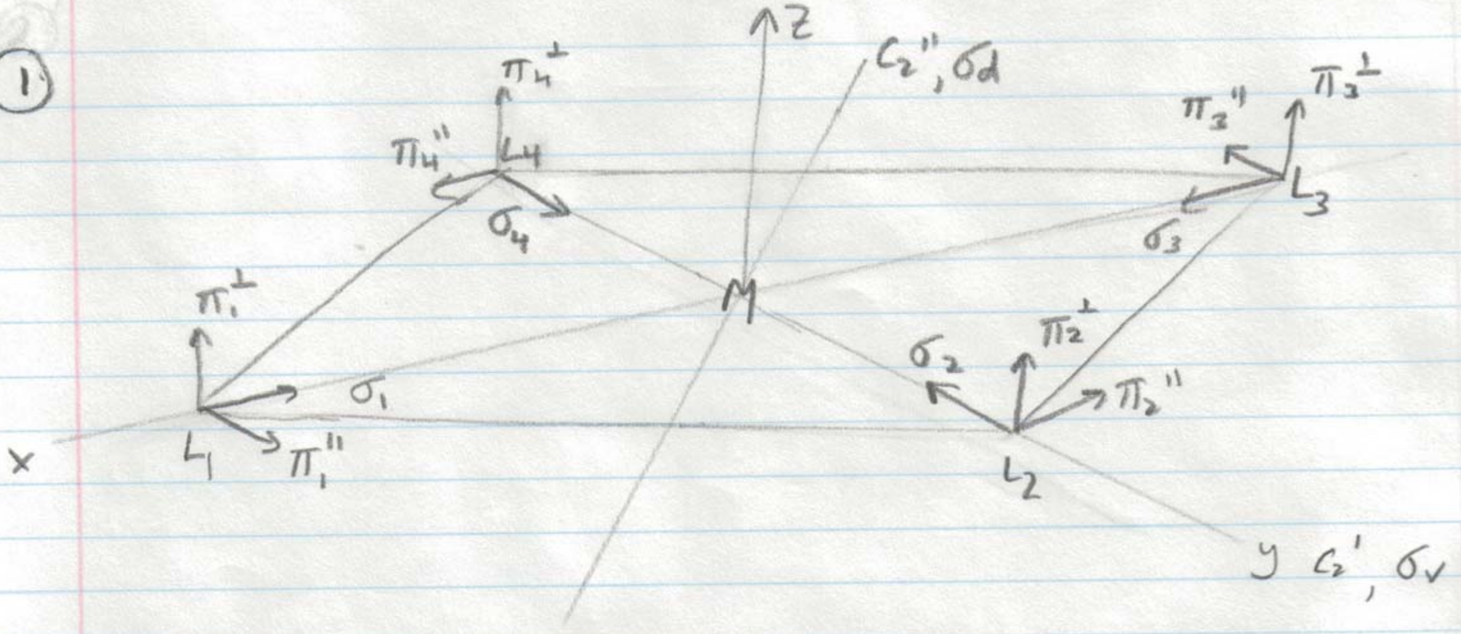
C734b 2008
Solutions Problem Set #5

(1)



a) From character table

$$\Gamma_s = A_{1g}$$
$$\Gamma_p = A_{2u} \oplus E_u$$
$$\Gamma_d = A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$$

b) First, $\pi^{\perp}, \pi^{\parallel}$ orbitals could be considered together but unlike O_h there are no operations in D_{4h} which transform $\pi^{\parallel} \leftrightarrow \pi^{\perp}$. Thus they could be considered separately which is what is done here.

$$\Gamma_\sigma : \chi(\Gamma_\sigma) = \{ \begin{array}{cccccccccc} E & 2C_4 & C_2 & 2C_2' & 2C_2'' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\ 4 & 0 & 0 & 2 & 0 & 0 & 0 & 4 & 2 & 0 \end{array} \}$$

$a_{1g} = 1/16\,[(1)(1)(4) + (2)(1)(2) + (1)(4)(1) + (2)(1)(2)] = 1$
$a_{2g} = 1/16\,[4 - 4 + 4 - 4] = 0$
$b_{1g} = 1/16\,[4 + 4 + 4 + 4] = 1$
$b_{2g} = 1/16\,[4 - 4 + 4 - 4] = 0$
$e_g = 1/16\,[8 + 0 - 8 + 0] = 0$
$a_{1u} = 1/16\,[4 + 4 - 4 - 4] = 0$
$a_{2u} = 1/16\,[4 - 4 - 4 + 4] = 0$
$b_{1u} = 1/16\,[4 + 4 - 4 - 4] = 0$
$b_{2u} = 1/16\,[4 - 4 - 4 + 4] = 0$
$e_u = 1/16\,[8 + 8] = 1$

$\therefore \Gamma_\sigma = A_{1g} \oplus B_{1g} \oplus E_u$

$$\chi(\Gamma_{\pi^\perp}) = \{ \begin{array}{cccccccccc} E & 2C_4 & C_2 & 2C_2' & 2C_2'' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\ 4 & 0 & 0 & -2 & 0 & 0 & 0 & -4 & 2 & 0 \end{array} \}$$

$a_{1g} = 1/16\,[4 - 4 - 4 + 4] = 0$
$a_{2g} = 1/16\,[4 + 4 - 4 - 4] = 0$
$b_{1g} = 1/16\,[4 - 4 - 4 + 4] = 0$
$b_{2g} = 1/16\,[4 + 4 - 4 - 4] = 0$
$e_g = 1/16\,[8 + 0 + 8 + 0] = 1$
$a_{1u} = 1/16\,[4 - 4 + 4 - 4] = 0$
$a_{2u} = 1/16\,[4 + 4 + 4 + 4] = 1$
$b_{1u} = 1/16\,[4 - 4 + 4 - 4] = 0$
$b_{2u} = 1/16\,[4 + 4 + 4 + 4] = 1$
$e_u = 1/16\,[8 - 8] = 0$

$\therefore \Gamma_{\pi^\perp} = A_{2u} \oplus B_{2u} \oplus E_g$

Hilroy

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\chi(\Gamma_{\pi''}) = \{$	4	0	0	-2	0	0	0	4	-2	0 $\}$

$\therefore\ a_{1g} = 1/16\,[4-4+4-4] = 0$

$a_{2g} = 1/16\,[4+4+4+4] = 1$

$b_{1g} = 1/16\,[4-4+4-4] = 0$

$b_{2g} = 1/16\,[4+4+4+4] = 1$

$e_g = 1/16\,[8-8] = 0$

$a_{1u} = 1/16\,[4-4-4+4] = 0$

$a_{2u} = 1/16\,[4+4-4-4] = 0$

$b_{1u} = 1/16\,[4-4-4+4] = 0$

$b_{2u} = 1/16\,[4+4-4-4] = 0$

$e_u = 1/16\,[8+8] = 1$

$\therefore\ \Gamma_{\pi''} = A_{2g} \oplus B_{2g} \oplus E_u$.

$\therefore$ metal

s A_{1g}

p $A_{2u} \oplus E_u$

d $A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$

ligand

$p\sigma$: $A_{1g} \oplus B_{1g} \oplus E_u$

$p\pi^{\perp}$: $A_{2u} \oplus B_{2u} \oplus E_g$

$p\pi''$: $A_{2g} \oplus B_{2g} \oplus E_u$

Possible combinations of metal and ligand orbitals.

1.) $a_1 s + c_1 d_{z^2} + b_1 p\sigma$ — A_{1g}

2.) $a_2 d_{x^2-y^2} + b_2 p\sigma$ — B_{1g}

3.) $a_3 p_x + b_3 p\sigma$
$a_4 p_y + b_4 p\sigma$ $\Big\}$ E_u

4.) $a_5 p_z + b_5 p\pi^{\perp}$ — A_{2u}

5.) $b_6 p\pi^{\perp}$ — B_{2u} (non-bonding)

6.) $a_6 d_{xz} + b_7 p\pi^{\perp}$
$a_7 d_{yz} + b_8 p\pi^{\perp}$ $\Big\}$ E_g

7.) $b_9 p\pi''$ — A_{2g} (non-bonding)

8.) $a_8 d_{xy} + b_{10} p\pi''$ — B_{2g}

9.) $a_9 p_x + b_{11} p\pi''$
$a_{10} p_y + b_{12} p\pi''$ $\Big\}$ E_u

If coefficients have same sign $\Rightarrow$ bonding ; opposite signs $\Rightarrow$ antibonding.

d) Projection Operator: $P_j \propto \sum_{\hat{T}} \chi_j(T)^* \hat{T}$

1) σ-bonding orbitals: using σ_1 as starting f^n

i) $a_{1g} = N(A_{1g})[\underset{E}{(1)\sigma_1} + \underset{2C_{4z}}{(1)(\sigma_2+\sigma_4)} + \underset{C_{2z}}{(1)\sigma_3} + \underset{2C_2'}{(1)(\sigma_1+\sigma_3)} + \underset{2C_2''}{(1)(\sigma_2+\sigma_4)} + \underset{i}{(1)\sigma_3}$

$+ \underset{2S_4}{(1)(\sigma_2+\sigma_4)} + \underset{\sigma_h}{(1)\sigma_1} + \underset{2\sigma_v}{(1)(\sigma_1+\sigma_3)} + \underset{2\sigma_d}{(1)(\sigma_2+\sigma_4)}]$

$= N(A_{1g})[4\sigma_1 + 4\sigma_2 + 4\sigma_3 + 4\sigma_4] = N'(A_{1g})[\sigma_1+\sigma_2+\sigma_3+\sigma_4]$

in ZOA $\quad N'^2[1+1+1+1] = 1 \Rightarrow N' = 1/2$

$\therefore a_{1g} = \frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$

ii) $b_{1g} = N(B_{1g})[\sigma_1 - (\sigma_2+\sigma_4) + \sigma_3 + (\sigma_1+\sigma_3) - (\sigma_2+\sigma_4) + \sigma_3 - (\sigma_2+\sigma_4) + \sigma_1$
$+ (\sigma_1+\sigma_3) - (\sigma_2+\sigma_4)]$

$= 4N(B_{1g})[\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) = N'(B_{1g})(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
in ZOA $\quad N' = 1/2 \quad \therefore b_{1g} = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$

iii) $e_u = N(E_u)[2\sigma_1 - 2\sigma_3 - 2\sigma_3 + 2\sigma_1] = N(E_u)[4\sigma_1 - 4\sigma_3] = N'(E_u)(\sigma_1 - \sigma_3]$
in ZOA $\quad N' = 1/\sqrt{2} \quad \therefore e_u(1) = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3)$

by cyclic permutation $\quad e_u(2) = 1/\sqrt{2}(\sigma_2 - \sigma_4)$

2) i) $p\pi^\perp$ - bonding orbitals. Using $\pi_1^\perp$ as starting f^n

$a_{2u} = N(A_{2u})[\pi_1^\perp + (\pi_2^\perp + \pi_4^\perp) + \pi_3^\perp - (-\pi_1^\perp - \pi_3^\perp) - (-\pi_2^\perp - \pi_4^\perp) - (-\pi_3^\perp)$
$- (-\pi_2^\perp - \pi_4^\perp) - (-\pi_1^\perp) + (\pi_3^\perp + \pi_1^\perp) + (\pi_2^\perp + \pi_4^\perp)]$

$= N(A_{2u})[4\pi_1^\perp + 4\pi_2^\perp + 4\pi_3^\perp + 4\pi_4^\perp] = N'(A_{2u})[\pi_1^\perp + \pi_2^\perp + \pi_3^\perp + \pi_4^\perp]$

in ZOA: $a_{2u} = \frac{1}{2}(\pi_1^\perp + \pi_2^\perp + \pi_3^\perp + \pi_4^\perp)$

ii) $b_{2u} = N(B_{2u})\,[\pi_1^{\perp} - (\pi_2^{\perp} + \pi_4^{\perp}) + \pi_3^{\perp} - (-\pi_1^{\perp} - \pi_3^{\perp}) + (-\pi_2^{\perp} - \pi_4^{\perp}) - (-\pi_3^{\perp})$
$+ (-\pi_2^{\perp} - \pi_4^{\perp}) - (-\pi_1^{\perp}) + (\pi_3^{\perp} + \pi_1^{\perp}) - (\pi_2^{\perp} + \pi_4^{\perp})\,]$

$= N(B_{2u})\,[4\pi_1^{\perp} - 4\pi_2^{\perp} + 4\pi_3^{\perp} - 4\pi_4^{\perp}] = N'(B_{2u})(\pi_1^{\perp} - \pi_2^{\perp} + \pi_3^{\perp} - \pi_4^{\perp})$

in ZOA $\quad b_{2u} = \frac{1}{2}[\pi_1^{\perp} - \pi_2^{\perp} + \pi_3^{\perp} - \pi_4^{\perp}]$

iii) $e_g(1) = N(E_g)\,[2\pi_1^{\perp} - 2\pi_3^{\perp} + 2(-\pi_3^{\perp}) - 2(-\pi_1^{\perp})] = N(E_g)[4\pi_1^{\perp} - 4\pi_3^{\perp}]$
$= N'(E_g)[\pi_1^{\perp} - \pi_3^{\perp}] \Rightarrow$ in ZOA $\quad e_g(1) = \frac{1}{\sqrt{2}}(\pi_1^{\perp} - \pi_3^{\perp})$

by cyclic permutation $\quad e_g(2) = \frac{1}{\sqrt{2}}(\pi_2^{\perp} - \pi_4^{\perp})$

3) $p\pi^{\parallel}$ - bonding orbitals ; using $\pi_1^{\parallel}$ as starting f^n.

i) $a_{2g} = N(A_{2g})[\pi_1^{\parallel} + (\pi_2^{\parallel} + \pi_4^{\parallel}) + (\pi_3^{\parallel}) - (-\pi_1^{\parallel} - \pi_3^{\parallel}) - (-\pi_2^{\parallel} - \pi_4^{\parallel}) + \pi_3^{\parallel} + (\pi_2^{\parallel} + \pi_4^{\parallel})$
$+ \pi_1^{\parallel} - (-\pi_3^{\parallel} - \pi_1^{\parallel}) - (-\pi_2^{\parallel} - \pi_4^{\parallel})\,]$

$= N(A_{2g})\,[4\pi_1^{\parallel} + 4\pi_2^{\parallel} + 4\pi_3^{\parallel} + 4\pi_4^{\parallel}] = N'(A_{2g})\,[\pi_1^{\parallel} + \pi_2^{\parallel} + \pi_3^{\parallel} + \pi_4^{\parallel}]$

in ZOA: $\quad a_{2g} = \frac{1}{2}[\pi_1^{\parallel} + \pi_2^{\parallel} + \pi_3^{\parallel} + \pi_4^{\parallel}]$

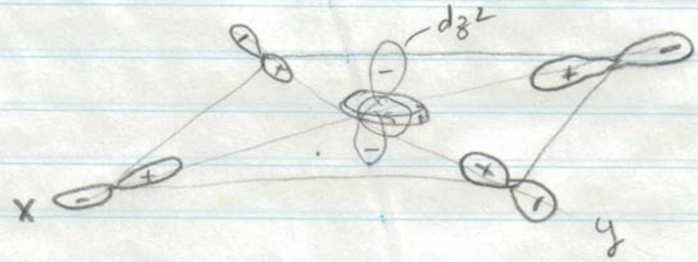
ii) $b_{2g} = N(B_{2g})(\pi_1^{\parallel} - (\pi_2^{\parallel} + \pi_4^{\parallel}) + \pi_3^{\parallel} - (-\pi_1^{\parallel} - \pi_3^{\parallel}) + (-\pi_2^{\parallel} - \pi_4^{\parallel}) + (\pi_3^{\parallel}) - (\pi_2^{\parallel} + \pi_4^{\parallel})$
$+ \pi_1^{\parallel} - (-\pi_1^{\parallel} - \pi_3^{\parallel}) + (-\pi_4^{\parallel} - \pi_2^{\parallel})\,]$
$= N(B_{2g})[4\pi_1^{\parallel} - 4\pi_2^{\parallel} + 4\pi_3^{\parallel} - 4\pi_4^{\parallel}] = N'(B_{2g})(\pi_1^{\parallel} - \pi_2^{\parallel} + \pi_3^{\parallel} - \pi_4^{\parallel}]$
in ZOA: $\quad b_{2g} = \frac{1}{2}(\pi_1^{\parallel} - \pi_2^{\parallel} + \pi_3^{\parallel} - \pi_4^{\parallel})$

iii) $e_u(1) = N(E_u)[2\pi_1^{\parallel} - 2\pi_3^{\parallel} - 2\pi_3^{\parallel} + 2\pi_1^{\parallel}] = N(E_u)[4\pi_1^{\parallel} - 4\pi_3^{\parallel}] = N'(E_u)[\pi_1^{\parallel} - \pi_3^{\parallel}]$
in ZOA $\quad e_u(1) = 1/\sqrt{2}\,(\pi_1^{\parallel} - \pi_3^{\parallel})$

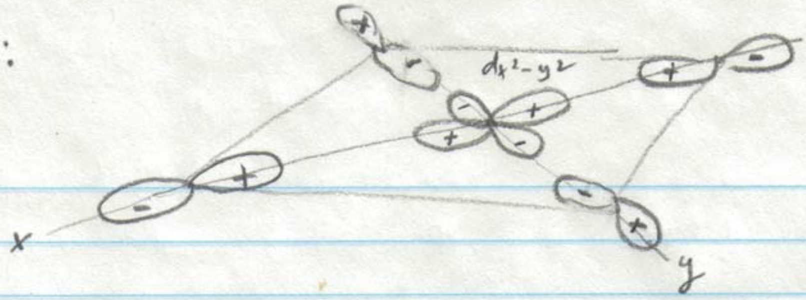
by cyclic permutation $\quad e_u(2) = 1/\sqrt{2}\,(\pi_2^{\parallel} - \pi_4^{\parallel})$

Sketches

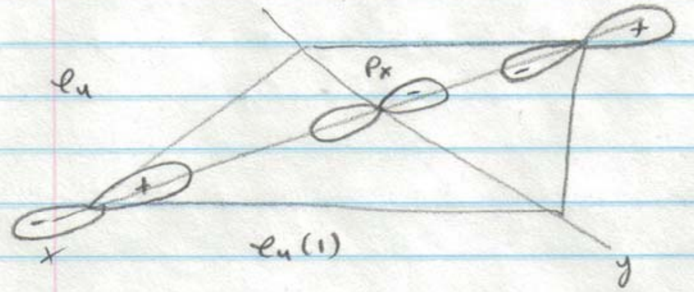
1.) σ - bonding. $\quad a_{1g}$



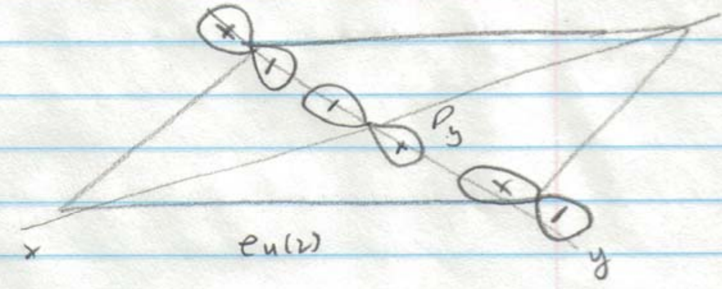
b_{1g} :



e_u



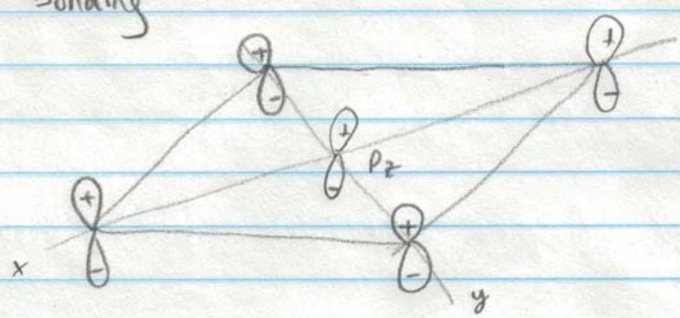
$e_u(1)$



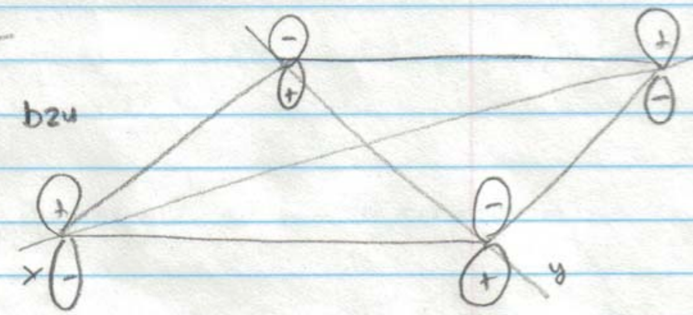
$e_u(2)$

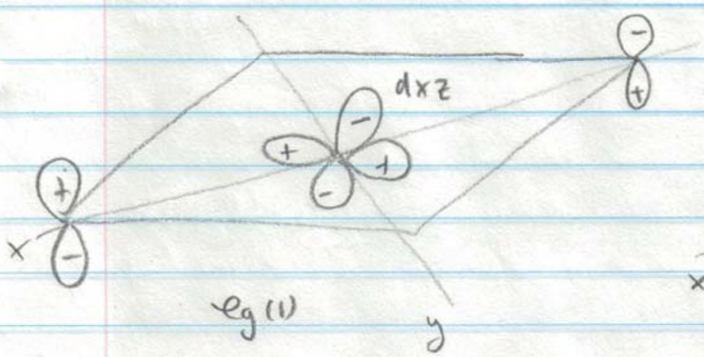
2.) $\pi^{\perp}$ - bonding

a_{2u}

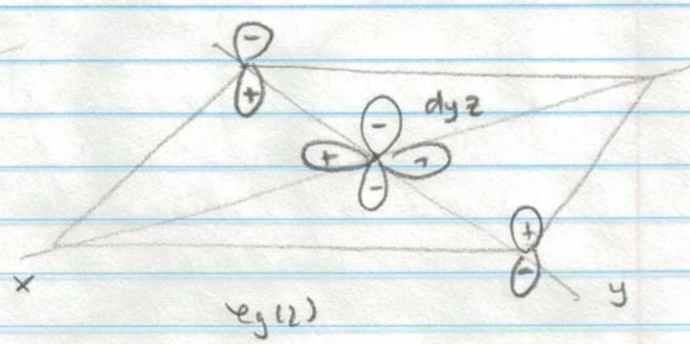


b_{2u}





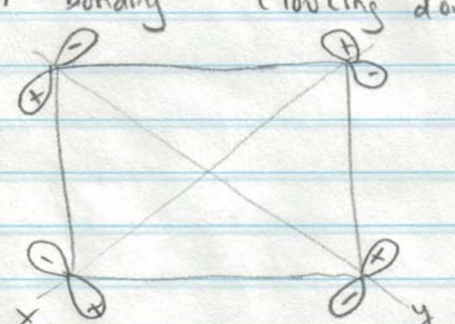
$e_g(1)$



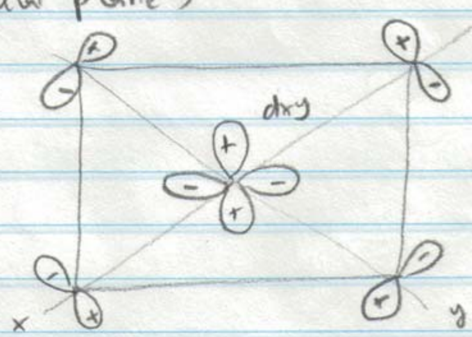
$e_g(2)$

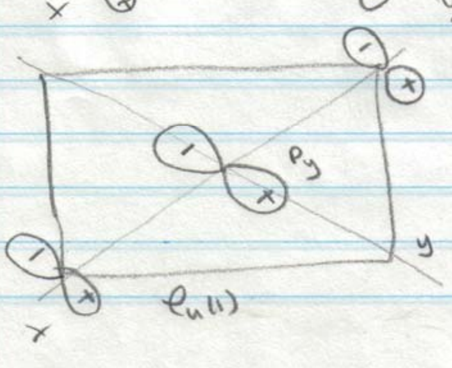
3.) $\pi^{\parallel}$ - bonding (looking down molecular plane)

a_{2g} :

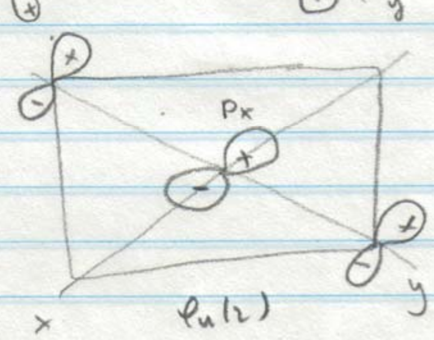


b_{2g} :



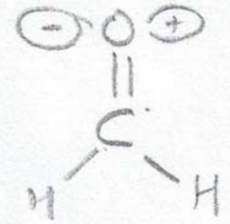


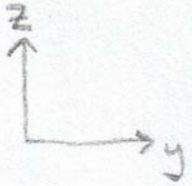
$e_u(1)$



$e_u(2)$

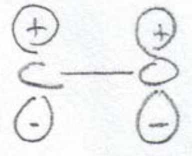
(2)





C_{2v}

a) According to character table p_y transforms as y which transforms as B_2

for π, π^* use  as basis set.

C_{2v}	E	C_{2z}	$\sigma_v(xz)$	$\sigma_v'(yz)$
$p_x(C)$	1	-1	1	-1
$p_x(O)$	1	-1	1	-1
Γ_π	2	-2	2	-2

Reduction in C_{2v} yields $\Gamma_\pi = 2B_1$

$\therefore$ π transforms as B_1 and π^* transforms as B_1

b) $\pi^* \leftarrow n$ transition symmetry allowed by electric dipole if $B_1 \otimes B_2$ contains x, y and/or z

$$\chi(B_1 \otimes B_2) = \begin{array}{cccc} E & C_2 & \sigma_v & \sigma_v' \\ \{1 & 1 & -1 & -1\} \end{array} = A_2 \not\subset x, y, z$$

$\therefore$ transition is not symmetry allowed.

note: in reality $b_2^2 \to b_1 b_2$

$\Rightarrow {}^1A_1 \to {}^1A_2$

assuming $\Delta S = 0$

$A_2 \otimes A_1 = A_2 \not\subset \Gamma_{x,y,z}$

$\therefore$ forbidden

c) Use short cut method. $\Gamma_{3N} = \chi_{\Gamma_{xyz}} \cdot N_R$

$$\begin{array}{lcccc} & E & C_2 & \sigma_v & \sigma_v' \\ \Gamma_{xyz} = \{ & 3 & -1 & 1 & 1 \} \\ \therefore \Gamma_{3N} = \{ & 12 & -2 & 2 & 4 \} \end{array}$$

reduction in C_{2v} $\rightarrow$ $\Gamma_{3N} = 4A_1 \oplus A_2 \oplus 3B_1 \oplus 4B_2$

$\Gamma_{trans} = A_1 \oplus B_1 \oplus B_2$; $\Gamma_{ROT} = A_2 \oplus B_1 \oplus B_2$

from character table.

$\therefore \Gamma_{3N-6} = 3A_1 \oplus B_1 \oplus 2B_2 \quad \equiv$ 6 normal modes.

d) ground vibration wavef^n is totally symmetric $\Rightarrow$ it transforms as A_1

$\therefore$ electronic transition becomes allowed vibronically if

$$\Gamma(Q_k) \otimes B_1 \otimes B_2 \quad \text{contains } x, y, \text{ or } z$$

$$\Rightarrow \Gamma(Q_k) \otimes A_2 \text{ contains } x, y, z$$

or if $\Gamma(A_2) \otimes \Gamma(x,y,z) \subset \Gamma(Q_k)$

$\therefore$ $A_1 \otimes A_2 = A_2 \quad \not\subset \; x, y, z \Rightarrow A_1$ modes don't work.

$B_1 \otimes A_2 = B_2$ which transforms as y

$B_2 \otimes A_2 = B_1$ which transforms as x

$\therefore B_1, B_2$ modes work.

4 a) D_{3h}: $\Gamma_{xyz} = E' \oplus A_2''$

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	$h=12$
$\therefore \Gamma_{xyz}$	3	0	−1	1	−2	1	
$\Gamma_{3N} = \Gamma_{xyz} \cdot N_R$	9	0	−1	3	0	1	

Reduction in D_{3h}

$a_1' = \frac{1}{12}[9\times1\times1 + 3\times-1\times1 + 1\times3\times1 + 3\times1\times1] = 1$

$a_2' = \frac{1}{12}[9\times1\times1 + 3\times-1\times-1 + 1\times3\times1 + 3\times1\times-1] = 1$

$e' = \frac{1}{12}[9\times2\times1 + 1\times3\times2] = 2$

$a_1'' = \frac{1}{12}[9\times1\times1 + 3\times-1\times1 + 1\times3\times-1 + 3\times1\times-1] = 0$

$a_2'' = \frac{1}{12}[9\times1\times1 + 3\times-1\times-1 + 1\times3\times-1 + 3\times1\times1] = 1$

$e'' = \frac{1}{12}[9\times1\times2 + 1\times3\times-2] = 1$

$\therefore \Gamma_{3N} = A_1' \oplus A_2' \oplus 2E' \oplus A_2'' \oplus E''$

$- \Gamma_{xyz} = E' \oplus A_2$; $- \Gamma_{ROT} = E'' \oplus A_2'$

$\therefore \Gamma_{3N-6} = A_1' \oplus E'$

b) $D_{\infty h}$ $\therefore\ \Gamma_{xyz} = \Sigma_u^+ \oplus \Pi_u$

	E	$2C_\infty^\phi$	$\infty\sigma_v$	i	$2S_\infty^\phi$	∞C_2
Γ_{xyz}	3	$1+2\cos\phi$	1	−3	$-1+2\cos\phi$	−1
$N_R\Gamma_{xyz}$	9	$3+6\cos\phi$	3	−3	$-1+2\cos\phi$	−1
$-\Gamma_{xyz}$	3	$1+2\cos\phi$	1	−3	$-1+2\cos\phi$	−1
$-\Gamma_{R_x,R_y}$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0

$\therefore\ \Gamma_{vib} = \Gamma_{3N} - (5) = 4 \quad 2+2\cos\phi \quad 2 \quad -2 \quad 2\cos\phi \quad 0$

by inspection:

$\Pi_u =$	2	$2\cos\phi$	0	−2	$2\cos\phi$	0
$\Sigma_u^+ =$	1	1	1	−1	−1	−1
$\Sigma_g^+ =$	1	1	1	1	1	1
	4	$2+2\cos\phi$	2	−2	$2\cos\phi$	0

$\therefore\ \Gamma_{vib} = \Sigma_g^+ \oplus \Sigma_u^+ \oplus \Pi_u.$

c) C_{2v} : $\Gamma_{xyz} = A_1 \oplus B_1 \oplus B_2$

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{xyz}	3	−1	1	1
$\Gamma_{3N} = \Gamma_{xyz}\cdot N_R$	9	−1	3	1

Reduction in C_{2v}

$a_1 = \frac{1}{4}\left[9\times1\times1 + -1\times1\times1 + 1\times3\times1 + 1\times1\times1\right] = 3$

$a_2 = \frac{1}{4}\left[9\times1\times1 + 1\times-1\times1 + 1\times3\times-1 + 1\times1\times-1\right] = 1$

$b_1 = \frac{1}{4}\left[9\times1\times1 + 1\times-1\times-1 + 1\times3\times1 + 1\times1\times-1\right] = 3$

$b_2 = \frac{1}{4}\left[9\times1\times1 + 1\times-1\times-1 + 1\times3\times-1 + 1\times1\times1\right] = 2$

$\therefore\ \Gamma_{3N} = 3A_1 \oplus A_2 \oplus 3B_1 \oplus 2B_2$

$-\Gamma_{xyz} = A_1 \oplus B_1 \oplus B_2$

$-\Gamma_{ROT} = A_2 \oplus B_1 \oplus B_2$

$\therefore\ \Gamma_{vib} = 2A_1 \oplus B_1.$

) if $\Gamma(Q_k) \subset \Gamma_{xyz} \Rightarrow$ vibrationally allowed.

a) $A_1' \not\subset \Gamma_{x,y,z}$, $E' \subset \Gamma_{xy}$ $\therefore$ only one E' mode allowed

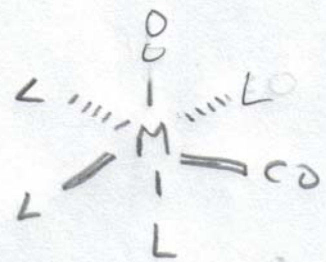
b) $\Sigma_g^+ \not\subset \Gamma_{x,y,z}$, $\Sigma_u^+, \Pi_u \subset \Gamma_{xyz}$ $\therefore$ 2 modes allowed.

c) $A_1 \subset \Gamma_z$ $B_1 \subset \Gamma_x$ $\therefore$ 3 modes allowed.

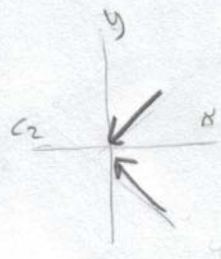
$\therefore$ 3 bands observed $\Rightarrow$ O_3 has C_{2v} structure.

b) for C_{2v} structure
$A_1 \subset \Gamma_{x^2, y^2, z^2}$ $B_1 \subset \Gamma_{xy}$ $\Rightarrow$ would 3
coincident bands in Raman spectrum

④ a) trans - $ML_4(CO)_2$



using CO ≡ stretching vectors



$\equiv C_{2v}$ symmetry

C_{2v}	E	C_2	$\sigma_v(xy)$	$\sigma_v'(xz)$
Γ_{CO}	2	0	2	0

$h = 4$

$a_1 = \frac{1}{4}[(1)(2)(1) + (1)(2)(1)] = 1$

$a_2 = \frac{1}{4}[(1)(2)(1) + (1)(2)(-1)] = 0$

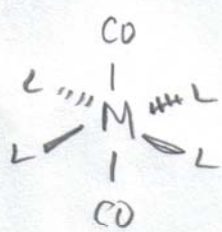
$b_1 = \frac{1}{4}[(1)(2)(1) + (1)(2)(1)] = 1$

$b_2 = \frac{1}{4}[(1)(2)(1) + (1)(2)(-1)] = 0$

$\therefore \Gamma_{CO} = a_1 \oplus b_1$

both ir active.

cis - $ML_4(CO)_2$



using CO ≡ stretching vectors

$D_{\infty h}$.

$D_{\infty h}$	E	$2C_\infty^\phi$	...	$\infty\sigma_v$	i	$2S_\infty^\phi$	...	∞C_2
Γ_{CO}	2	2		2	0	0		0

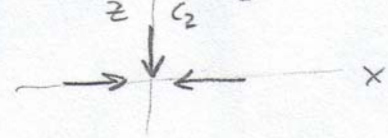
by inspection $\Gamma_{CO} = \Sigma_g^+ \oplus \Sigma_u^+$

Σ_g^+ ir inactive but Σ_u^+ is ir active.

$\therefore$ trans will have 2 modes but cis will have one.

(4) b) fac - $ML_3(CO)_3$ when examing the CO stretching modes only has C_{3v} symmetry (modes represented by arrows)

while mer - $ML_3(CO_3)$ has C_{2v} symmetry



fac - $ML_3(CO)_3$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{CO}	3	0	1

$h = 6$

$$\therefore a_1 = \frac{1}{6}[(1)(3)(1) + (3)(1)(1)] = 1$$

$$a_2 = \frac{1}{6}[(1)(3)(1) + (3)(1)(-1)] = 0$$

$$e = \frac{1}{6}[(1)(3)(2) + (3)(1)(0)] = 1$$

$$\therefore \Gamma_{CO} = a_1 \oplus e$$

mer - $ML_3(CO)_3$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{CO}	3	1	3	1

$h = 4$

$$a_1 = \frac{1}{4}[(1)(3)(1) + (1)(1)(1) + (1)(3)(1) + (1)(1)(1)] = 2$$

$$a_2 = \frac{1}{4}[(1)(3)(1) + (1)(1)(1) + (1)(3)(-1) + (1)(1)(-1)] = 0$$

$$b_1 = \frac{1}{4}[(1)(3)(1) + (1)(1)(-1) + (1)(3)(1) + (1)(1)(-1)] = 1$$

$$b_2 = \frac{1}{4}[(1)(3)(1) + (1)(1)(-1) + (1)(3)(-1) + (1)(1)(1)] = 0$$

$$\therefore \Gamma_{CO} = 2a_1 \oplus b_1$$

From character table.

a_1 and e modes are both IR active $\Rightarrow$ would see 2 bands for fac - $ML_3(CO)_3$

a_1 and b_1 modes are both IR active $\Rightarrow$ would see 3 bands for mer - $ML_3(CO)_3$.