M. Sc. (Chemistry) Examination, 2022

(4th Semester, CBCS)

Inorganic Chemistry Special

Paper – XIII-I

Time : Two hours | Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each Unit.

UNIT: I-4131

(Answer All Questions)

1. Find out the splitting of ^3F state under O_h symmetry. 3
2. Evaluate the symmetries of IR and Raman vibrations of NH_3. 4
3. Determine the spin-allowed and spin-forbidden transitions for the polarized crystal spectrum of $Cs_2[CuCl_4]$. [Where $^2B_2$ is the ground state] 5
4. Construct the spin orbit coupling correlation diagram for square planar Ag(II) complexes. 8

T_d	D_{2d}
A_1	A_1
A_2	B_1
E	$A_1 + B_1$
T_1	$A_2 + E$
T_2	$B_2 + E$

Partial Character table for O

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

Character table for C_{3v} point group

C_{3v}	E	$2C_3(z)$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2,\ z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_v)$	$(x^2 - y^2, xy)(xz, yz)$

Character table for D_{2d} point group

D_{2d}	E	$2S_4$	$C_2(z)$	$2C_2'$	$2\sigma_d$		
A_1	+1	+1	+1	+1	+1		$x^2+y^2,\ z^2$
A_2	+1	+1	+1	−1	−1	R_z	
B_1	+1	−1	+1	+1	−1		x^2-y^2
B_2	+1	−1	+1	−1	+1	z	xy
E	+2	0	−2	0	0	$(x,\ y)(R_x,\ R_y)$	$(xy,\ yz)$

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	$\sqrt{2}$	0	0	0	−2	$-\sqrt{2}$
Γ_7	E_3'	2	$-\sqrt{2}$	0	0	0	−2	$\sqrt{2}$

D_{4h}	D_4'
A_{1g}	A_1'
B_{1g}	B_1'
B_{2g}	B_2'
E_g	E_1'

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

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5. Consider a square planar complex compound, $[PtF_4]^{2-}$.

a) Determine the LGOs of the four terminal F atoms using projection operator. (Character Table may be consulted). 5

Character table for D_4 point group

	E	$2C_4(z)$	$C_2(z)$	$2C_2'$	$2C_2''$	linear functions rotations	quadratic functions
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	–1	1	z, R_z	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	1		xy
E	2	0	–2	0	0	$(x,y)(R_x,R_y)$	(xz, yz)

b) Write down the Mulliken symbol of the valence AOs of Pt atom and draw a qualitative molecular orbital energy level diagram of $[PtF_4]^{2-}$ with clear depiction of FMOs. 5

c) Predict the geometry of CH_2 and NH_2 in their ground and first excited states with the aid of appropriate Walsh diagram. 4

d) Explain the following phenomena: 3×2

i) Aurophilicity

ii) Platinum exists in nature as native metal, nonetheless it can form M(IV) among Group 10.