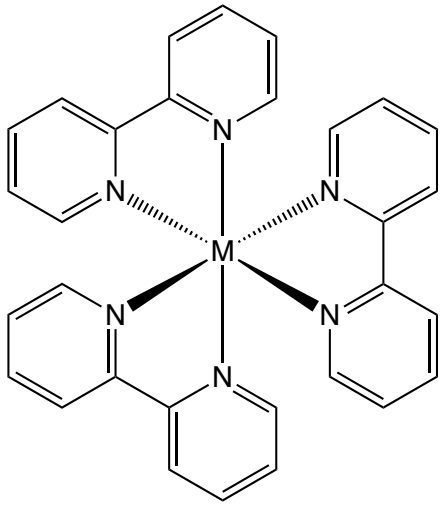
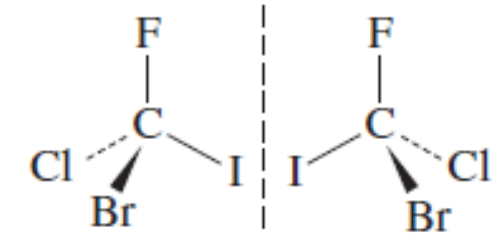
APPLICATIONS OF POINT GROUPS AND CHARACTER TABLES

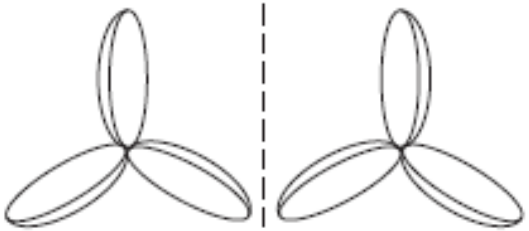
MFT Ch 4

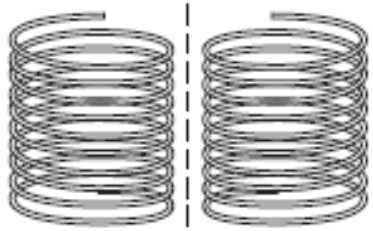
Application 1: Chirality

- A chiral molecule does not necessarily have no symmetry
- No mirror planes or inversion centers
- Either contains only the identity E, or only C_n (proper) rotation axes (belong to point groups C_n, where n = 1,2,3,4, etc., or D_n)





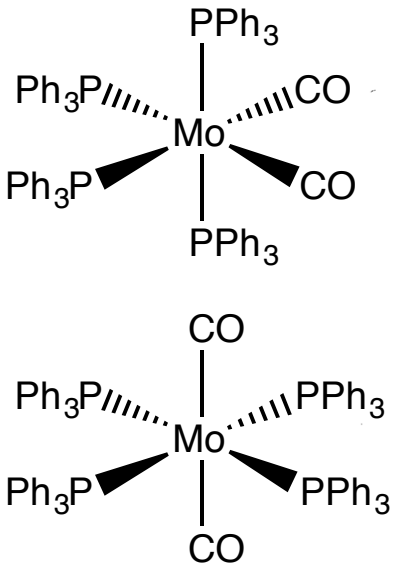




Application 2: Molecular Vibrations and Vibrational Spectroscopy

- Character tables are very useful for analyzing molecular vibrations and predicting peaks in Infrared and Raman spectra of a molecule

IR spectra (CO region) of *cis* vs *trans* $Mo(PPh_3)_4(CO)_2$



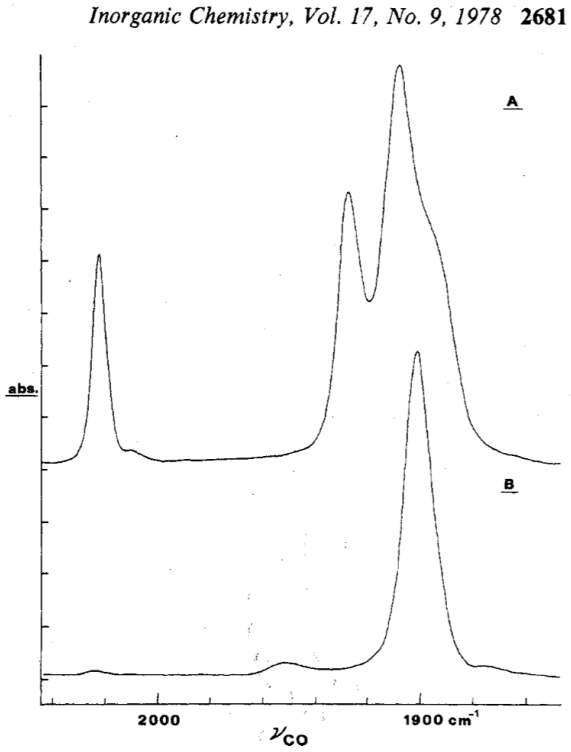
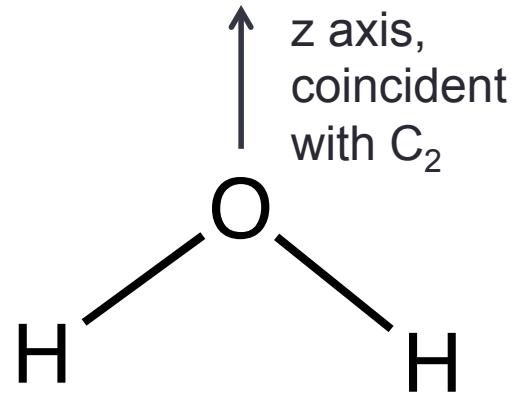


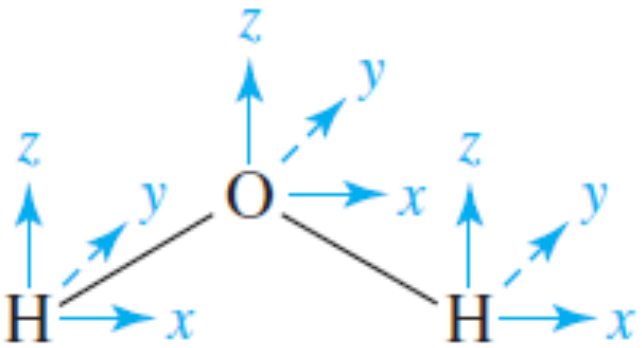
Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $Mo(CO)_4[PPh_3]_2$: A, *cis*-$Mo(CO)_4[PPh_3]_2$; B, *trans*-$Mo(CO)_4[PPh_3]_2$.

Application 2: Molecular Vibrations and Vibrational Spectroscopy

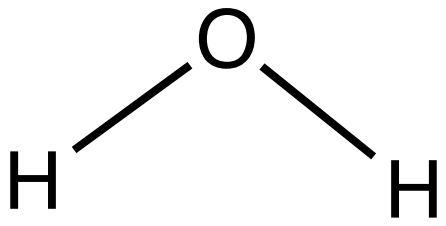
- Character tables are very useful for analyzing molecular vibrations and predicting peaks in Infrared and Raman spectra of a molecule
- Example: H_2O (C_{2v})



- Each of the three atoms can move in all three directions (x,y,z) a total of 9 transformations
- Also known as 9 degrees of freedom



Application 2: Molecular Vibrations and Vibrational Spectroscopy



- A molecule with N atoms has 3N degrees of freedom
  - Translational modes: T_x, T_y, and T_z (movement of the whole body)
  - Rotational modes: R_x, R_y, and R_z (rotations of the whole body)
  - Vibrational modes: displacement of atoms from their mean positions

- H_2O, N = 3 has 3 x 3 = 9 degrees of freedom

Normal modes/fundamental vibrations

- A vibrational mode is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner (and some can be detected by IR, Raman)

- **Non-linear molecules** have 3N – 6 vibrational modes
  - 3N – (T_x, T_y, T_z) – (R_x, R_y, R_z)
- **Linear molecules** have 3N – 5 vibrational modes
  - 3N – (T_x, T_y, T_z) – (R_x, R_y)

  (rotation around z-axis does not change molecule, so doesn't count)

- H_2O: 3 x 3 -6 = 3 vibrational modes

Symmetry and vibrational motions

- We can use character tables to understand the different vibrational motions a molecule has

- Each of these motions will have a certain symmetry that will correspond to one of the irreducible representations

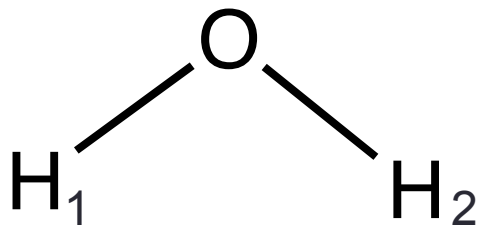
Finding vibrational modes

1) **Find Γ_{3N}** The first step in this process is making a ***reducible representation*** of all possible molecular motions Γ_{3N} (aka Γ_{total})

a) **Generate Γ_{xyz}**, which represents the x, y, and z coordinate axes of the molecule. This tracks how the orientation of atoms change with each symmetry operation. Equal to the sum of irreducible representations for x, y, and z

b) **Determine number of unmoved atoms.** How many atoms stay in the same place when a symmetry operation is applied?

c) **Multiply 1 and 2 to generate Γ_{3N}**



Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Matching Functions	
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_{xyz}				
unmoved atoms				
Γ_{3N}				

Finding vibrational modes

2) **Use the reduction formula** *to determine irreducible representations that make up reducible representation* Γ_{3N}

$$\left(\begin{array}{l}\text{Number of irreducible}\\ \text{representations of}\\ \text{a given type}\end{array}\right) = \frac{1}{order}\sum_{R}\left[\left(\begin{array}{l}\text{number}\\ \text{of operations}\\ \text{in the class}\end{array}\right)\times\left(\begin{array}{l}\text{character of}\\ \text{reducible}\\ \text{representation}\end{array}\right)\times\left(\begin{array}{l}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{array}\right)\right]$$

$n_{(x_y^z)}$

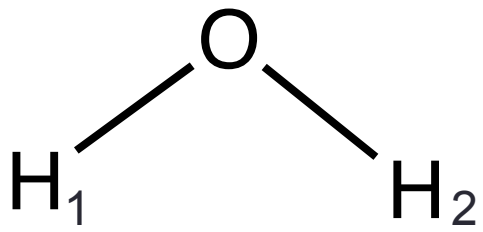
(1/h)

sum

class coefficient

character of reducible representation (you have just derived this)

character of irreducible representation (from character table)



h =

Character Table

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

n (A_1) =

n (A_2) =

n (B_1) =

n (B_2) =

Γ_{3N} =

Finding vibrational modes

3) **Determine which representations represent translational and rotational movements, the remaining are vibrations**

Γ_{3N} =

$\Gamma_{translational}$ =

(correspond to x,y,z representations)

$\Gamma_{rotational}$ =

(correspond to R_x, R_y, R_z representations)

$\Gamma_{vibrational}$ =

(all remaining representations)

Finding vibrational modes

4) **Determine if any of the vibrations are IR or Raman active**

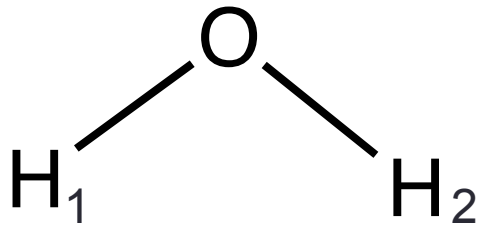
a) **Infrared (IR) active:** if vibration results in a **change in dipole moment** of molecule

In terms of group theory, a vibrational mode is IR active if it corresponds to an irreducible representation that has the **same symmetry as x, y, and z** (the Cartesian coordinates)

b) **Raman active:** if vibration results in **change in polarizability** of molecule

In terms of group theory, a vibrational mode is Raman active if it corresponds to an irreducible representation that has the **same symmetry as xy, xz, yz, x^2, y^2, z^2, or a combination of these**

c) **Some vibrations can be both IR and Raman active**



Character Table

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

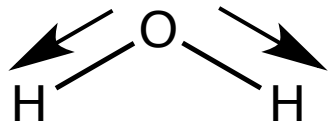
Γ_{vib} =

IR active?

Raman Active?

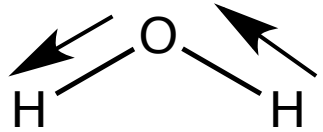
The three vibrational modes of H_2O

- Symmetric stretch



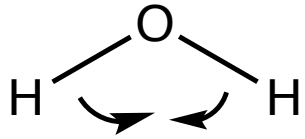
3700 cm^{-1}, A_1

- Asymmetric stretch



3600 cm^{-1}, B_1

- Symmetric bend



1600 cm^{-1}, A_1

A_1 and B_1 describe vibrations in symmetry terms-we derived this!

Useful resource: ChemEd DL: Models 360

http://www.chemeddl.org/resources/models360/models.php?pubchem=962

Finding vibrational modes

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2) **Use the reduction formula** *to determine irreducible representations that make up reducible representation* Γ_{3N}

3) **Determine which representations represent translational and rotational movements, the remaining are vibrations**

4) **Determine if any of the vibrations are IR or Raman active**

Beyond H_2O

- H_2O is a very simple example that can be handled 'by inspection'

- However, things get more complicated ones larger molecules are involved

Molecule	# of atoms	# of molecular motions (3N)	# of vibrations (3N – 6 or 3N -5)
H_2O			
PH_3			
CO_3^{2-}			
XeF_4			
B_2H_6			

http://www.chemeddl.org/resources/models360/models.php?pubchem=11533782

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Example: BF_3

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
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	

Example: B_2H_6