PG – 201

II Semester M.Sc. Degree Examination, June 2016
(CBCS)
CHEMISTRY
C – 204 : Spectroscopy – I

Time : 3 Hours Max. Marks : 70

*Instruction : Answer question No. 1 and **any five** of the remaining.*

1. Answer **any ten** of the following : (10×2=20)

a) By matrix multiplication, find out the equivalent symmetry operation for the following products :
$C_2\sigma_h$ and C_2i

b) Give the meaning of subgroup and write the subgroups for C_{2h} and D_{2h}-point groups.

c) Explain the term 'transition probability integral'.

d) How many irreducible representations are possible for C_{2h}-point group ? Justify your answer.

e) Why are pure rotational spectra studied only in the gaseous states of atoms and molecules ?

f) Distinguish between harmonic and anharmonic oscillators with the help of their potential energy curves.

g) How are molecules classified based on the three principal moments of inertia ?

h) How many stretching and bending modes are present in CO_2 and SO_2 molecules ?

i) Define the term polarizability, and why are spherical top molecules have polarizability surfaces.

j) CO molecule vibrates with a frequency of 1700 cm^{-1}. Express this energy in kJ/mole.

k) Explain the terms vibrational relaxation and internal conversion.

l) How are σ-, π- and δ- molecular orbitals formed ?

P.T.O.

2. a) An MX_6 molecule belongs to the O_h-point group. Find the point groups that will result if the molecule is changed into MX_5Y and cis-and trans-MX_4Y_2

b) How do the functions X, Y and Z transform in the point group C_{2v} ? Name the corresponding irreducible representations.

c) How does electromagnetic radiation interact with molecules ? What are its consequences ?

(3+3+4=1

3. a) Write a note on labelling of irreducible representations.

b) Using the following character table, find the direct products and their irreducible components for $A_1 \times A_2$ and $B_1 \times E$.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	−1	1	1	−1
B_2	1	−1	1	−1	1
E	2	0	−2	0	0

(4+6=1

4. a) The three consecutive lines in the rotational spectrum of $H^{79}Br$ are observed at 84.544, 101.355 and 118.152 cm^{-1}. Calculate the bondlength of the molecule.

b) How does the breakdown of the Born-Oppenheimer approximation affect the P and R branch lines in the vibration-rotation spectrum of a diatomic molecule ?

(4+6=10

5. a) Explain the terms : overtones, combination bands and Fermiresonance.

b) Draw a schematic diagram of Michelson interferometer and discuss the experimental technique. List the advantages of FT technique. (4+6=10)

6. a) Derive the expression for the Raman shifts of the pure rotational Raman lines of a linear molecule.

b) Outline the concept of normal modes of vibration of a molecule. Sketch shematically the normal modes of AB_3-planar molecule and comment on its IR and Raman activity.

(4+6=10)

7. a) Explain predissociation by depicting Morse curves of a particular molecule in two different excited states intersect.

b) State the Frank-Condon principle. In what way it is useful in explaining the intensities of vibrational structures ? (4+6=10)

8. a) A strong infrared absorption band is observed at 2991 cm^{-1} for $^{1}H^{35}Cl$ molecule. Calculate the force constant for this molecule.

b) Draw the energy level diagram and show how the energy of the $1s\sigma_g$ and $1s\sigma_u^*$ orbitals varies with the distance between the nuclei. (4+6=10)