Reg. No.:

Date & session:

ST. JOSEPH'S UNIVERSITY, BENGALURU - 27
M.Sc. (CHEMISTRY) – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2022
(Examination conducted in December 2022)
CH 7421 – SPECTROSCOPIC METHODS OF ANALYSIS I

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.

PART-A

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

1. Define fluorescence.
2. What is direct product? Carry out $A_u \times B_{1u}$ operation using a D_{2h} character table. The D_{2h} character table is provided at the end of this question paper.
3. Give an example of two operations which commute with each other.
4. Write an expression for transition moment integral. Explain the terms involved in it.
5. Draw the energy level diagram indicating Stokes and anti-Stokes lines.
6. Which molecule/s among the following is/are microwave active: OCS, CO_2. Give reason.
7. The rotational energy level of CO shows a series of equidistant lines spaced 3.842 cm^{-1} apart. Obtain the rotational energy level from which the most intense spectral line arises at 45 ^oC.
8. Explain Fermi resonance in IR spectroscopy.
9. The line spacing in P and R branches of CO_2 molecule is found to be 4B instead of 2B. Give reason.
10. Explain Born-Oppenheimer approximation in electronic spectroscopy.

PART-B

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

11. a) Generate the reducible representation of H_2O molecule. Decompose this reducible representation to irreducible representation using the reduction formula and write the linear combinations of the Mulliken symbols. Calculate the symmetry species of the normal modes of vibration. H_2O molecule belongs to C_{2v} point group. The character table for C_{2v} point group is provided at the end of this question paper.
    b) Show mathematically S_n axis generates '2n' operations, when n = odd. **(8+4)**

12. a) Sketch the normal modes of vibration of CO_2 molecule and show the changes in the polarizability ellipsoids of CO_2 during its vibrations in Raman spectroscopy. Indicate the Raman active 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) Discuss and depict the effect of isotopic substitution on the rotational energy levels of diatomic molecule such as carbon monoxide.

b) The vibrational frequency of $^{14}N^{35}Cl$ molecule is 817.358 cm^{-1}. Calculate the force constant and zero point energy (in cm^{-1}) of the molecule.

Given: mass of $^{14}N = 2.32586 \times 10^{-27}$ kg; mass of $^{35}Cl = 5.8871 \times 10^{-27}$ kg.

c) Based on Frank Condon principle, draw the electronic excitation using Morse curve and their corresponding intensities in the case of

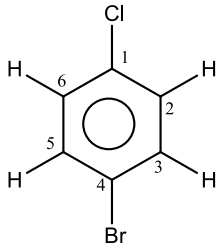
i) $r_e' = r_e''$ and

ii) $r_e' < r_e''$, where r_e' and r_e'' represent equilibrium internuclear distance in the upper and the lower electronic states, respectively. **(4+4+4)**

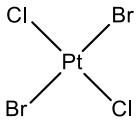
PART-C

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

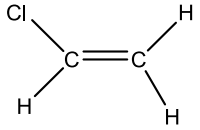
14. a) There are three molecular structures given below. Identify the principal axis in each of them? Also mention through which atoms does the principal axis pass.



a



b



c

b) The bonding molecular orbital of ethylene molecule in the ground state with a single electron has an assigned Mulliken symbol as B_{3u}. What will be the Mulliken symbol of this bonding molecular orbital in the ground state, if there are two electrons in it? Ethylene belongs to D_{2h} point group. The character table for D_{2h} is given at the end of this question paper. **(3+ 2)**

15. a) Justify that symmetric stretching of an AB_3 planar molecule is Raman active and IR inactive.

b) Two adjacent lines in the rotational absorption spectrum of $^{14}N^{1}H$ are at 98.036 cm^{-1} and 130.714 cm^{-1}. Calculate the rotational constant, B. Assign these lines to their appropriate J″ to J′ transition. **(2+3)**

16. The equilibrium vibrational frequency of a molecule is 215 cm^{-1} and the anharmonicity constant x_e is 0.003.

i) Calculate the vibrational wavenumber, $\bar{\nu}$, corresponding to the fundamental vibration of the molecule.

ii) Derive an expression for wavenumber, $\bar{\nu}$, corresponding to the hot band transition (v = 1 to v = 2) of the molecule and calculate the value of $\bar{\nu}$, for this transition.

iii) Comment on the intensities of hot band transition with respect to that of fundamental transition, in general. **(1+3+1)**

C_{2v} character table

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} character table

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	
