M. Sc. Chemistry Examination, 2022

(4th Semester)

Inorganic Chemistry Special

Paper – XIII-I

Time : Two hours Full Marks : 50

Use a separate answer script for each Unit.

UNIT: I-4131

(Answer All Questions)

1. Find out the splitting of ^2D state under O_h symmetry. 3
2. Evaluate the symmetries of IR and Raman vibrations of CH_4. 5
3. Construct the correlation diagram of d^2 system under O_h. 12
4. Show that in $[CoCl_4]^{2-}$; $^4A_2 \rightarrow {}^4T_2$ transition is electronically forbidden whereas $^4A_2 \rightarrow {}^4T_1$ transition is electronically allowed. 5

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 T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

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Character table for D_{4h} point group

D_{4h}	E	$2C_4(z)$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-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

O_h	D_{4h}	C_{2v}
A_{1g}	A_{1g}	A_1
A_{2g}	B_{1g}	A_2
E_g	$A_{1g} + B_{1g}$	$A_1 + A_2$
T_{1g}	$A_{2g} + E_g$	$A_2 + B_1 + B_2$
T_{2g}	$B_{2g} + E_g$	$A_1 + B_1 + B_2$

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5. Consider a tetrahedral complex compound, $[NiCl_4]^{2-}$:

a) Determine the LGOs of the terminal atoms using projection operator method. (Character Table may be consulted). Write Mulliken notation of the valence AOs of metal atom and draw a qualitative molecular orbital energy level diagram of a tetrahedral complex. 4+4

Table 1: Character table for T_d point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)

b) Why is s–p mixing important in H_2O molecule? Justify your arguments in the light of group theory. 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) How do the relativistic effects cause the stabilization of valence *s* and *p* AOs, while destabilization of *d* and *f* orbitals in case of heavier transition elements. 2

e) Explain the following phenomena (***any two***): 3×2

i) Aurophilicity

ii) Gold can form stable auride ion.

iii) The Au(III) complexes are more common unlike Ag(III) species.