ADVANCED CHEMISTRY

INORGANIC CHEMISTRY - WINTER - WEEK 4

Chapter 4

(14)

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
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
Γ_2	6	4	6	2	0

(a) Order = $1+2+1+2+2=\underline{\underline{8}}$ (total # of symm. operations)

(b) $\sum \chi_i(E).\chi_i(A_1) = 2.1 + 0.2.1 + (-2)\,1.1. + 0(1)(2) + 0(1)(2)$

$= 2 - 2 = \underline{\underline{0}}$

$\Rightarrow$ E is orthogonal to A_1

$\sum \chi_i(E)\chi_i(A_2) = 2.1 + 0.2.1. + (-2).1 + 0(-1)(2) + 0(-1)(2)$

$= 2-2=0$

$\Rightarrow$ E is orthogonal to A_2

$\sum \chi_i(E)\,\chi_i(B_1) = 2.1 + (0)(-1)(2) + (-2)(1) + (0)(1)(2) + 0(-1)(2)$

$= 2-2=0$

$\Rightarrow$ E is orthogonal to B_1

$$\sum \chi_i(E)\chi_i(B_2) = (2)(1) + (0)(-1)(2) + (-2)(1)(1) + 0(-1)(2) + 0(1)(2) = 2-2=0$$

E is orthogonal to B_2

$\therefore$ E is orthogonal to each of the other irreducible representations in the D_{2d} point group.

(c) For A_1

$$\sum \chi_i^2(A_1) = 1^2 + 2(1)^2 + 1^2 + 2(1)^2 + 2(1)^2 = \underline{\underline{8}}$$

For A_2 $\sum \chi_i^2(A_2) = 1^2 + 2(1)^2 + 1^2 + 2(-1)^2 + 2(-1)^2 = \underline{\underline{8}}$

For B_1 $\sum \chi_i(B_1)^2 = 1^2 + (-1)^2 \cdot 2 + 1^2 + 2(1)^2 + 2(-1)^2 = \underline{\underline{8}}$

For B_2 $\sum \chi_i(B_2)^2 = 1^2 + (-1)^2 \cdot 2 + 1^2 + 2(-1)^2 + 2(1)^2 = \underline{\underline{8}}$

For E $\sum \chi_i(E)^2 = 2^2 + 2(0)^2 + 1(-2)^2 + 2(0)^2 + 2(0)^2$
$= \underline{\underline{8}}$

(d) $\left.\begin{array}{l}\text{\# of times } A_1 \text{ is} \\ \text{in } \Gamma_1\end{array}\right] = \frac{1}{8}\left[(6 \cdot 1 \cdot 1) + 0(2)(1) + 2 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1 + 2 \cdot 2 \cdot 1\right]$

$= \frac{1}{8}\left[6 + 2 + 4 + 4\right] = 2$

$\left.\begin{array}{l}\text{\# of times } A_2 \text{ is} \\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{8}\left[6 \cdot 1 \cdot 1 + 0 \cdot 2 \cdot (1) + 2(1)(1) + 2(2)(-1) + 2 \cdot 2 \cdot (-1)\right] = \frac{1}{8}(6 + 2 - 4 - 4) = \underline{\underline{0}}$

$$\left.\begin{array}{l}\#\text{ of times } B_1 \text{ is} \\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{8}\Big[6(1)(1) + (0)(2)(-1) + (2)(1)(1) + (2)(2)(1) + (2)(2)(-1)\Big]$$

$$= \frac{1}{8}\left(6 + 2 + 4 \cancel{+} -4\right) = 1$$

$$\left.\begin{array}{l}\#\text{ of times } B_2 \text{ is} \\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{8}\Big[6(1)(1) + (0)(2)(-1) + (2)(1)(1) + (2)(2)(-1) + (2)(2)(1)\Big]$$

$$= \frac{1}{8}\left[6 + 2 - 4 + 4\right] = 1$$

$$\left.\begin{array}{l}\#\text{ of times } E \text{ is} \\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{8}\Big[(6)(1)(2) + (0)(2)(0) + (2)(1)(-2) + (2)(2)(0) + (2)(2)(0)\Big]$$

$$= \frac{1}{8}\left(12 - 4\right) = 1$$

$$\therefore \quad \Gamma_1 = 2A_1 + B_1 + B_2 + E$$

(note that dimensionality of Γ $(=6)$ = sum of the dimensionalities of $2A_1$, B_1, B_2 and E.)

$$\left.\begin{array}{l}\#\text{ of times } A_1 \text{ is} \\ \text{in } \Gamma_2\end{array}\right\} = \frac{1}{8}\Big[6\cdot 1\cdot 1 + 4\, 1\cdot 2 + 6\cdot 1\cdot 1 + 2\cdot 2\cdot 1 + (0)\, 2\cdot 1\Big]$$

$$= \frac{1}{8}\left(6 + 8 + 6 + 4\right) = 3$$

$$\left.\begin{array}{l}\#\text{ of times } A_2 \text{ is} \\ \text{in } \Gamma_2\end{array}\right\} = \frac{1}{8}\Big[6\cdot 1\cdot 1 + 4\cdot 1\cdot 2 + 6\cdot 1\cdot 1 + 2\cdot(-1)(2) + (0)(-1)(2)\Big]$$

$$\ldots) = 2$$

$$\left.\begin{array}{l}\#\text{ of times } B_1\\ \text{is in } \Gamma_2\end{array}\right\} = \frac{1}{8}\left[6\cdot1\cdot1 + 4\cdot(-1)(2) + 6(1)(1) + (2)(1)(2) + (0)(-1)(2)\right]$$

$$= \frac{1}{8}(6 - 8 + 6 + 4) = 1$$

$$\underline{\underline{\Gamma_2 = 3A_1 + 2A_2 + B_1}}$$

$$\left(\begin{array}{l}\text{dimensionality}\\ \text{of } \Gamma_2\end{array} = \text{dimensionality of } (3A_1 + 2A_2 + B_1)\right)$$

(15)

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
Γ_1	6	3	2
Γ_2	5	−1	−1

$$\left.\begin{array}{l}\#\text{ of times } A_1 \text{ is}\\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{6}\left[6\cdot1\cdot1 + 3\cdot1\cdot2 + 2\cdot1\cdot3\right]$$

$$= \frac{1}{6}(6+6+6) = \underline{\underline{3}}$$

$$\left.\begin{array}{l}\#\text{ of times } A_2 \text{ is}\\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{6}\left(6\cdot1\cdot1 + 3\cdot1\cdot2 + 2(-1)\cdot3\right)$$

$$= \frac{1}{6}(6 + 6 - 6) = \underline{1}$$

$$\left.\begin{array}{l}\#\text{ of times } E \text{ is}\\ \text{in } \Gamma_1\end{array}\right\} = \frac{1}{6}\left[6\cdot 2\cdot 1 + 3(-1)(2) + 2\cdot(0)(3)\right]$$

$$= \frac{1}{6}(12-6) = 1$$

$$\therefore \quad \Gamma_1 = 3A_1 + A_2 + E$$

$$\#\text{ of times } A_1 \text{ is in } \Gamma_2 = \frac{1}{6}\left[5\cdot 1\cdot 1 + (-1)\,1\cdot(2) + (-1)(1)3\right]$$

$$= \frac{1}{6}(5-2-3) = 0$$

$$\#\text{ of times } A_2 \text{ is in } \Gamma_2 = \frac{1}{6}\left[5\cdot 1 + (-1)(+1)(2) + (-)(-1)(3)\right]$$

$$= \frac{1}{6}\left[\overset{5}{\cancel{10}} - 2 + 3\right) = 1$$

$$\#\text{ of times } E \text{ is in } \Gamma_2 = \frac{1}{6}\left[5\cdot 2\cdot 1 + (-1)(-1)(2) + (-1)\,0\cdot(3)\right]$$

$$= \frac{1}{6}\left[10+2\right] = 2$$

$$\Gamma_2 = A_2 + 2E$$

<u>O_h group</u>

$$\left.\begin{array}{l}\#\text{ of times } A_{1g}\\ \text{is in } \Gamma\end{array}\right\} = \frac{1}{48}\left[\begin{array}{l}6\cdot 1\cdot 1 + 0\cdot 1\cdot 8 + 0\cdot 1\cdot 6 + 2\cdot 1\cdot 6 + 2\cdot 1\cdot 3 +\\ 0\cdot 1\cdot 1 + 0\cdot 1\cdot 6 + 0\cdot 1\cdot 8 + 4\cdot 1\cdot 3 + 2\cdot 1\cdot 6\end{array}\right]$$

$$= \frac{1}{48}\left(6 + 12 + 6 + 12 + 12\right) = 1$$

$$\#\text{ of times } E_g \Big\} = \frac{1}{\ }\Big[6\cdot 2\cdot 1 + 0\cdot(-1)(8) + 0\cdot 0\cdot 6 + 2\cdot 0\cdot 6 +$$

$$\ldots\ 0(-1)\cdot 8 +$$

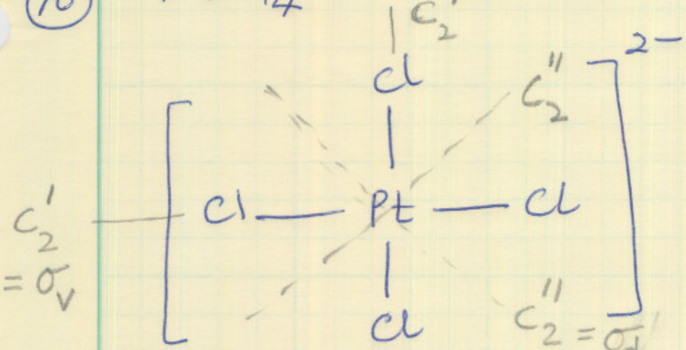
$$= \frac{1}{48}\left(12 + 12 + 24\right) = 1$$

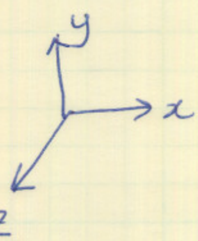
$$\left.\begin{array}{l}\#\text{ of times } T_{1u} \text{ is} \\ \text{in } \Gamma\end{array}\right\} = \frac{1}{48}\Big[3.6.1 + 0.0.8 + 0.(-1).6 + (2).1.6 + 2(-1).3. + 0.(-3).1 + 0.(-1).6 + 0.0.8 + 4.1.3 + 2.1.6\Big]$$

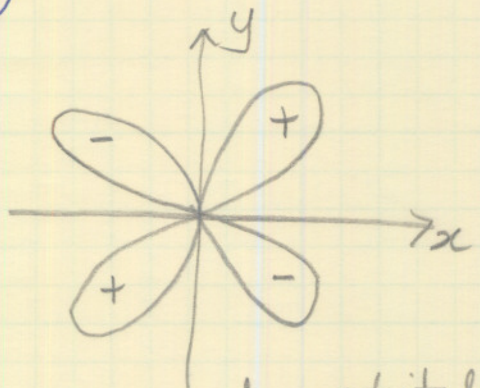
$$= \frac{1}{48}\left(18 + 12 - 6 + 12 + 12\right) = 1$$

$$\Gamma = A_{1g} + E_g + T_{1u}$$

(16) $PtCl_4^{2-}$ ion, has D_{4h} symmetry





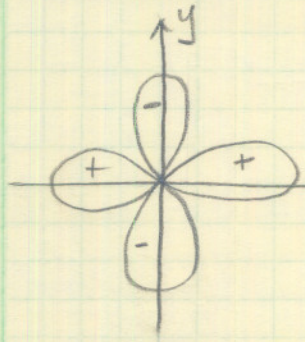


d_{xy} orbital

Check how the d_{xy} orbital transforms under the symmetry operations of the D_{4h} point group.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
d_{xy}	1	−1	1	−1	1	1	−1	1	−1	1

It is clear from the above that the d_{xy} orbital has B_{2g} symmetry.



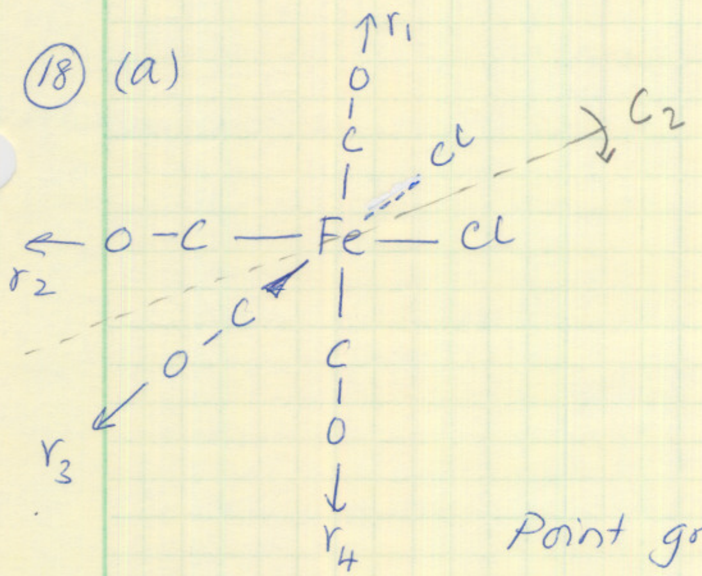
$d_{x^2-y^2}$

Check how the $d_{x^2-y^2}$ orbital transforms under the symmetry operations of the D_{4h} point group.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$d_{x^2-y^2}$	1	−1	1	1	−1	1	−1	1	1	−1

It is clear from the above that the $d_{x^2-y^2}$ orbital has B_{1g} symmetry.

(18) (a)



Select the basis set to represent the C−O stretching vibrations (vectors r_1, r_2, r_3 and r_4).
(You could also just take the four arrows as your basis set).

Point group is C_{2v}.
Generate Γ to represent the basis set in the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	
B_1	1	−1	1	−1	x
B_2	1	−1	−1	1	y
Γ	4	0	2	2	

Reduce Γ to its irreducible components

$$\#\text{ of times } A_1 \text{ is in } \Gamma = \frac{1}{4}\left[4.1.1 + 2.1.1 + 2.1.1\right] = 2$$

$$\#\text{ of times } B_1 \text{ is in } \Gamma = \frac{1}{4}\left[4.1.1 + 0.(-1).1 + 2.1.1. + 2.(-1)(1)\right] = 1$$

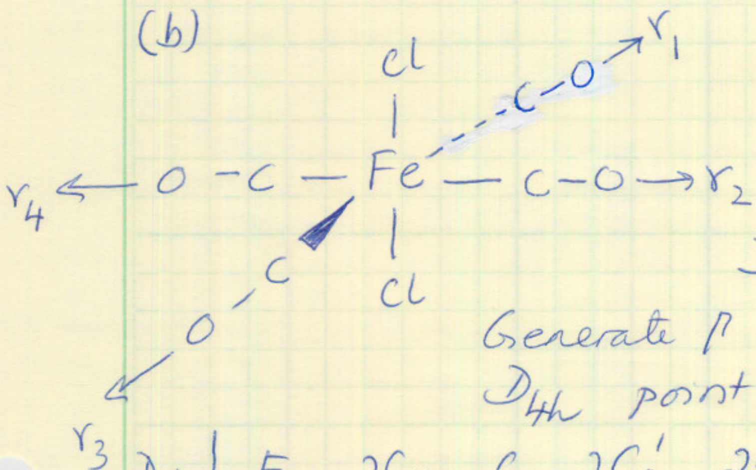
$$\#\text{ of times } B_2 \text{ is in } \Gamma = \frac{1}{4}\left[4.1.1 + 0(-1).1 + 2(-1)(1) + 2(1)(1)\right] = 1$$

$$\Gamma = \underbrace{2A_1 + B_1 + B_2}_{}$$

4 vibrational modes

two with A_1 symmetry — IR active (transforms as z)
one with B_1 symmetry — IR active (transforms as x)
one with B_2 symmetry — IR active (transforms as y)

(b)



The vectors r_1, r_2, r_3, r_4 represent the C—O stretching vibrations (basis set).

D_{4h} point group.

Generate Γ to represent the basis set in the D_{4h} point group.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

$$\left.\begin{array}{l}\text{\# of times } A_{1g} \text{ is}\\ \text{in } \Gamma\end{array}\right\} = \frac{1}{16}\Big[4\cdot1\cdot1 + 0\cdot1\cdot2 + 0\cdot1\cdot1 + 2\cdot1\cdot2 + 2\cdot1\cdot0 + 1\cdot1\cdot0 + 2\cdot1\cdot0 + 1\cdot1\cdot4 + 2\cdot2\cdot1 + 2\cdot0\cdot1\Big]$$

$$= \frac{1}{16}\left(4+4+4+4\right) = 1$$

$$\text{\# of times } B_{1g} \text{ is in } \Gamma = \frac{1}{16}\Big(1\cdot1\cdot4 + (-1)\cdot2\cdot0 + 1\cdot1\cdot0 + 2\cdot1\cdot2 + 2\cdot(-1)(0) + 1\cdot1\cdot(0) + 2(-1)(0) + (1)(1)4 + 2\cdot1\cdot2 + 2(-1)(0)\Big]$$

$$= \frac{1}{16}\left(4+4+4+4\right) = 1$$

$$\text{\# of times } E_u \text{ is in } \Gamma = \frac{1}{16}\Big(2\cdot1\cdot4 + 0\cdot2\cdot0 + (-2)(1)(0) + 0\cdot2\cdot2 + 0\cdot2\cdot0 + (-2)1\cdot0 + 2\cdot0\cdot0 + 2\cdot1\cdot4 + 0\cdot2\cdot2 + 0\cdot2\cdot0\Big)$$

$$= \frac{1}{16}\left[8+8\right] = 1$$

$$\Gamma = \underbrace{A_{1g} + B_{1g} + E_u}_{\text{4 CO stretching vibrations}}$$

One with A_{1g} symmetry, one with B_{1g} symmetry, two with E_u symmetry.

E_u transforms as (x, y). Hence the two vibrations with E_u symmetry are IR active.

Those vibrations with A_{1g} and B_{1g} symmetries are not IR active –