M. Sc. Chemistry Examination, 2017

(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. Determine the number of frequencies, their symmetrics, IR, Raman activities of CH_4 molecule and hence assign the CH and HCH vibrations. 6+2
2. Describe the First Order Jahn-Teller distortion in $[Ni(H_2O)_6]^{2+}$ with the help of Group Theory.
   [Normal Modes of Vibrations : $\mathbf{A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}}$] 5
3. Find out the vibronically allowed and forbidden transitions for the polarized crystal spectrum of ***trans*-$\mathbf{[Co(en)_2Cl_2]^+}$** [Where $^1A_{1g}$ is the ground state] 8
4. Show that the D term of free d^1 system split into $^2T_{1g} + {}^2E_g$ in octahedral ligand fields. 4

O	E	$8C_3$	$6C'_2$	$6C_4$	$3C_2 = (C_4)^2$		quadratic functions
A_1	+1	+1	+1	+1	+1		$x^2+y^2+z^2$
A_2	+1	+1	-1	-1	+1		-
E	+2	-1	0	0	+2		$(x^2-y^2, 2z^2-x^2-y^2)$
T_1	+3	0	-1	+1	-1	(x, y, z) (R_x, R_y, R_z)	-
T_2	+3	0	+1	-1	-1	-	(xy, xz, yz)

D_{4h}	E	$2C_4(z)$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
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	(x, y)	-

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	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	-	-
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)

O_h	D_{4h}
$^1A_{1g}$	$^1A_{1g}$ (ground state)
$^1T_{1g}$	$^1A_{2g} + {}^1E_g$
$^1T_{2g}$	$^1B_{2g} + {}^1E_g$

UNIT - I - 4132

5. a) Construct the LGOs of H_2O group theoretically.

   b) Determine the valence orbitals of O atom in water with justification.

   c) Draw the molecular orbital energy level diagram along with the respective orbital of water with and without considering s-p mixing. Hence compare and comment on the nature of HOMO and HOMO - 1 for both cases. 2+2+6

6. a) Draw Walsh diagram of H_3^+ and H_3^- and hence predict the geometry of $H_3^{\bullet}$.

   b) Determine the geometry of BH_2 and NH_2 in their first excited states. 3+3

7. a) Briefly discuss direct and indirect relativistic effects and their consequences on the size and energy of orbitals.

   b) Unlike their lighter congeners, osmium, iridium and platinum show oxidation state 'IV'. Explain.

   c) Account for the coloration of silver and gold. 3+3+3