M. Sc. Chemistry Examination, 2019

(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 ^3F state under D_{4h} Symmetry. 5
2. Evaluate the symmetries of IR and Raman vibrations of H_2O. 5
3. Determine the spin-allowed and spin-forbidden transitions for the polarized crystal spectrum of $K_3[Cr(C_2O_4)_3]$. [Where $^4A_2$ is the ground state and $^4A_1$, $^4A_2$ and ^4E are the excited states] 6
4. Construct the spin orbit coupling correlation diagram for square planer Ag(II) complexes. 6
5. $[VF_6]^{3-}$, which has absorption bands at 14,800 and 23,250 cm^{-1}, plus a third band in the ultraviolet. Calculate Δ_0 and B. 3

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 C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
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

Character table for D_3 point group

	E	$2C_3$ (z)	$3C'_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

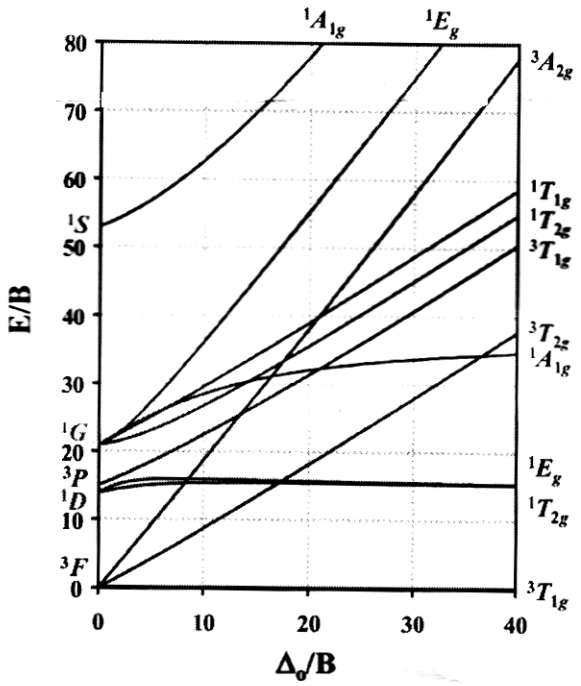
Partial Character table for O

O	E	$8C_3$	$6C'_2$
A_2	1	1	-1
T_1	3	0	-1
T_2	3	0	1

Character Table of D_4'

				RC_2	$2RC'_2$	$2RC''_2$	R	$2RC_4$
	D'_4	E	$2C_4$	C_2	$2C'_2$	$2C''_2$		
Γ_1	A'_1	1	1	1	1	1	1	1
Γ_2	A'_2	1	1	1	-1	-1	1	1
Γ_3	B'_1	1	-1	1	1	-1	1	-1
Γ_4	B'_2	1	-1	1	-1	1	1	-1
Γ_5	E'_1	2	0	-2	0	0	2	0
Γ_6	E'_2	2	√2	0	0	0	-2	-√2
Γ_7	E'_3	2	-√2	0	0	0	-2	√2

d^2 Tanabe-Sugano Diagram



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	2π/3	π/2
D_J	2J + 1	0	1 (*J* = ½, 7/2 ....)	√2 (*J* = ½, 9/2 ....)
			-1 (*J* = 3/2, 9/2 ....)	0 (*J* = 3/2, 7/2 ....)
			0 (*J* = 5/2, 11/2 ....)	-√2 (*J* =5/2, 13/2 ....)
J = 1/2	2	0	1	√2
J = 3/2	4	0	-1	0
J = 5/2	6	0	0	-√2

UNIT - I - 4132

6. a) Group theoretically determine the LGOs for NH_3 by means of projection operator method and depict the individual LGOs. 3+2

   b) Write down the Mulliken symbol of the valence AOs of N atom in NH_3 and draw a qualitative molecular orbital energy level diagram of NH_3 molecule considering with and without s-p mixing (Character table of C_{3v} point group may be consulted). 2+6

   c) Draw the Walsh diagram for AH_2 molecule considering two limiting geometries viz. linear and angular and hence predict the geometry of BeH_2^+ and BH_2 in their ground and first excited states. 6

   d) Explain any two of the followings :

      (i) Electronegativity of gold ($x_{Au} = 2.54$ in Pauling scale) is copmparable to that of iodine ($x_1 = 2.66$).

      (ii) Sixth period elements usually show two units below the respective group valence.

      (iii) In transition metal-dihydrogen chemistry, metal-hydride description becomes more significant down the group. 2×3

Character table for C_{3V} point group

C_{3V}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0
$\Gamma_{r.v.x.}$	3	0	1