Register no.

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27

M.Sc. Chemistry – I SEMESTER

END SEMESTER EXAMINATION: OCTOBER 2021

CH 7418/CH 7421 – SPECTROSCOPIC METHODS OF ANALYSIS–I

Examination conducted in Jan-Mar 2022

Time- 2.5 hrs **Max Marks-70**

This paper contains THREE printed pages and THREE parts

Some useful constants: $h = 6.626 \times 10^{-34}$ Js ; $k = 1.381 \times 10^{-23}$ J/K ; $c = 2.99810^{10}$ cm/s; Atomic mass of an element = mass number x 1.66×10^{-27} kg; $1 cm^{-1}$ = 11.958 J/mol.

Part A

Answer any SIX from the following. **6×2=12**

1. What is Fermi resonance? Explain using a suitable example.
2. Explain predissociation of a molecule using Morse potential energy diagram.
3. Calculate the most populated state of a rigid diatomic rotor having rotational constant value of 14.9 cm^{-1} at 300 K.
4. State Frank – Condon principle and explain one of its applications.
5. How many classes are there in a C_{2v} and C_{3v} point group?
6. Define phosphorescence.
7. What are reducible representations? Give an example.
8. Write the matrix representations for C_3 and C_2^x.

Part B

Answer any FOUR from the following. **12×4=48**

9. a) 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. Also calculate zero-point energy.

b) Explain influence of rotation on the perpendicular vibrations of a symmetric top molecule. **(6 + 6)**

10. a) Discuss the rotational spectrum of a non-rigid diatomic rotor.
b) B value of $^{1}H^{35}Cl$ is 10.5909cm^{-1}. Calculate B value of $^{1}H^{37}Cl$ and $^{2}D^{35}Cl$.

(8 + 4)

11. a) Discuss the rotational fine structure of a particular vibration-electronic transition for a diatomic molecule, R, P and Q branches of lines (assume B' is not equal to B").
b) The spectrum arising from transitions between two states of a diatomic molecule shows the $v_{0,0}$ line at 21248 cm^{-1} and a convergence limit at 42017 cm^{-1}. The dissociation into one ground state atom and one excited atom, the excitation energy of the latter being 11012 cm^{-1}, calculate the exact dissociation energy of the two states. **(8 + 4)**

12. a) Show that the characters of the various irreducible representations of C_{2v} point group obey the corollaries of GOT.

b) Sketch the polarizability ellipsoids of H_2O molecule in vibrational Raman spectroscopy. Indicate the Raman activity of the different modes of vibration. **(6+6)**

13.a) With the help of a flowchart show how molecules can be classified into various symmetry point group.

c) Using reduction formula, obtain the linear combinations of the irreducible representation for the below data. The character table for C_{3v} is provided at the end of the question paper.

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma_{3N(RR)}$	12	0	2

(6+6)

14. a) Γ_{3N} representation of D_{3h} point group is given in terms of its irreducible representation components.

$\Gamma_{3N} = A_1' + A_2' + 3E' + 2A_2'' + E''$

Which of the above irreducible representation correspond to vibrational modes? Which of the vibrational modes are IR and/or Raman active. (The character table of D_{3h} point group is provided at the end of this paper.)

b) Mathematically prove S_4 has four operations.

c) Show there are three σ_v planes, one C_3^1 and one C_3^2 axes in an ammonia molecule.

(4+4+4)

Part C

Answer any TWO from the following. **5×2=10**

15. a) Deduce the term symbols for the following singlet transition states of hydrogen molecule. i) $(1s\sigma_g\,2p\sigma_g)$ and ii) $(1s\sigma_g\,2p\pi_u)$

b) Show that C_6 axis is not an independent symmetry element in case of staggered ethane but S_6 is an independent symmetry element. **(3+2)**

16. The P(1) and R(5) lines of $^{7}Li^{1}H$ are observed 90.2 cm^{-1} apart. Calculate the bond length of the molecule.

17. a) A molecule AB_2 has the following IR and Raman spectra.

cm^{-1}	IR	Raman
3756	Very strong; perpendicular	Weak, depolarized
3652	Strong; parallel	Strong, polarized
1592	Very strong; parallel	Very weak

The rotational fine structure of the IR bands is complex and does not show simple PR or PQR characteristics. Comment on the molecular structure and assign the observed lines to specific molecular vibrations as far as possible.

b) Fix the point groups of the following: i) $[Co(en)_3]^{3+}$ ii) cis-$[Co(en)_2Cl_2]^{+}$ and iii) trans-$[Co(en)_2Cl_2]^{+}$; where 'en' is ethylene diamine. **(2+3)**

Character tables

D_3h	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2 – y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz. yz)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A1	1	1	1	Z	x^2+y^2, z^2
A2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)