M. Sc. Chemistry Examination, 2018

(4th Semester)

Inorganic Chemistry Special

Paper - XIII-I

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - I - 4131

1. Find out the splitting of ^2D state under D_{4th} Symmetry. 4
2. Evaluate the symmetries of IR and Raman Vibrations of NH_3. 4
3. An aqueous solution of $[Cr(NH_3)_6]^{3+}$ displays two high intensity spin allowed bands at 21550 cm^{-1} and 28500 cm^{-1}, respectively. Deduce the values of Δ_0 and B. 3
4. Explain logically the term "double group". Construct the spin orbit coupling correlation diagram for $[T_i (H_2O)_6]^{3+}$. 3+6
5. Discuss the Jahn-Teller theorem using group theory and hence explain the Jahn-Teller distortion in VCl_4. 3+2

Character table for D_4

	E	$2C_4$ (z)	C_2 (z)	2C'$_2$	2C''$_2$
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

Character table for group T_d

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	+1	+1	+1	+1	+1
A_2	+1	+1	+1	-1	-1
E	+2	-1	+2	0	0
T_1	+3	0	-1	+1	-1
T_2	+3	0	-1	-1	+1

Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

Character Table of D_{2d}

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
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

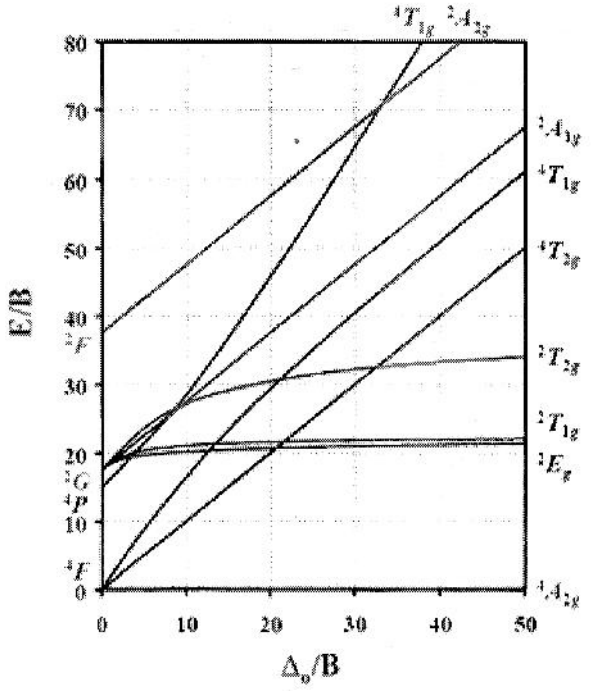
Character Table of O'

			$3RC_2$			$6C_2'$	R	$8RC_3$	$6RC_4$
	O'	E	$3C_2$	$8C_3$	$6C_4$	$6C_2$			
Γ_1	A_1'	1	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	-1	-1	1	1	-1
Γ_3	E_1'	2	2	-1	0	0	2	-1	0
Γ_4	T_1'	3	-1	0	1	-1	3	0	1
Γ_5	T_2'	3	-1	0	-1	1	3	0	-1
Γ_6	E_2'	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$
Γ_7	E_3'	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$
Γ_8	$F_{3/2}$	4	0	-1	0	0	-4	1	0

Characters of the matrix representatives D_J or D_S for half-integral *J or S*

	E	C_2	C_3	C_4
α	0	π	$2\pi/3$	$\pi/2$
D_J	$2J+1$	0	1 (J = ½, 7/2 ....)	$\sqrt{2}$ (J = ½, 9/2 ....)
			-1 (J = 3/2, 9/2 ....)	0 (J = 3/2, 7/2 ....)
			0 (J = 5/2, 11/2 ....)	$-\sqrt{2}$ (J =5/2, 13/2 ....)
J = 1/2	2	0	1	$\sqrt{2}$
J = 3/2	4	0	-1	0
J = 5/2	6	0	0	$-\sqrt{2}$

TS Diagram for d^3 system



UNIT - I - 4132

6. a) Condider an octahedral ML_6 molecule:

(i) Construct the expressions for LGOs among six ligands, L, forming σ -bonding with central metal atom, M.

(ii) Determine Mulliken notations of valance AOs of M.

(iii) Draw a qualitative moleculer orbital energy diagram of ML_6. 6+2+2

b) Construct a correlation diagram for energy of EH_3 molecule (consider two limiting geometries e.g., planar and pyramidal) and hence determine the geometry of BH_3, CH_3, NH_3, molecules in their ground and first excited states. 2+4

c) Rationalize the following phenomena with the aid of Relativistic Effects:

(i) Unlike the lighter congeners, higher valences (viz. IV) are more common for Os, Ir and Pt.

(ii) Compare and contrast : Argentophilicity and Aurophilicity

(iii) Compare the back-bonding ability in fifth and sixth row transition elements, 3×3

Character table of O point group

O	E	$8C_3$	$6C'_2$	$6C_4$	$3C_2 = (C_4)^2$
A_1	+1	+1	+1	+1	+1
A_2	+1	+1	-1	-1	+1
E	+2	-1	0	0	+2
T_1	+3	0	-1	+1	-1
T_2	+3	0	+1	-1	-1