This Class

4.4 Uses of Character Tables

Finish IR Water
Do IR of metal carbonyls

Chap 5: MO Theory (maybe)

Next Class

Chap 5: MO Theory

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

$$n(A_1) = {}^{1}/4 \bullet [(1)(1)(9) + (1)(1)(-1) + (1)(1)(3) + (1)(1)(1)]$$

C_{2v}	1E	$1C_2$	$1\sigma_v(xz)$	$1\sigma_v(yz)$		
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		

Irreducible representations for the motions of the atoms in H_2O Section 4.4

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		

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

these represent the symmetry of motions of the atoms in a H_2O molecule

Number of IR Active Vibrations in H_2O

rotation on the z axis

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		

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

$$\text{number of vibrational modes} = \left(\text{\# of ways of moving}\right) - \left(\text{translational movement}\right) - \left(\text{rotational movement}\right)$$

Translational movement: A_1 (movement along z axis) + B_1 (movement along x) + B_2 (movement along y axis)

Rotational movement: A_2 (rotation on z) + B_1 (rotation on y) + B_2 - rotation on x

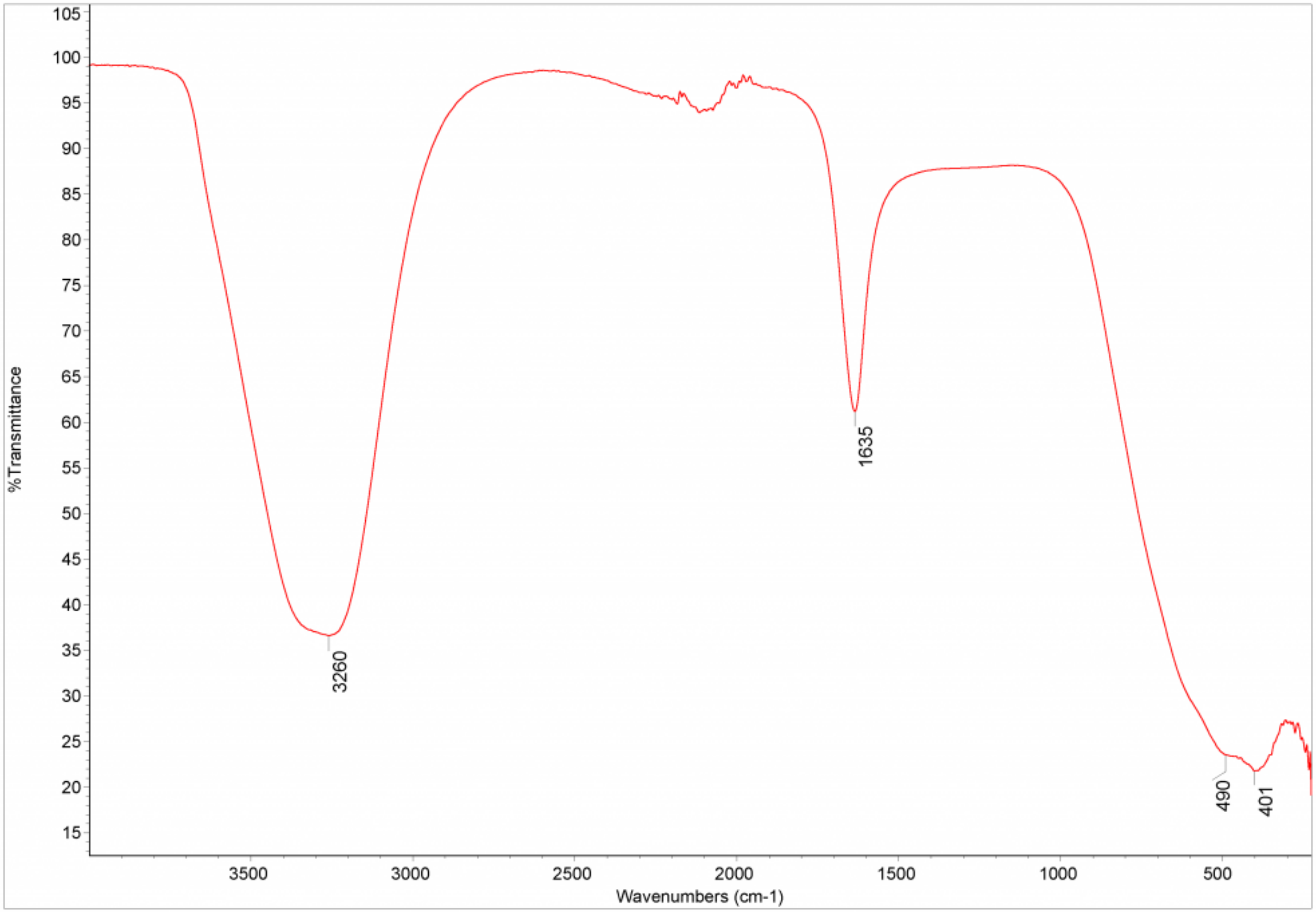
$$= \cancel{3}^{2}A_1 + \cancel{A_2} + \cancel{3}B_1 + \cancel{2B_2} - \cancel{A_1} - \cancel{B_1} - \cancel{B_2} - \cancel{A_2} - \cancel{B_1} - \cancel{B_2}$$

$$= 2A_1 + B_1$$ ✓ ✓

these vibrations move atoms along z axis dipole changing

\# ways of moving atoms = translate - rotate - vibrate

2 A_1 modes + 1 B_1 mode ⇒ 3 peaks



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

Intersted in # IR active vibrations, which are molecular motions

Find Pt Group C_{2v}

Do all symmetry operations on vectors describing motion to determine the reducible representation of the motions

Use linear algebra to find the irreducible representations (to find the symmetry of all the motions)

Analyze

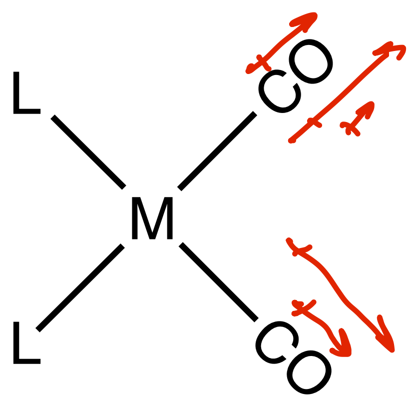
In this case we had to remove rotational motion + translational motion to find vibrational motions

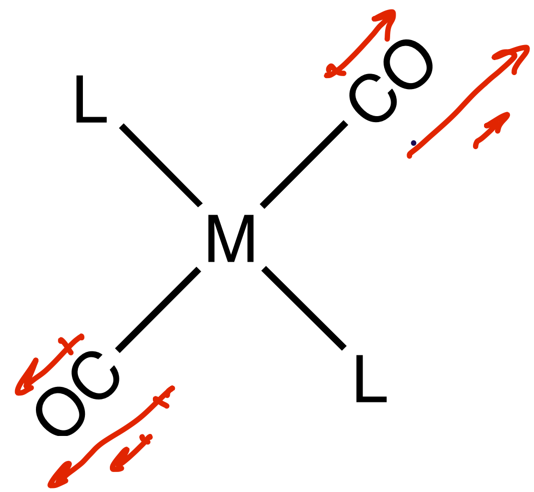
R_x, R_y, + R_z are rotations x, y, z motion along axes

remaining terms were vibrational motion

vibrations on x y z IR Active

How many C≡O stretching peaks will we see in the Infrared spectrum

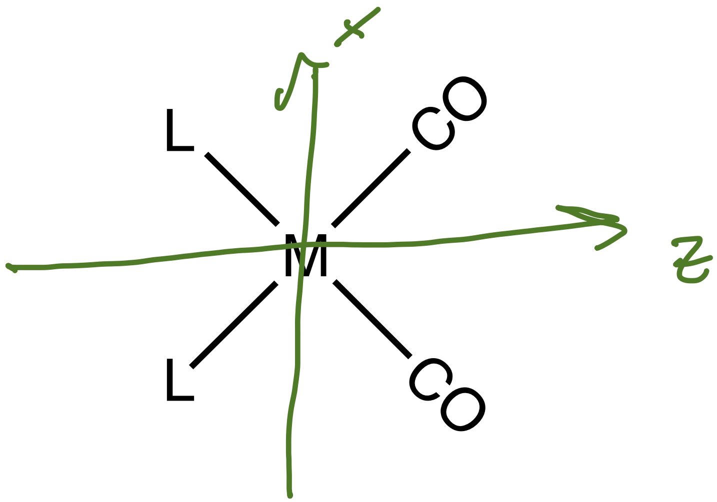


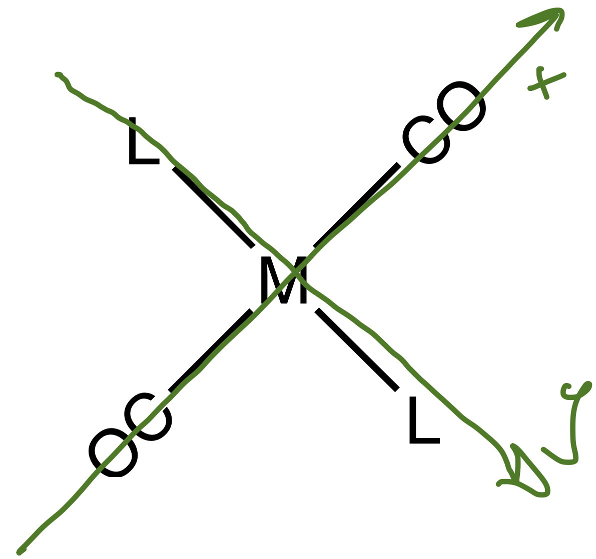


Pt. Group

C_{2v} D_{2h}

Interested in just 2 motions; the stretching of the 2 C≡O bonds.

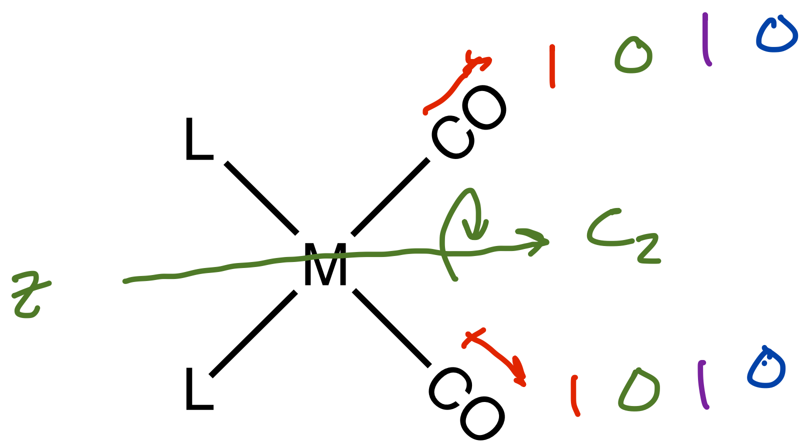


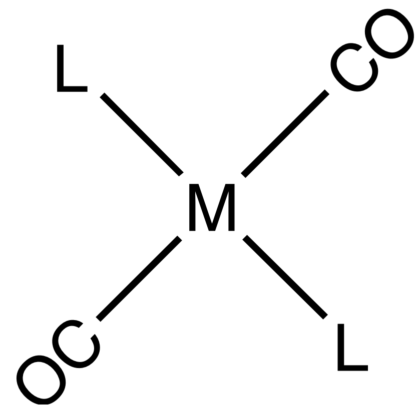


y out of plane

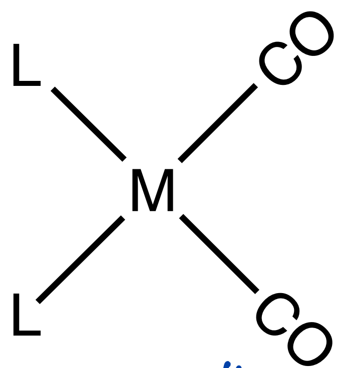
z out of plane

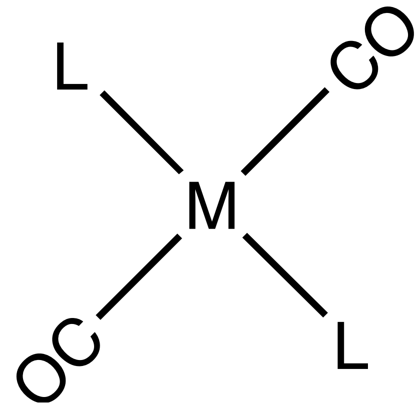
Carbonyl Stretching Bands in Metal Compounds: Determine Reducible Representation





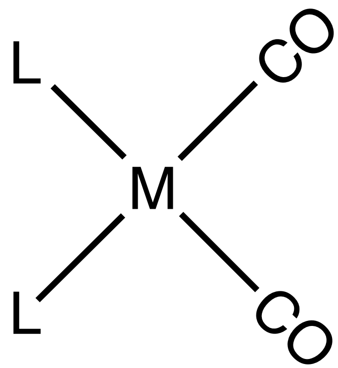
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ	2	0	2	0		

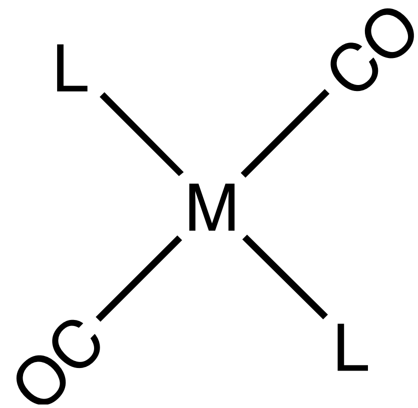




by "inspection"

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		



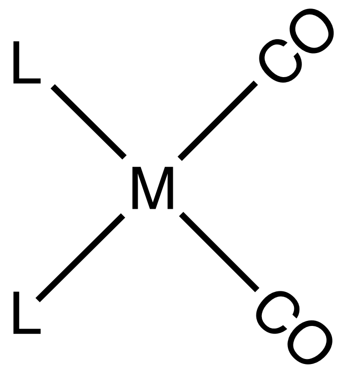


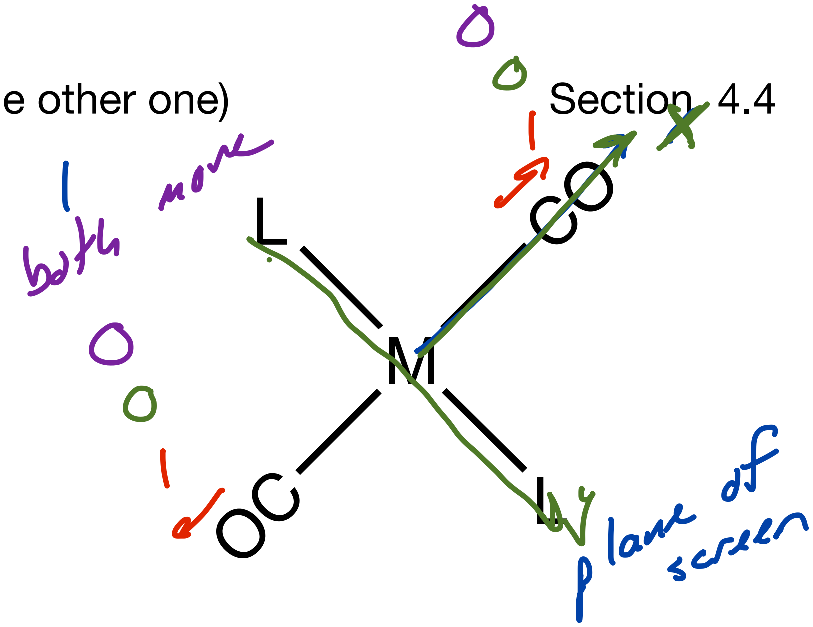
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ	2	0	2	0		

$\Gamma = A_1 + B_1$

C moves (dipole on z axis — IR active
moves on x — IR active

Carbonyl Stretching Bands in Metal Compounds (now the other one)





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		

not IR active

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		

1 (beside A_g)

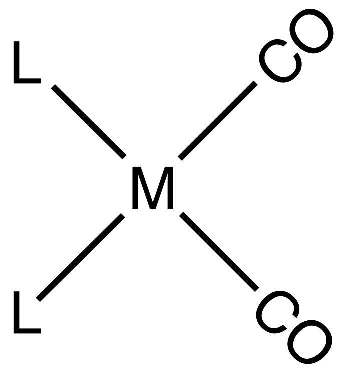
IR active

$$\# A_g = \frac{1}{8}(1\cdot1\cdot2 + 1\cdot1\cdot0 + 1\cdot1\cdot0 + 1\cdot1\cdot2 + 1\cdot1\cdot0 + 1\cdot1\cdot2 + 1\cdot1\cdot2 + 0) = 1$$

since we now know 1 stretching vibration has A_g symmetry we know, by inspection, that $\Gamma = B_{3u} + A_g$

1 stretching vibration with A_1 symmetry

1 stretching vibration with B_1 symmetry

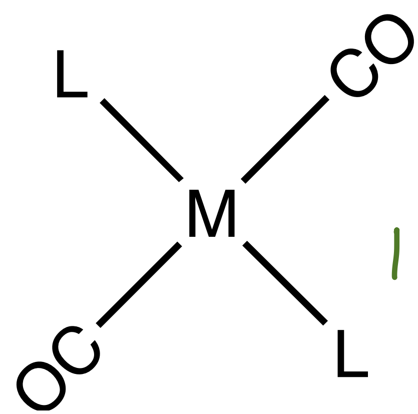


both are IR active

2 peaks

C_{2v} pt group $\Gamma = A_1 + B_1$

D_{2h} pt group $\Gamma = A_g + B_{3u}$



1 peak

1 stretching vibration with A_g symmetry

1 stretching vibration with B_{3u} symmetry

Find irreducible representants / move dipole on x, y, or z axis

only this one is IR active