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14 (CHM-1) 106

2021
(Held in 2022)

CHEMISTRY

Paper : CH-106

(Symmetry and Group Theory in Chemistry)

Full Marks : 40

Time : Two hours

***The figures in the margin indicate
full marks for the questions.***

1. Answer **any one** of the following questions :

- (a) Group multiplication table for an arbitrary group of order 6 is given below. Find the subgroups and the classes in this group. 3

$G_6^{(2)}$	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>F</i>
<i>E</i>	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>F</i>
<i>A</i>	<i>A</i>	<i>E</i>	<i>D</i>	<i>F</i>	<i>B</i>	<i>C</i>
<i>B</i>	<i>B</i>	<i>F</i>	<i>E</i>	<i>D</i>	<i>C</i>	<i>A</i>
<i>C</i>	<i>C</i>	<i>D</i>	<i>F</i>	<i>E</i>	<i>A</i>	<i>B</i>
<i>D</i>	<i>D</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>F</i>	<i>E</i>
<i>F</i>	<i>F</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>E</i>	<i>D</i>

Contd.

- (b) Show that there can be only one group of order 'h', where h is a prime number.

3

- (c) Define class and subgroup of a mathematical group.

3

2. Answer **any one** of the following questions :

- (a) Define symmetry elements. Identify the point group of allene. Mention the *symmetry elements* present in a tetrahedral molecule.

2+1+2=5

- (b) Write out all the operations generated by ferrocene molecule in its staggered configuration. Why do we not have S_n point groups with n being odd?

3+2=5

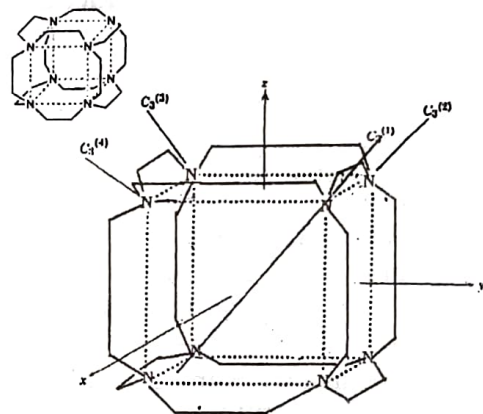
- (c) Find out the resultant point group on addition of σ_h , to the point group C_4 . What is the point group of the crown-shaped S_8 molecule?

3+2=5

3. Answer **any two** of the following questions :
5×2=10

- (a) The molecule Dodeca (ethylene) octamine, as shown in the *figure* below belongs to the symmetry point group O. For the group O, show that the sets of function (x, y, z) and (xy, xz, yz) correspond to the irreducible representation T_1 and T_2 respectively.

5



O	E	$8C_3$	$3C_2 (= C_1)$	$6C_4$	$6C_2$
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

- (b) State great orthogonality theorem and prove that the sum of the characters in any irreducible representation equals order of the group, h , which is

$$\sum_R [\chi_i(R)]^2 = h. \quad 5$$

- (c) Derive the complete matrices for all the representations of the group C_{3v} . 5

- (d) Fill in the blanks: 5

- (i) The result of the product of $C_2(x)$ and $C_2(y)$ is ____.
- (ii) The product $\sigma^{xy} \cdot S_4(z)$ is ____.
- (iii) The product of reflection and inversion is ____.
- (iv) When there is a rotation axis C_n and a plane containing it, there must be n such planes separated by angles of ____.
- (v) The inversion and ____ or rotation always commute.

4. Answer **any two** of the following questions :
5×2=10

- (a) Considering the eigenfunctions for $2p_x$ and $2p_y$, 5

$$p_x = \Psi_r \sin \theta \cos \phi$$

$$p_y = \Psi_r \sin \theta \sin \phi$$

show that these two eigenfunctions indeed form the basis for E irreducible representation in D_3 point group.

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

- (b) For spectroscopic techniques like circular dichroism and magnetic circular dichroism it is necessary to know what electronic transitions are magnetic dipole allowed. The operators for this have the symmetry properties of R_x , R_y and R_z . For a tetrahedral molecule of T_d symmetry, check whether the transitions A_2 to T_1 , E to T_2 and E to E are magnetic dipole allowed transitions. (Hint: Transition moment integral $\int \psi_i \mu \psi_j d\tau$ may be used) 5

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	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z)

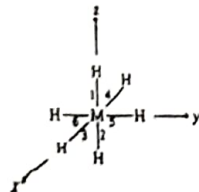
- (c) Identify the irreducible representations to which the normal modes of vibration of water molecule belong. Comment on the IR and Raman activity of the normal modes.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
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

- (d) For a hypothetical octahedral molecule given below, find the reducible representation considering the six σ -bonding atomic orbitals of the H atoms as basis and show that A_{1g} , E_g and T_{1u} are the irreducible components of the said reducible representation. Identify the metal orbitals taking part in the sigma bonding. Show that the SALCs

$$1\sqrt{2}(\sigma_1 - \sigma_2), 1\sqrt{2}(\sigma_3 - \sigma_4) \text{ and}$$

$1\sqrt{2}(\sigma_5 - \sigma_6)$ form the basis for the T_{1u} irreducible representation.



Character tables are provided.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(-C_4)$	I	$6S_6$	$8C_6$	$3\sigma_h$	$6\sigma_d$	
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	$(2x^2 - y^2 - z^2)(x^2 - y^2)$
E_g	2	-1	0	0	2	2	0	-1	2	0	(p_x, p_y, p_z)
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(x, y, z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	-1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	(x, y, z)
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

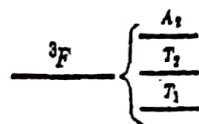
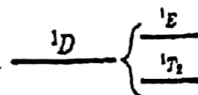
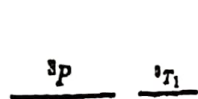
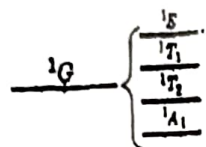
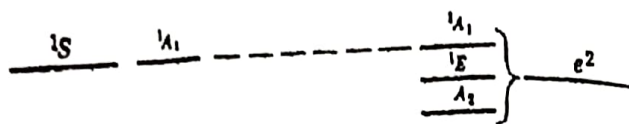
O	E	$8C_3$	$3C_2(=C_1)$	$6C_4$	$6C_2$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	$(2x^2 - y^2 - z^2, x^2 - y^2)$
E	2	-1	2	0	0	$(R_x, R_y, R_z); (x, y, z)$
T_1	3	0	-1	1	-1	(xy, xz, yz)
T_2	3	0	-1	-1	1	

- (e) State the symmetry based selection rules for electronic, IR and Raman spectroscopy.

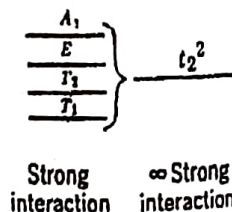
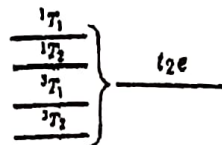
5. Answer **any two** of the following questions :

$$3 \times 2 = 6$$

- (a) Given below is the incomplete correlation diagram for d^2 configuration. Identify the spin multiplicities for the terms in it and draw the connecting lines.



Free Ion Weak Interaction



Strong interaction ∞ Strong interaction

(b) One of the SALC for sigma bonding in square planer complex is

$$\Psi = 1/2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4).$$

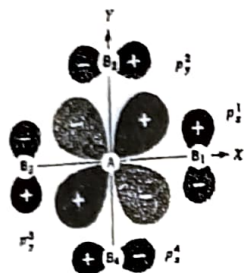
Identify the irreducible representation for the SALC. 3

D_{4h}	E	$2C_4$	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	R_z	$x^2 + y^2, z$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
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)	(xy, 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)	

(c) For an MX_4 molecule having a flattened tetrahedral structure of D_{2d} symmetry, identity the splitting pattern of p and d orbitals. 3

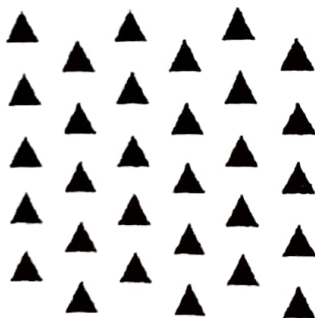
D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1		$x^2 - y^2$
B_1	1	-1	1	1	-1		xy
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	$(x, y); (R_x, R_y)$	xz, yz

- (d) Write the SALC for the π orbital in a square planar complex matching the d_{xy} orbital of central metal atom. Diagram below may be used. 3



6. Answer **any three** of the following questions :
2×3=6

- (a) Show the possible unit cells for the following lattice : 2



- (b) Name the crystal system with crystal parameters $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$. 2
- (c) How many point and space groups one can find for two-dimensional lattice? 2
- (d) Mention the essential symmetry elements for cubic crystal systems. 2
- (e) Define space groups. 2
- (f) What are the symmetry elements for point symmetry in crystals? 2