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

M.Sc. Chemistry – I SEMESTER

SEMESTER EXAMINATION: JANUARY 2021

OCH/CH 7418 – SPECTROSCOPIC METHODS OF ANALYSIS – I

Time- 2 1/2 hrs **Max Marks-70**

This paper contains FOUR printed pages and THREE parts

Some useful constants: $h = 6.626 \times 10^{-34}$ Js ; $k = 1.381 \times 10^{-23}$ J/K ; $c = 2.99810^{8}$ m/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 out of the following EIGHT questions: **6 × 2 = 12 Marks**

1. Explain the difference between r_{eq} and r in the parabolic curve of energy plotted against the extension or compression of the bond of a diatomic molecule obeying Hooke's law.
2. Intensity of first overtone is weaker than the fundamental vibration. Explain.
3. The average spacing between successive rotational lines of CO molecule is 3.8626 cm^{-1}. Determine the transition which gives the most intense line at 300 K.
4. What is the average period of rotation of a diatomic molecule (B = 10.618 cm^{-1}) if it is in the J = 8 state.
5. Write the matrix representation of C_2^z and i.
6. What is the symmetry condition for molecular chirality?
7. Give two properties of conjugate elements.
8. Explain improper axis of rotation with an example.

PART-B

Answer any FOUR out of the following SIX questions: **4 × 12 = 48 Marks**

9. a) What is predissociation? How would you account for it?

   b) The absorption spectrum of a diatomic molecule shows vibrational structure which becomes a continuum at 59126cm^{-1}, the upper electronic state dissociates into one ground state atom and one excited atom (the excitation energy of which measured from the atomic spectrum is 17576cm^{-1}). Estimate the dissociation energy of the ground state diatomic molecule in joule per mole.

   c) Deduce the term symbols for the following singlet transition states of hydrogen molecule.

   i) $(1s\sigma_g 2p\sigma_g)$ ii) $(1s\sigma_g 2p\pi_u)$

   d) State and explain Frank – Condon principle. (3+3+3+3)

10. a) Discuss the rotational spectra of non – rigid heteronuclear diatomic molecules.

b) What are hot bands? Why are they called so?

c) Alternate lines of P and R branches of acetylene are less intense. Why? (6+3+3)

11. a) The IR spectrum of a symmetric AB_2 molecule gives 3 prominent lines. Check whether the molecule is bent or linear.

b) The Q branch of the vibrational spectrum of CH_3Cl consists of a series of lines on both sides of the band centre whereas that of a linear molecule is a single intense line. Explain.

c) Calculate the energy in cm^{-1} of the photon absorbed when NO molecule goes 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 = 1904 cm^{-1}, anharmonicity constant = 0.00733, bond length = 0.1151nm and its reduced mass = 12.3075 x 10^{-27} kg. (3+4+5)

12. a) Sketch the polarizability ellipsoids of H_2O molecule in vibrational Raman spectroscopy. Indicate the Raman activity of the different modes of vibration.

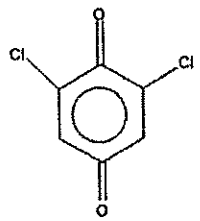
b) Deduce the matrix representation for any rotation operation C_n with the angle of rotation θ. (6+6)

13. a) Γ_{3N} representation generated by all the vectors X, Y, Z for C_{2h} point group is given as follows:

C_{2h}	E	C_2	i	σ_h
Γ_{3N}	12	0	0	4

The character table of C_{2h} is given at the end. Get the irreducible components of Γ_{3N}. How many of its vibrations are IR active and how many are Raman active?

b) Show step-wise determination of point group for the below molecule.



2,6-dichloroquinone

14.a) Give the mathematical form of GOT and explain the terms involved.

b) Draw the Huckle-molecular orbital energy level diagram of ethylene molecule. Obtain the symmetry species for the ground state and the excited state of the molecule. Assign the bands at 164 nm (intense), 200 nm (weak) and 270 nm (extremely weak). The character table of D_{2h} point group is given at the end.

[4+8]

PART-C

Answer any TWO out of the following THREE questions: 2 × 5 = 10 Marks

15. (a) A rotational absorption line of a symmetric top molecule is split into five lines in presence of an electric field of several hundred volts / m. Identify the J values of both upper and lower rotational levels of the transition. Assume k (represent the angular momentum about the top axis) values in both upper and lower rotational levels is 1.

(b) Calculate the moment of inertia of a H_2O molecule around its twofold axis of rotation (the bisector of HOH angle). Bond angle and bond length of the molecule are 104.6^0 and 95.7 pm.

Note:

$I = \sum m_i r_i^2$, where r_i is the perpendicular distance of the atom i from the axis of rotation.

Mass of H = 1.67×10^{-27} kg and $\sin 52.3^0 = 0.79$ (2+3)

16. a)The P(1) and R(5) lines of diatomic molecule, X-Y are observed 90.2 cm^{-1} apart. Calculate the bond length of the molecule. Assume the reduced mass of the molecule is 1.4535×10^{-27} kg.

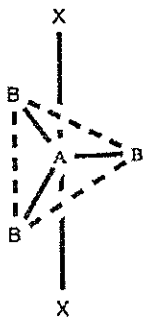
b) Justify that the staggered ethane belongs to D_{3d} point group. (3+2)

17. a) A molecule AB_4 belongs to T_d point group. Deduce the point symmetry if it is changed to AB_3X, AB_2X_2, ABXYZ.

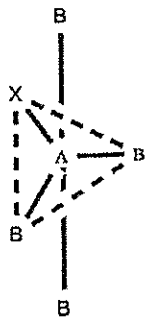
b) Two molecular structures are given below. Which is the principal axis for them? Also from which atoms do the principal axis pass? Which point group do they belong?

(3+2)

i)



ii)



C_{2h}	A_g	B_g		x^2, y^2, z^2, xy
			R_z	xz, yz
E	1	1	R_x, R_y	
C_2	1	−1	z	x, y
i	−1	1		
σ_h	−1	−1	R_x, R_y	

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