(15) **Today**

4.4 Uses of Character Tables

Next Class (16)

4.4 Uses of Character Tables

(17) **Second Class from Today**

5.1 Formation of Molecular Orbitals

5.2 Homonuclear Diatomic Molecules

Third Class from Today (18)

5.2 Homonuclear Diatomic Molecules

5.3 Heteronuclear Diatomic Molecules

IR active vibrations in H_2O

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
Γ	9	-1	3	1		

reducible representations

summary of all the symmetry associated with the movement of the atoms in H_2O

Find which irreducible representations to find symmetry for individual motions not as a group order = 1 + 1 + 1 + 1 = the number of operations in all classes

number of irreducible representations of a given type needed = $^1/_{order}\ \Sigma_{classes}$ [(# operations in class)(χ of the irreducible representation)(χ of the reducible representation)]

$n(A_1) = 1/4 \cdot [(1)(1)(9) + (1)(1)(-1) + (1)(1)(3) + (1)(1)(1)]$

$n(A_1) = 3$

C_{2v}	1 E	1 C_2	1 $\sigma_v(xz)$	1 $\sigma_v(yz)$		
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
Γ	9	-1	3	1		

order = $1^2 + 1^2 + 1^2 + 1^2$ = sum of the squares of the χ under E number of irreducible representations of a given type needed = $^1/_{order}\ \Sigma_{classes}$ [(# operations in class)(χ of the irreducible representation)(χ of the reducible representation)]

n must be a whole #
if it's not, double check your math

$$n(A_2) = {}^1/_4 \cdot [(1)(1)(9) + (1)(1)(-1) + (1)(-1)(3) + (1)(-1)(1)]$$

9 −1 −3 −1

9−5 = 4

C_{2v}	1 E	1 C_2	1 $\sigma_v(xz)$	1 $\sigma_v(yz)$		
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
Γ	9	-1	3	1		

$n(A_2) = 1$

$$\text{number of irreducible representations of a given type needed} = {}^{1}/_{\text{order}} \Sigma_{\text{classes}} \left[\left(\begin{array}{c} \# \\ \text{operations} \\ \text{in class} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{irreducible} \\ \text{representation} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{reducible} \\ \text{representation} \end{array} \right) \right]$$

$$n(B_1) = {}^{1}/\quad \bullet [(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )]$$

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
Γ	9	-1	3	1		

$$\text{number of irreducible representations of a given type needed} = {}^{1}/_{\text{order}}\, \Sigma_{\text{classes}} \left[\left(\begin{array}{c}\#\\ \text{operations}\\ \text{in class}\end{array}\right) \left(\begin{array}{c}\chi \text{ of the}\\ \text{irreducible}\\ \text{representation}\end{array}\right) \left(\begin{array}{c}\chi \text{ of the}\\ \text{reducible}\\ \text{representation}\end{array}\right) \right]$$

$$n(B_2) = {}^{1}/\quad \bullet [(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )]$$

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
Γ	9	-1	3	1		

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
Γ	9	-1	3	1		

if we had an A_2 vibration it would be IR in active

$\Gamma = 3A_1 + A_2 + 3B_1 + 2B_2$

all possible motions = vibration + translation + rotation

move along x, y, + z axes

number of vibrational modes = (# of ways of moving) − (translational movement) − (rotational movement)

~~A_1~~ A_1 A_1 ~~A_1~~ + ~~B_1~~ + ~~B_2~~   ~~A_2~~ + ~~B_1~~ + ~~B_2~~

~~A_2~~

~~B_1~~ ~~B_1~~ B_1

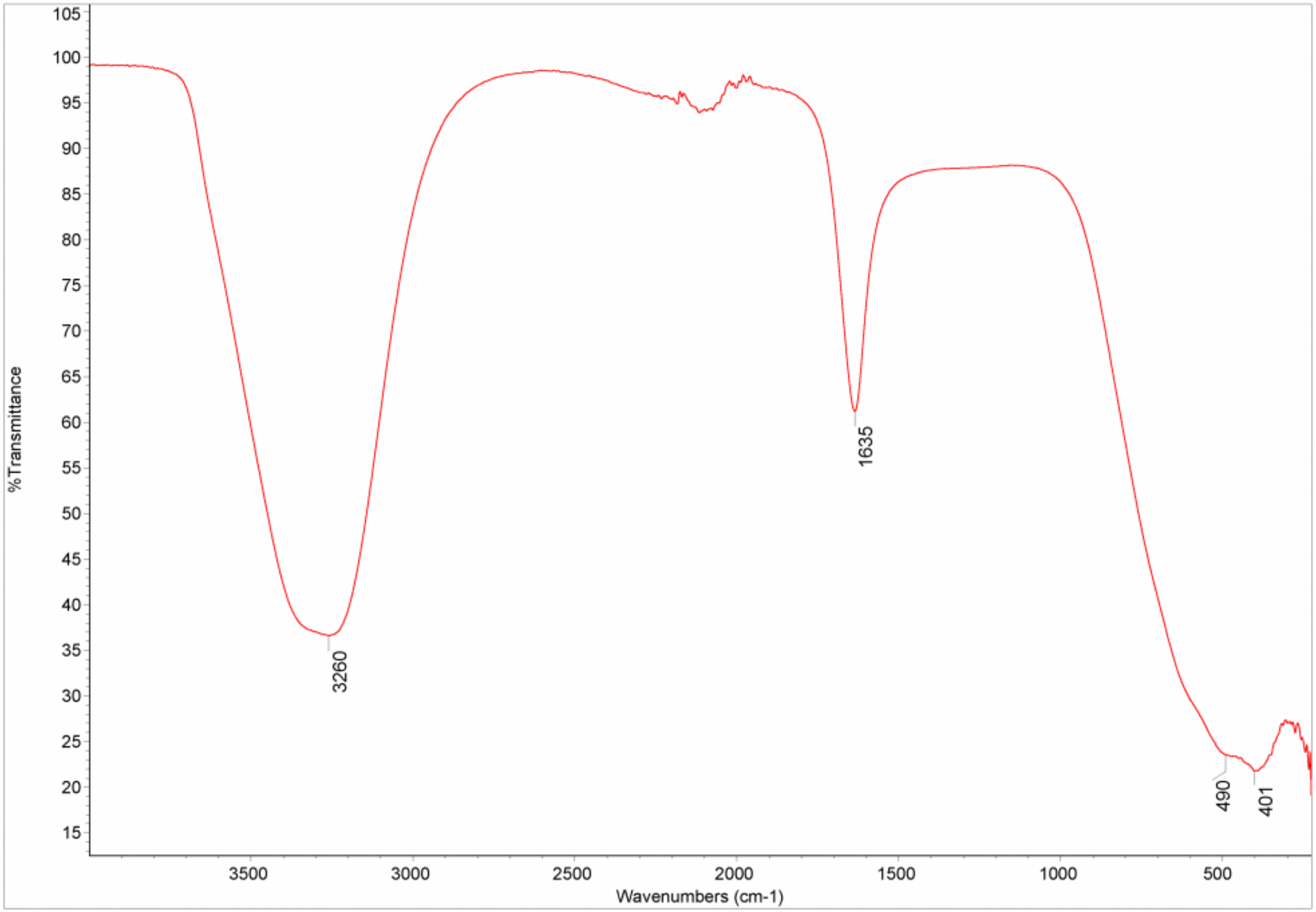
~~B_2~~ ~~B_2~~

3 IR active vibrations

3 peaks in IR spectrum

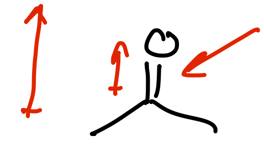
$2A_1 + B_1$ symmetry of vibrational modes

Summary IR Active Vibations in H_2O



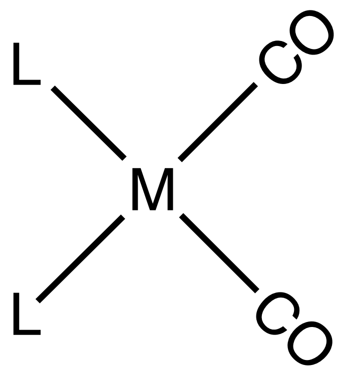
https://spectra.cs.ut.ee/conservation_materials/milli-q-water/

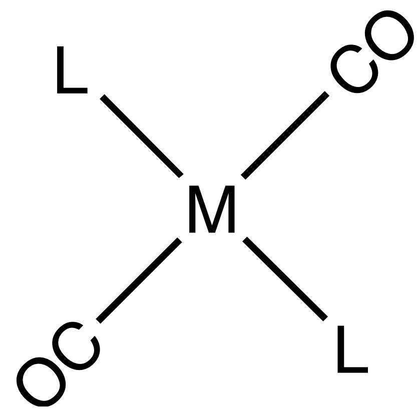
Carbonyl Stretching Bands in Metal Compounds: How Many?

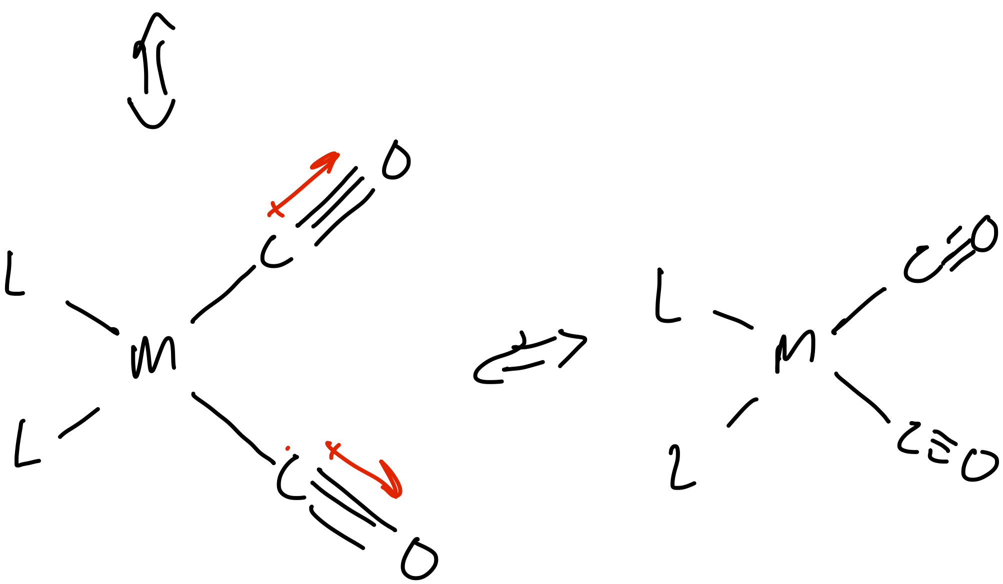


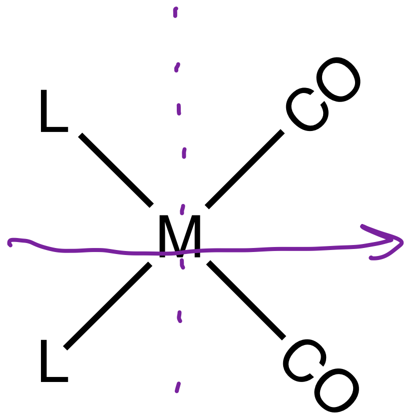
intense 1715 cm^{-1} IR absorbance

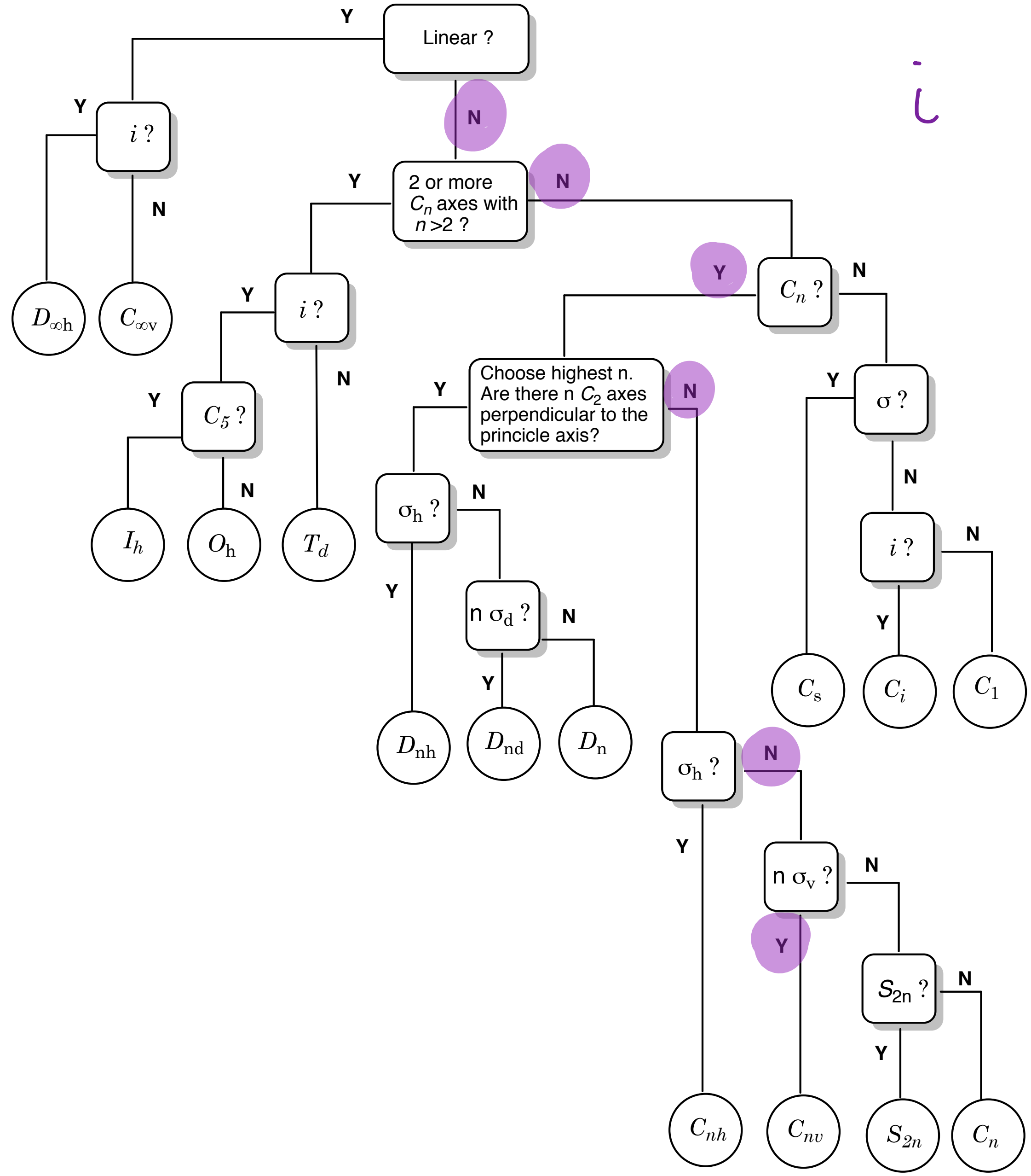
C≡O bonded to metal will stretch + can change the dipole of the molecule











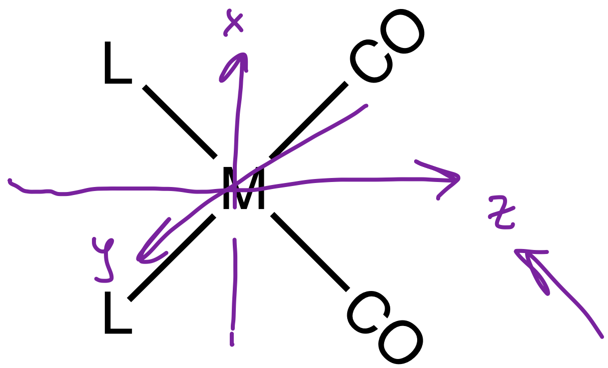
i

σ_h?
cut in half on line ⊥ to C_2? no

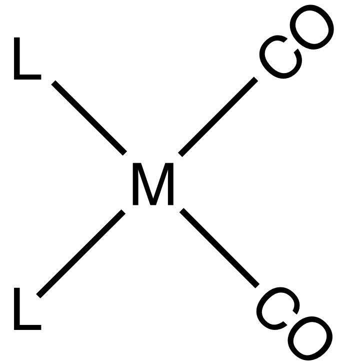
A σ_v contains the principle axis.
are there 2? yes

C_{2v}

C_{2h} principle axis = z axis



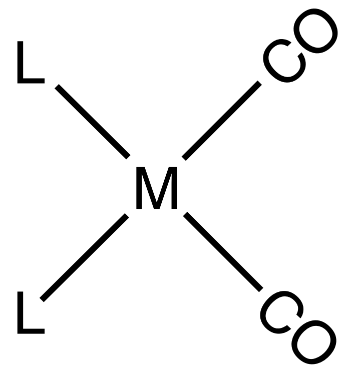
Carbonyl Stretching Bands in Metal Compounds: Determine Reducible Representation



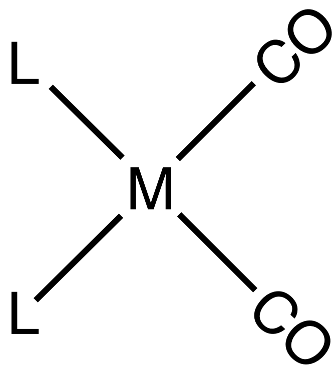
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Γ

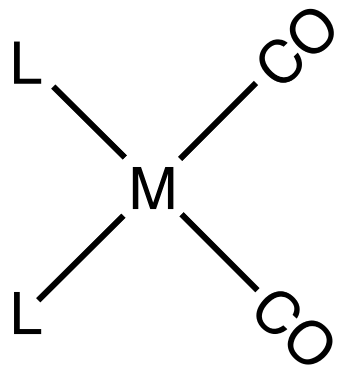
Carbonyl Stretching Bands in Metal Compounds: Determine Irreducible Representations that Combine to Form Reducible Representation

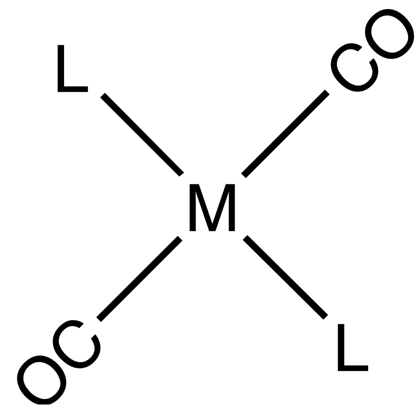


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ	2	0	2	0		



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
Γ	2	0	2	0		
Γ	=	A_1	+	B_1		





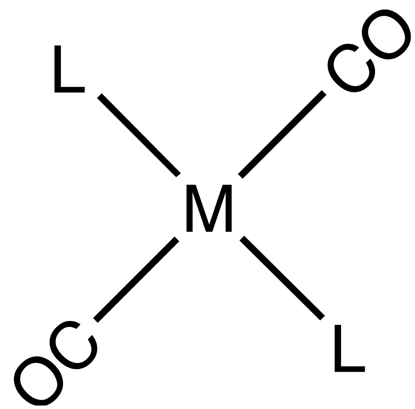
Find Point Group

Assign Axes

Determine Reducible Representation

Determine Irreducible Representations that Combine to Form Reducible Representation

Analyze Results



D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	$\sigma_h(xy)$	$\sigma_d(xz)$	$\sigma_d(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	
Γ	2	0	0	2	0	2	2	0		