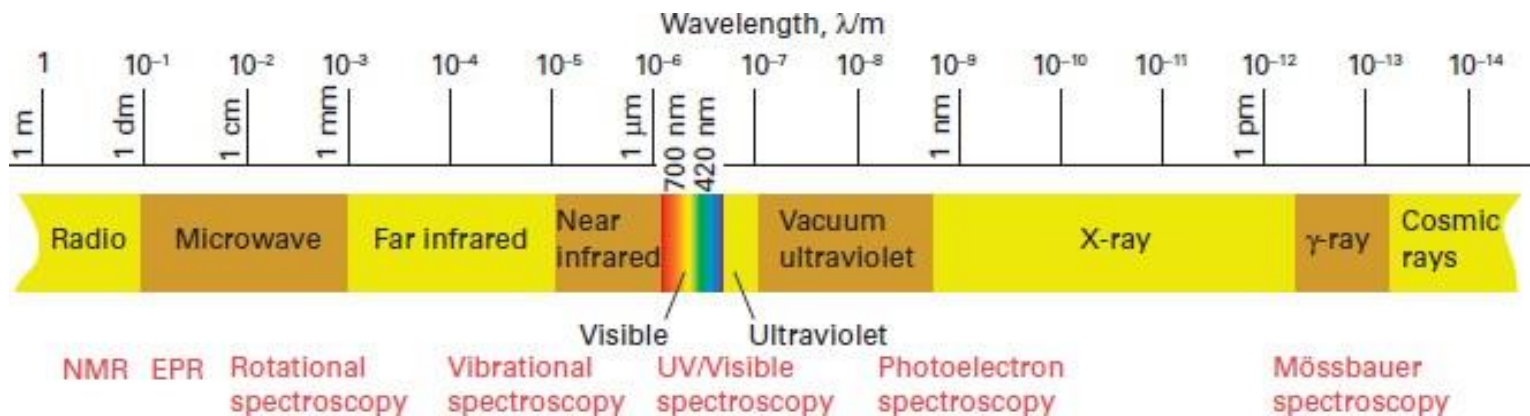# Vibrational Spectroscopy

(Part 5)

Infrared Spectroscopy

- The structure of new compounds that are isolated from natural sources or prepared in the lab must be determined (and/or verified).
  - Chemical analysis
  - Spectroscopy

- Spectroscopic techniques are non-destructive and generally require small amounts of sample

- Infrared spectroscopy:
  - Used to determine the functional groups present (or absent) in a molecule

Introduction

- Infrared spectroscopy (IR) or vibrational spectroscopy is an analytical tool, which, used to identifying how certain atoms are bonded to each other or how they are grouped in a molecule.

- A molecular vibration occurs when atoms in a molecule are in periodic motion; it turns out those different motions among different groups of atoms cause the molecule to absorb different amounts of energy. Studying these transitions can sometimes allow us to determine which kinds of atoms are bonded or grouped in an unknown compound.

- The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-infrared, mid- and far- infrared, named for their relation to the visible spectrum.
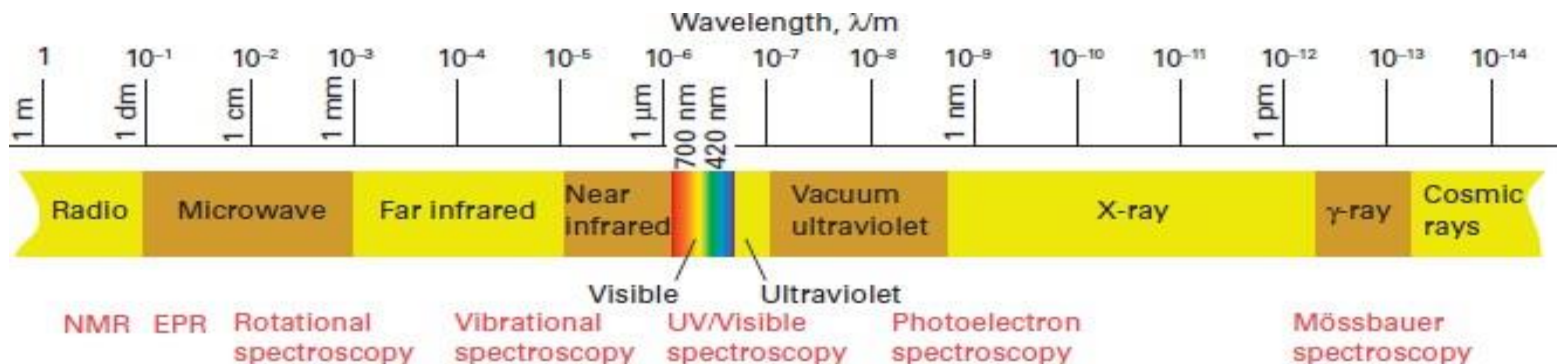
- The higher-energy (near-IR) approximately 14000–4000 cm^{-1} (0.8–2.5 µm wavelength) can excite overtone. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 µm) may be used to study the **fundamental vibrations and associated rotational-vibrational** structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 µm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

- The names and classifications of these sub regions are conventions and are only loosely based on the relative molecular or electromagnetic properties.

- **A pure rotation spectrum can only arise when the molecule possesses a permanent electric dipole moment.** **On the other hand, the vibrational spectra arise when the molecule possesses changing dipole moment.** Since molecular bond lengths remain constant in pure rotation, the magnitude of a molecule's dipole cannot change.

- **Dipole moment**: Dipole moment (μ) is the measure of net molecular polarity, which is the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges. **$\mu = Q \times r$**

Dipole Moments of Some Compounds

Compound   Dipole Moment (Debyes)
- NaCl   9.0   measured in the gas phase)
- CH_3Cl 1.87   active
- H_2O 1.85   active
- NH_3 1.47   active
- CO_2 0   inactive
- CCl_4 0   inactive

Vibration or rotation causes change in dipole moment
(Molecule must have change in dipole moment due to vibration to absorb IR radiation) Absorption causes increase in vibration amplitude (distance during vibration between two molecules)/rotation frequency (number of rotation of a repeating event per unit time).
Absorption of energy in the infrared region (v = 4000 - 200 cm-1) arises from changes in the vibrational energy of the molecules. There are two types of vibrations that cause absorptions in an IR spectrum.
Stretching involves rhythmical displacement along the bond axis such that the interatomic distance alternately increases and decreases (Figure 3A.1a).
Bending involves a change in bond angles between two bonds and an atom common to both

Degree of Freedom

- The mode of vibration depends on the nature of molecules. A molecule consisting of **n (i.e., number of atoms)** has a total of **3n (i.e., degrees of freedom)**, corresponding to the Cartesian coordinates (x and y values) of each atom in the molecule.
  - In a nonlinear molecule, 3 are rotational and 3 are translational and the remaining correspond to fundamental vibrations;
 - In a linear molecule, 2 are rotational and 3 are translational.

molecule	degrees of freedom
nonlinear	$3n - 6$
linear	$3n - 5$

Number of vibrations:

- **Vibrations:** Atoms of a molecule changing their relative positions without changing the position of the molecular center of mass.

Single Atom

- **Vibration:** Atoms of a molecule changing their relative positions without changing the position of the molecular center of mass.
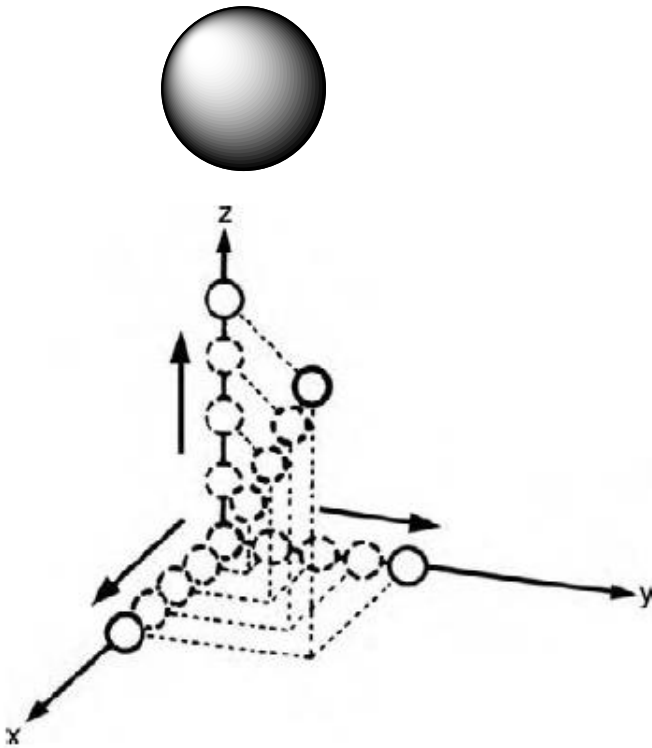
No Vibration
"It takes two to vibrate"

No Rotation
A point cannot rotate

Translation
Can move in x, y, and/or z

3 Degrees of Freedom (DOF)
0 Vibrations

Diatomic Molecule
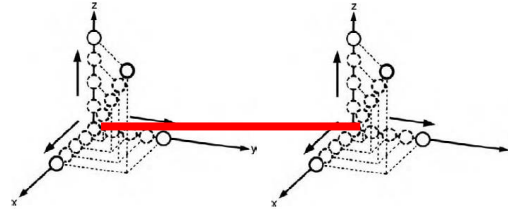
2 atoms x 3 DOF = 6 DOF

Translation
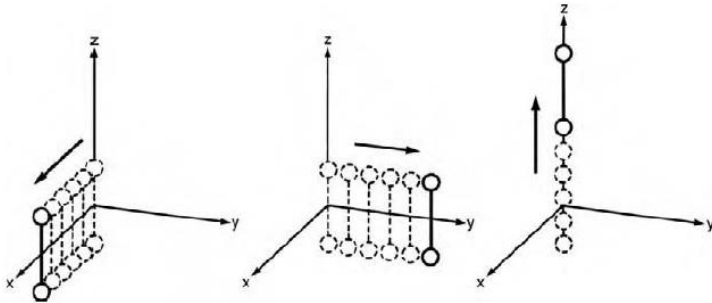
Rotation

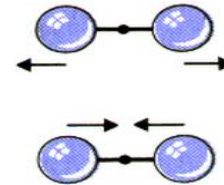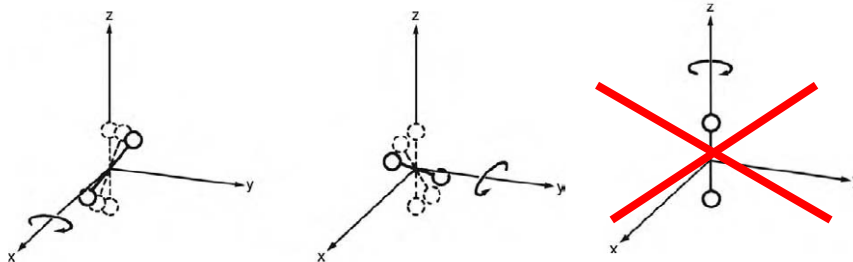

6 DOF
- 3 Translation
- 2 Rotation
  1 Vibration

For a Linear Molecule
# of Vibrations = 3N-5

Linear Triatomic Molecule

3 atoms x 3 DOF = 9 DOF

O=C=O
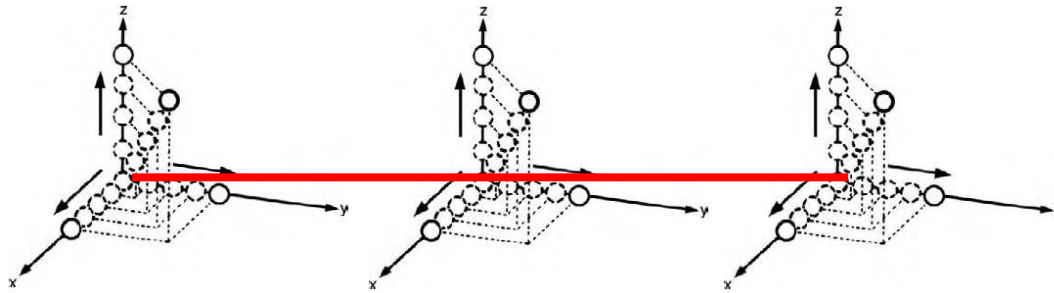
9 DOF
- 3 Translation
- 2 Rotation
  4 Vibration

For a Linear Molecule
of Vibrations = 3N-5

symmetric stretch

bend

bend

antisymmetric stretch
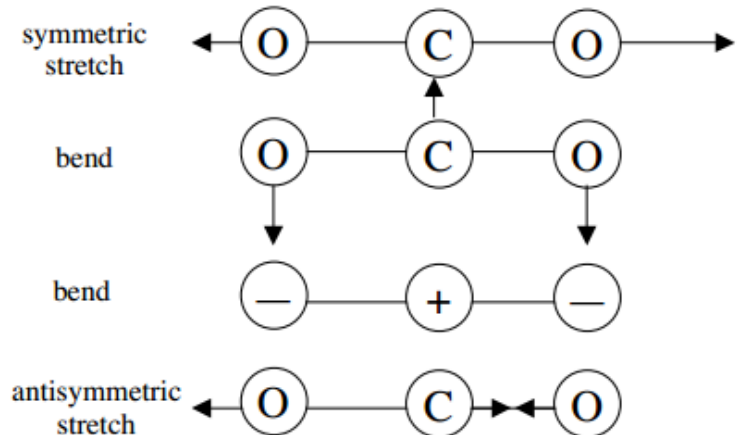
Argon (1% of the atmosphere)
3 DOF, 0 Vibrations

Nonlinear Triatomic Molecule
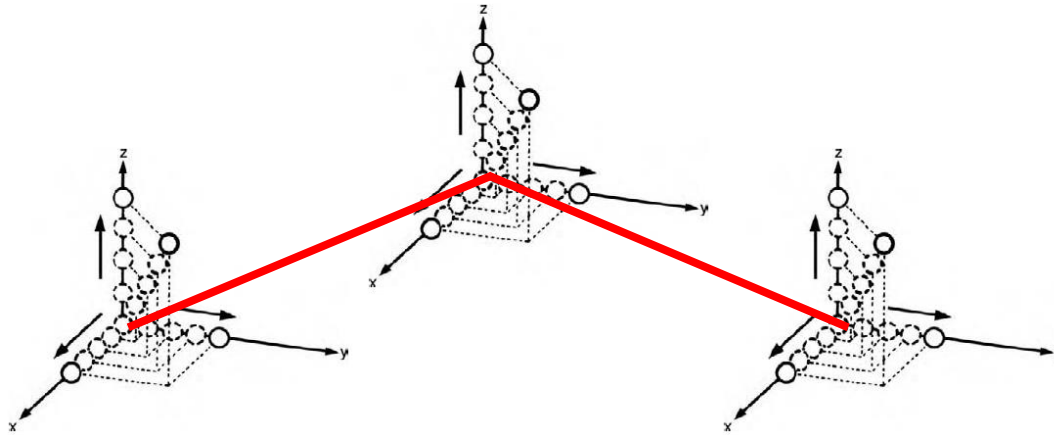
3 atoms x 3 DOF = 9 DOF

3 Translation
3 Rotation
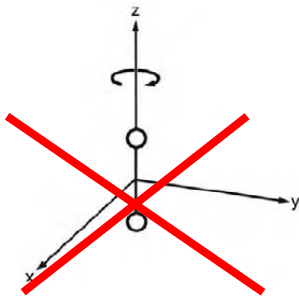
Linear   non-linear
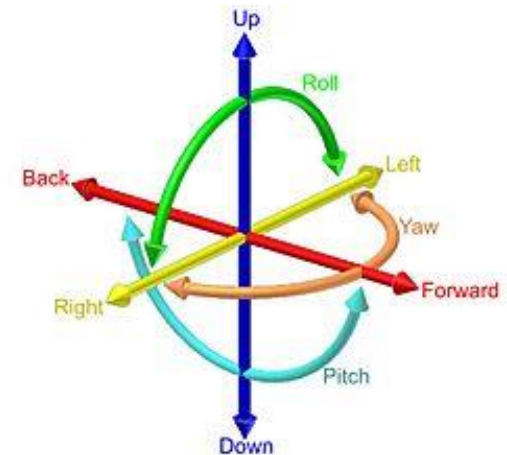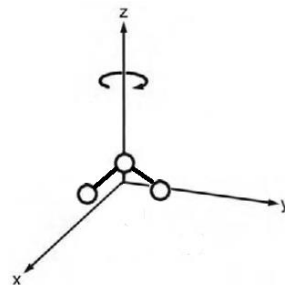
Nonlinear Triatomic Molecule
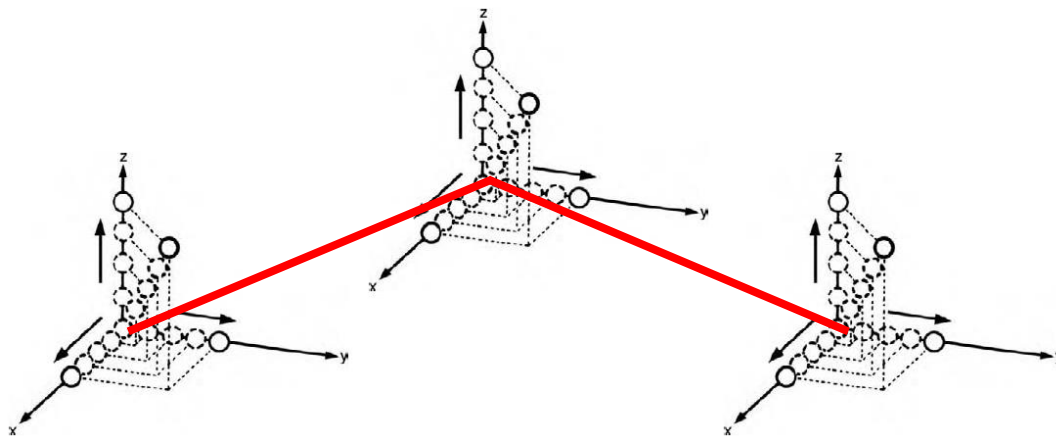
3 atoms x 3 DOF = 9 DOF

Trans$_z$

R$_z$

Trans$_y$
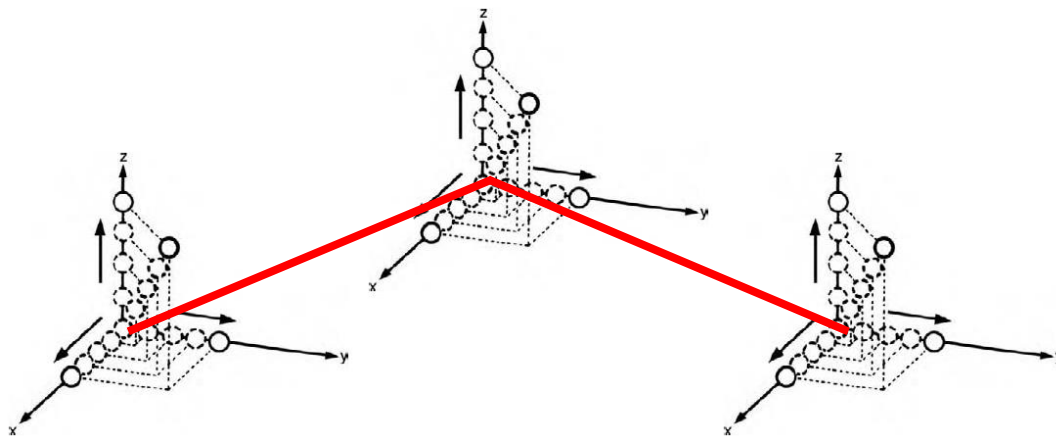
R$_x$

Trans$_x$

R$_y$
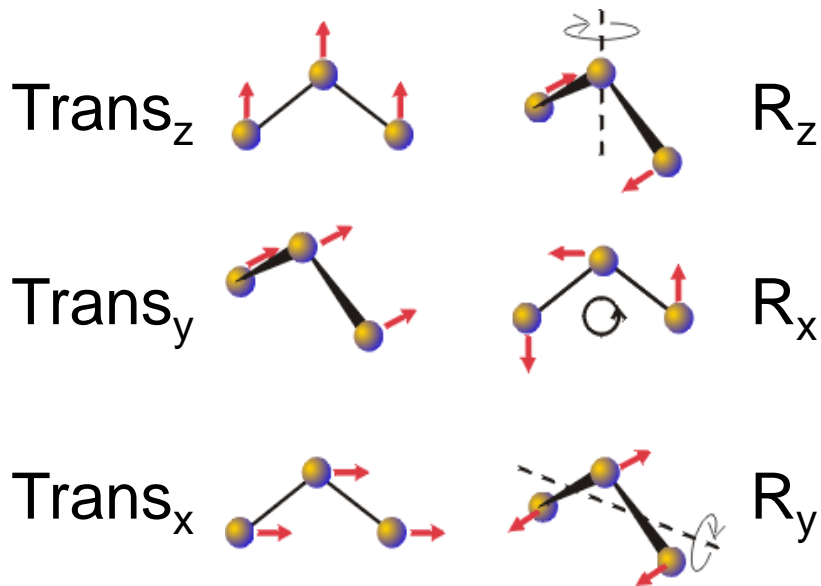
9 DOF
- 3 Translation
- 3 Rotation

3 Vibration

For a nonlinear Molecule
# of Vibrations = 3N-6

Nonlinear Triatomic Molecule

3 atoms x 3 DOF = 9 DOF

antisymmetric
stretch

symmetric
stretch

scissoring
bend
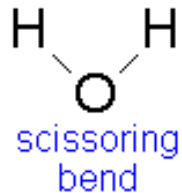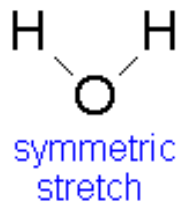
9 DOF
- 3 Translation
- 3 Rotation
3 Vibration

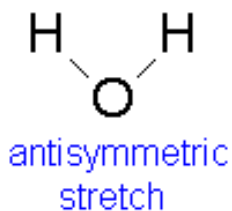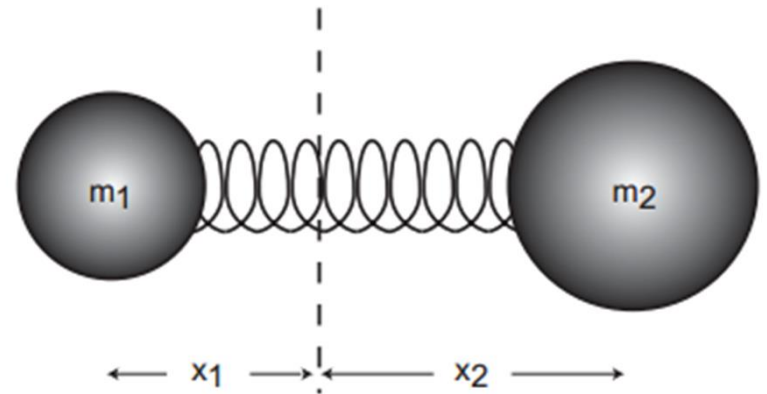For a nonlinear Molecule
# of Vibrations = 3N-6

Molecular Vibrations

- Atoms of a molecule changing their relative positions without changing the position of the molecular center of mass.

- Even at Absolute Zero!

- In terms of the molecular geometry these vibrations amount to continuously changing bond lengths and bond angles.

Center of Mass

$$x_{cm} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

Reduced Mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

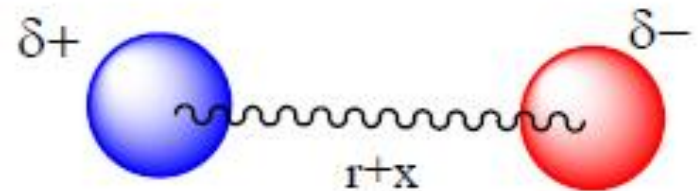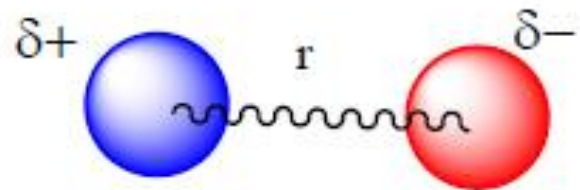# Molecular Vibrations

Hooke's Law

$$\Delta E = \tfrac{1}{2}kx^2$$
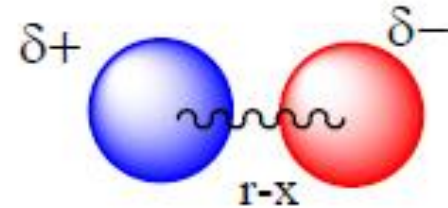
k = force constant
x = distance

Assumes
  It takes the same energy to stretch the bond as to compress it.
  The bond length can be infinite.

$\delta+$ $\delta-$
r-x

$\delta+$ r $\delta-$

$\delta+$ $\delta-$
r+x
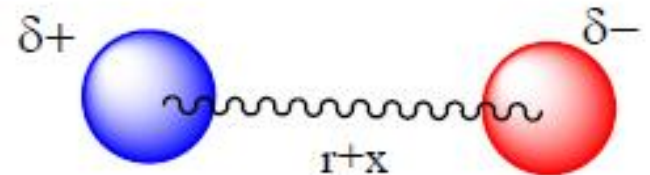
Molecular Vibrations

Vibration Frequency (n)

Related to:

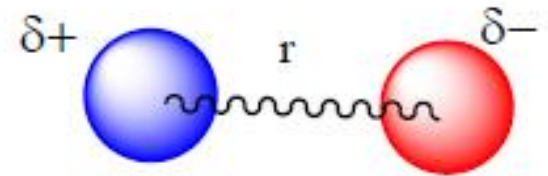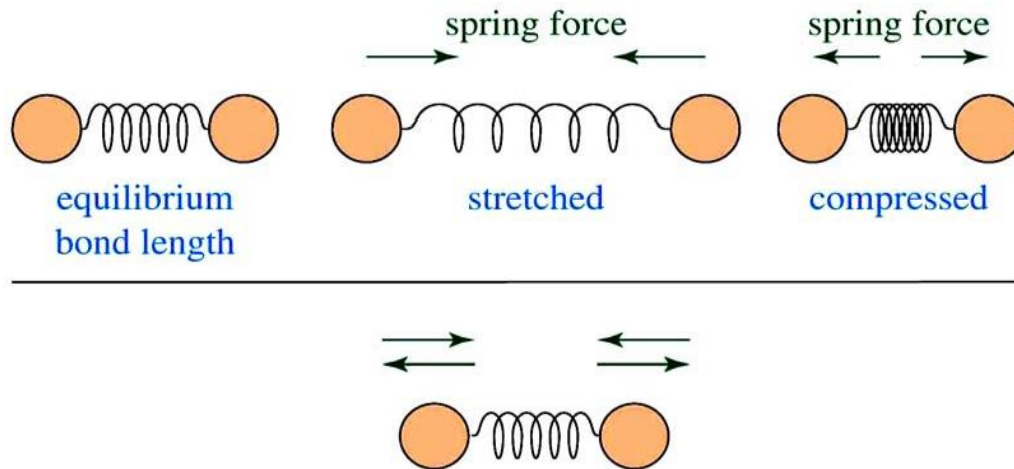$$\overline{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

v: Frequency in cm^{-1} 10
c: Velocity of light => 3 x 10 cm/s
k: Force constant => dynes /cm
m: Reduce mass of atoms in grams
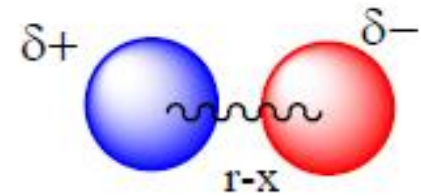
Molecular Vibrations
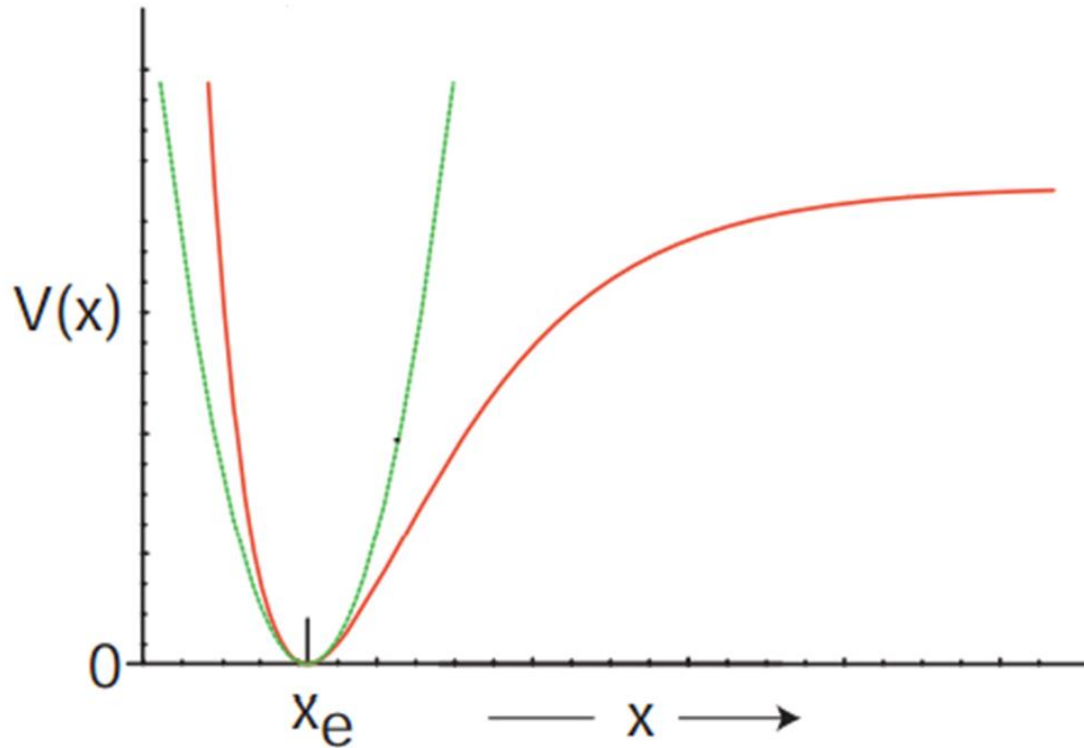
Sometimes a classical description is good
enough. Especially at low energies.

Infrared Spectroscopy

- The absorption of IR radiation increases the amplitude of the various types of bond vibrations.
  - Stretching
    - Symmetric
    - Asymmetric
  - Bending
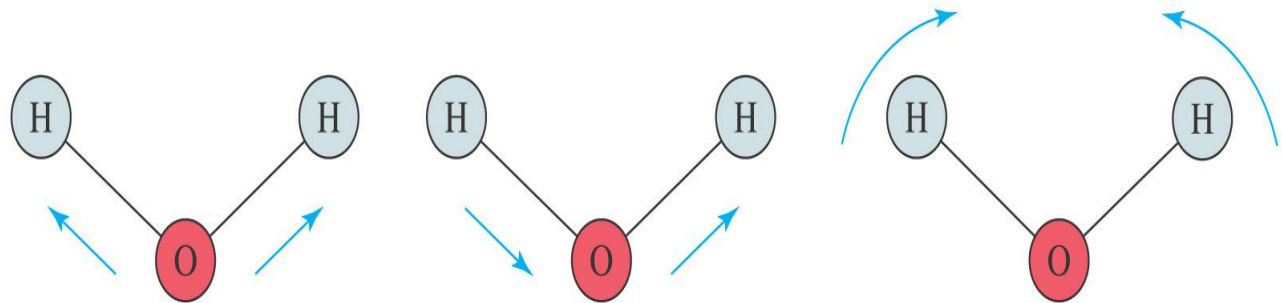
- Since energy is quantized, covalent bonds can vibrate/stretch only at certain allowed frequencies.

- The position of an absorption band correlates with the type of chemical bond.

Infrared Spectroscopy

- The frequency of an absorption band in an IR spectrum depends primarily on:

  - Type of vibration
    - Stretching vibrations: higher frequency
    - Bending vibrations: lower frequency

  - Masses of the atoms in a bond

    AW↑   Freq ↓

  - Strength of the bond or bond order

    BO ↑   Freq ↑

Dipole Moment

- The polarity of a bond has a significant impact on the intensity of an IR absorption band.
- Vibrations that cause a significant change in the dipole moment of a chemical bond lead to strong absorption bands.
- Vibrations that result in no change/very little change in dipole moment lead to very weak or no absorption band.
- Symmetrical bonds often exhibit very weak or no absorption band.
- IR spectrum results from a combination of all possible stretching and/or bending vibrations of the individual bonds and the whole molecule.
- Simple stretching: ~1600-4000 cm^{-1}.
- Complex vibrations: 600-1400 cm^{-1}, called the "fingerprint region."

6 Types of Vibrational Modes

Symmetric Stretch
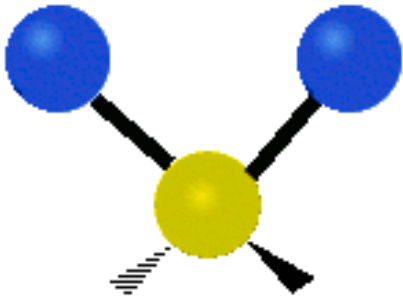
Assymmetric Stretch
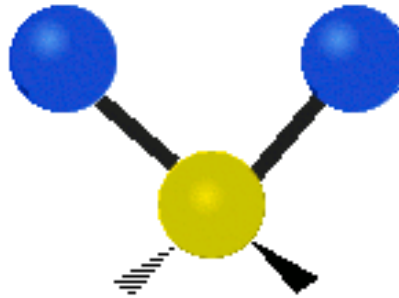
Wagging
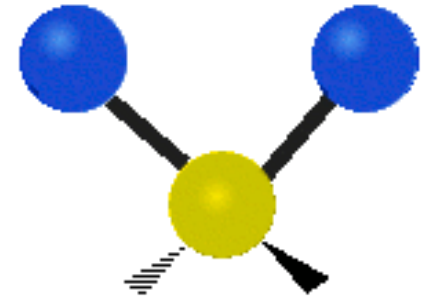
Twisting
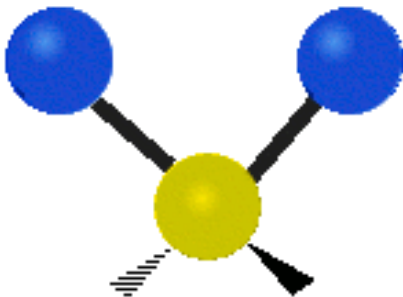
Scissoring
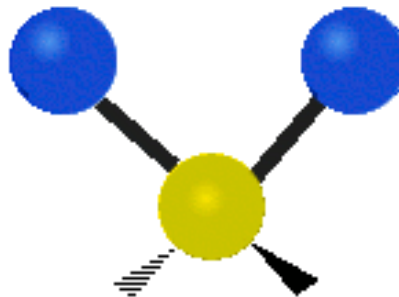
Rocking
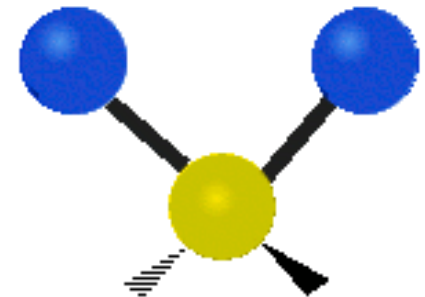
Vibrations and Group Theory

- What kind of information can be deduced about the internal motion of the molecule from its point-group symmetry?

- Each <u>normal mode of vibration</u> forms a basis for an <u>irreducible representation</u> of the point group of the molecule.

1. Find number/symmetry of vibrational modes.

2. Assign the symmetry of known vibrations.

3. What does the vibration look like?

4. Find if a vibrational mode is IR or Raman Active.

Finding Vibrational Modes

1. Assign a point group
2. Choose basis function (three Cartesian coordinates or a specific bond)
3. Apply operations
       -if the basis stays the same = +1
       -if the basis is reversed = -1
       -if it is a more complicated change = 0
4. Generate a reducible representation
5. Reduce to Irreducible Representation
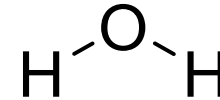6. Subtract Translational and Rotational Motion

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
    -if the basis stays the same = +1
    -if the basis is reversed = -1
    -if it is a more complicated change = 0

$H\!-\!O\!-\!H$

C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom 1: $x_1 = 1$
$y_1 = 1$
$z_1 = 1$

$\xrightarrow{\text{E}}$

Atom 2: $x_2 = 1$
$y_2 = 1$
$z_2 = 1$

Atom 3: $x_3 = 1$
$y_3 = 1$
$z_3 = 1$

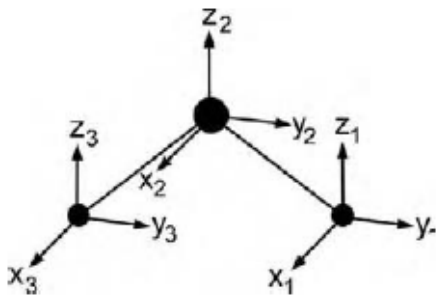| Atom:	1	2	3	
E	3 +	3 +	3	= 9

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations

-if the basis stays the same = +1

-if the basis is reversed = -1

-if it is a more complicated change = 0

$$H\diagdown\overset{O}{}\diagup H$$

C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom 1: $x_1 = 0$
$y_1 = 0$
$z_1 = 0$

C_2
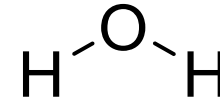
Atom 2: $x_2 = -1$
$y_2 = -1$
$z_2 = 1$

Atom 3: $x_3 = 0$
$y_3 = 0$
$z_3 = 0$

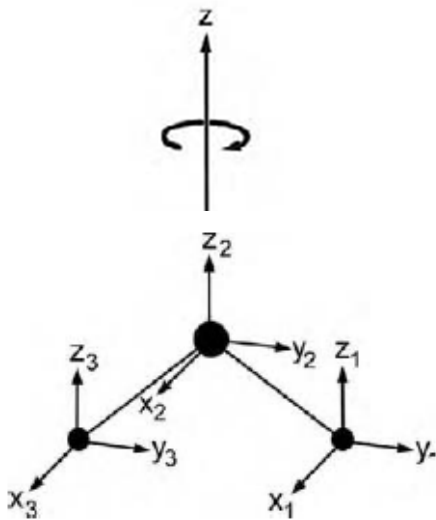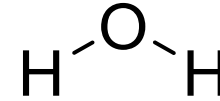| Atom:	1		2		3		
E	3	+	3	+	3	=	9
C_2	0	+	-1	+	0	=	-1

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
    - if the basis stays the same = +1
    - if the basis is reversed = -1
    - if it is a more complicated change = 0

$$H-O-H$$

C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom 1: $x_1 = 0$
$\qquad y_1 = 0$
$\qquad z_1 = 0$

$\xrightarrow{\sigma_{xz}}$

Atom 2: $x_2 = 1$
$\qquad y_2 = -1$
$\qquad z_2 = 1$

Atom 3: $x_3 = 0$
$\qquad y_3 = 0$
$\qquad z_3 = 0$

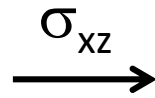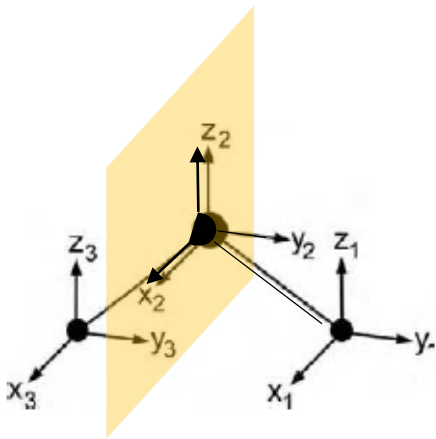| Atom:	1		2		3		
E	3	+	3	+	3	=	9
C_2	0	+	-1	+	0	=	-1
σ_{xz}	0	+	1	+	0	=	1

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations

     -if the basis stays the same = +1

     -if the basis is reversed = -1

     -if it is a more complicated change = 0

$$H-O-H$$

C_{2v} point group

Basis: x_{1-3}, y_{1-3} and z_{1-3}

$\xrightarrow{\sigma_{yz}}$

Atom 1: $x_1 = 1$

             $y_1 = 1$

             $z_1 = 1$

Atom 2: $x_2 = 1$

             $y_2 = 1$

             $z_2 = 1$

Atom 3: $x_3 = 1$

             $y_3 = 1$

             $z_3 = 1$

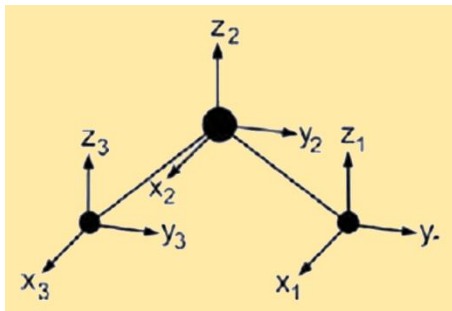| Atom:	1		2		3		
E	3	+	3	+	3	=	9
C_2	0	+	-1	+	0	=	-1
σ_{xz}	0	+	1	+	0	=	1
σ_{yz}	1	+	1	+	1	=	3

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations

    -if the basis stays the same = +1

    -if the basis is reversed = -1

    -if it is a more complicated change = 0

4. **Generate a reducible representation**

$$H \overset{\diagup O \diagdown}{\qquad} H$$
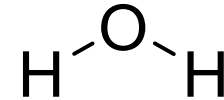
C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

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

Atom:	1		2		3		
E	3	+	3	+	3	=	9
C_2	0	+	-1	+	0	=	-1
σ_{xz}	0	+	1	+	0	=	1
σ_{yz}	1	+	1	+	1	=	3

Example: H$_2$O

1. Assign a point group
2. Choose basis function
3. Apply operations

    -if the basis stays the same = +1

    -if the basis is reversed = -1

    -if it is a more complicated change = 0
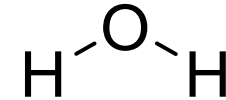4. Generate a reducible representation
5. **Reduce to Irreducible Representation**

H$-$O$-$H

C$_{2v}$ point group
Basis: x$_{1-3}$, y$_{1-3}$ and z$_{1-3}$

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

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Reducible Rep. $\longrightarrow$ **Irreducible Rep.**

Example: H$_2$O

Decomposition/Reduction Formula
$$a_i = (1/h) \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

order (h)

h = 1 + 1 + 1 + 1 = **4**

Γ   9   -1   1   3

$$a_{A1} = \frac{1}{4} \left[(1)(9)(1) + (1)(-1)(1) + (1)(1)(1) + (1)(3)(1) \right] = \frac{12}{4} = 3$$

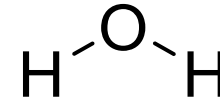$$a_{A2} = \frac{1}{4} \left[(1)(9)(1) + (1)(-1)(1) + (1)(1)(-1) + (1)(3)(-1) \right] = \frac{4}{4} = 1$$

$$a_{B1} = \frac{1}{4} \left[(1)(9)(1) + (1)(-1)(-1) + (1)(1)(1) + (1)(3)(-1) \right] = \frac{8}{4} = 2$$

$$a_{B2} = \frac{1}{4} \left[(1)(9)(1) + (1)(-1)(-1) + (1)(1)(-1) + (1)(3)(1) \right] = \frac{12}{4} = 3$$

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

Example: H$_2$O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - if the basis stays the same = +1
   - if the basis is reversed = -1
   - if it is a more complicated change = 0
4. Generate a reducible representation
5. Reduce to Irreducible Representation
6. **Subtract Rot. and Trans.**
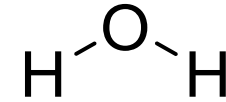
$$H-O-H$$

C$_{2v}$ point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

3 atoms x 3 DOF = 9 DOF
3N-6 = 3 Vibrations

Γ =   3A$_1$ + A$_2$ + 2B$_1$ + 3B$_2$

Trans = A$_1$ + B$_1$ + B$_2$

Rot = A$_2$ + B$_1$ + B$_2$

Vib = 2A$_1$ + B$_2$

| 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

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
   -if the basis stays the same = +1
   -if the basis is reversed = -1
   -if it is a more complicated change = 0
4. Generate a reducible representation
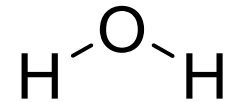5. Reduce to Irreducible Representation
6. Subtract Rot. and Trans.

H $-O-$ H

C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

Vibration = 2A₁ + B₂

ν_1 (3652 cm^{-1})
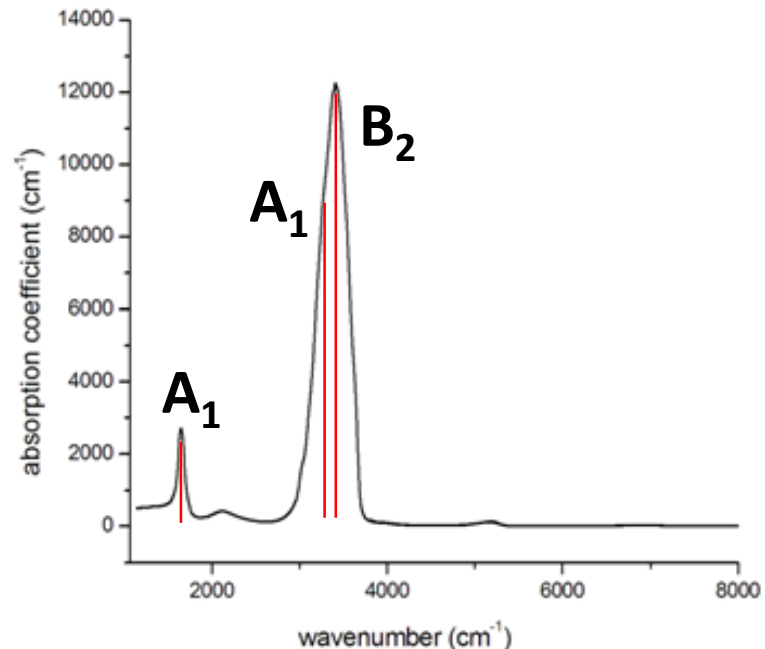
ν_2 (1595 cm^{-1})

ν_3 (3756 cm^{-1})
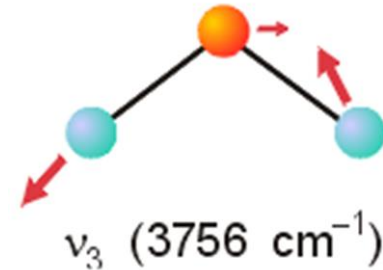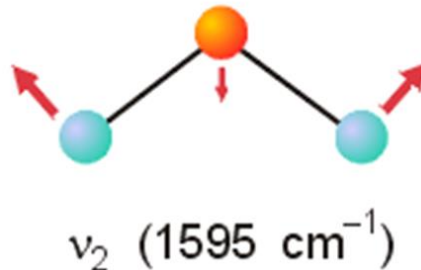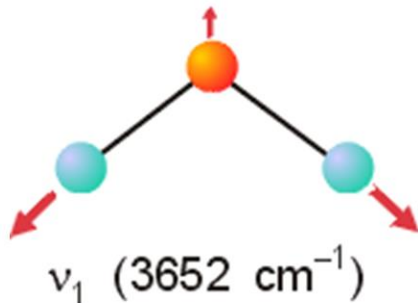
Example: H$_2$O

1. Start with a drawing of a molecule
2. Draw arrows
3. Use the Character Table
4. Predict a physically observable phenomenon

H $\diagdown$ O $\diagdown$ H

C$_{2v}$ point group
Basis: x$_{1-3}$, y$_{1-3}$ and z$_{1-3}$

Vibrations = 2A$_1$ + B$_2$

All three are IR active but that is not always the case.

B$_2$

A$_1$

A$_1$

absorption coefficient (cm^{-1})

14000
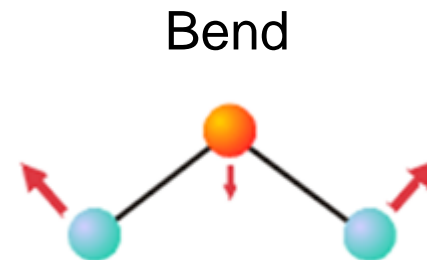12000
10000
8000
6000
4000
2000
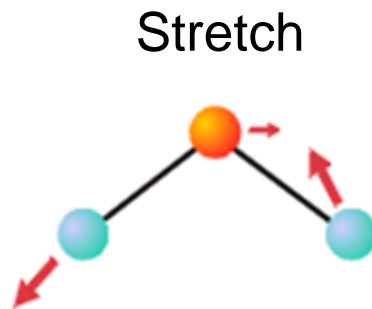0

2000   4000   6000   8000
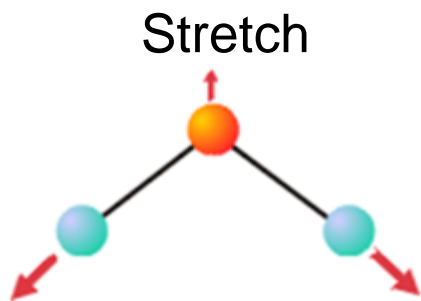
wavenumber (cm^{-1})

# Vibrations and Group Theory

1. Find number/symmetry of vibrational modes.

2. **Assign the symmetry of known vibrations.**

3. What does the vibration look like?

4. Find if a vibrational mode is IR or Raman Active.

2. Assign the Symmetry of a Known Vibrations

Stretch

Stretch

Bend

Vibrations = $2A_1$ + B_2

1. Assign a point group
2. Choose basis function (stretch or bend)
3. Apply operations
   - if the basis stays the same = +1
   - if the basis is reversed = -1
   - if it is a more complicated change = 0
4. Generate a reducible representation
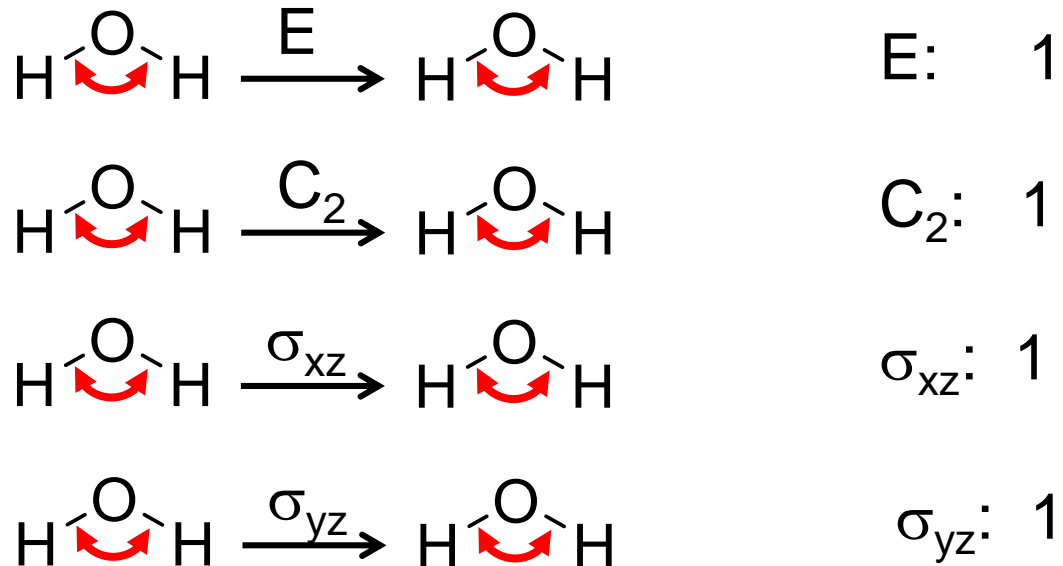5. Reduce to Irreducible Representation

Bend

H — O — H

Stretch

H — O — H
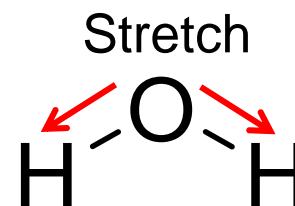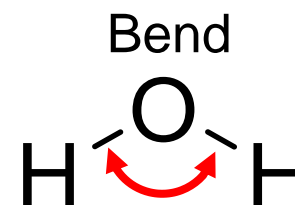
Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
   -if the basis stays the same = +1

   -if the basis is reversed = -1

   -if it is a more complicated change = 0
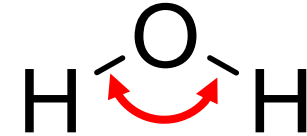
C_{2v} point group
Basis: Bend angle

E: 1

C_2:   1

σ_{xz}: 1

σ_{yz}: 1

Example: H$_2$O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - if the basis stays the same = +1
   - if the basis is reversed = -1
   - if it is a more complicated change = 0
4. Generate a reducible representation
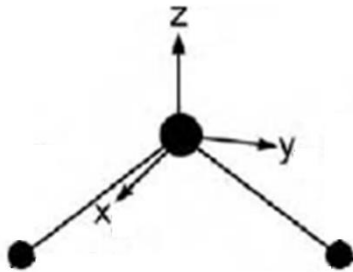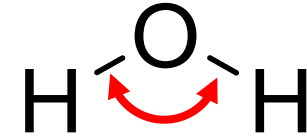5. Reduce to Irreducible Representation

C$_{2v}$ point group
Basis: Bend angle

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ	1	1	1	1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

Reducible Rep. ⟶ **Irreducible Rep.**

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2. Assign the Symmetry of a Known Vibrations

Stretch

Stretch

Bend

A_1

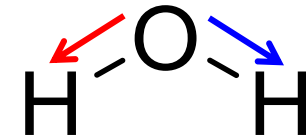**Vibrations = A_1 + B_2**

1. Assign a point group
2. Choose basis function (stretch or bend)
3. Apply operations
   - if the basis stays the same = +1
   - if the basis is reversed = -1
   - if it is a more complicated change = 0
4. Generate a reducible representation
5. Reduce to Irreducible Representation

Stretch

O

H   H

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
   -if the basis stays the same = +1
   -if the basis is reversed = -1
   -if it is a more complicated change = 0

C_{2v} point group
Basis: OH stretch

E:	2
C_2:	0
σ_{xz}:	0
σ_{yz}:	2

Example: H₂O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - if the basis stays the same = +1
   - if the basis is reversed = -1
   - if it is a more complicated change = 0
4. Generate a reducible representation
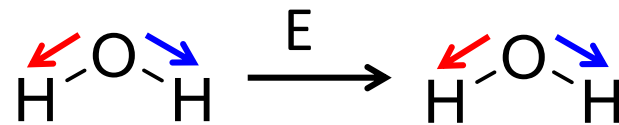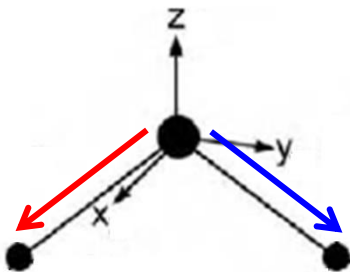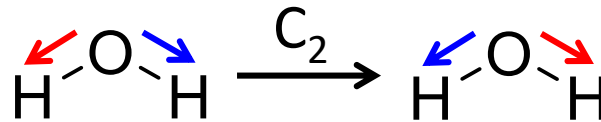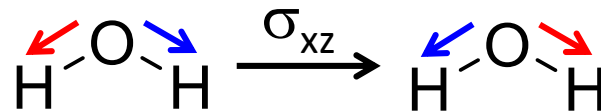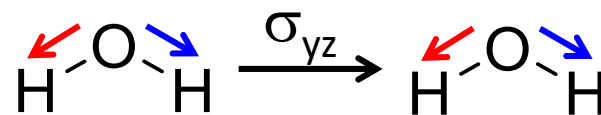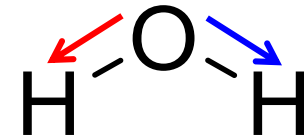5. Reduce to Irreducible Representation

C_{2v} point group
Basis: OH stretch

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ	2	0	0	2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Reducible Rep. $\longrightarrow$ **Irreducible Rep.**

Example: H$_2$O

Decomposition/Reduction Formula

$$a_i = (1/h) \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

order (h)

h = 1 + 1 + 1 + 1 = **4**

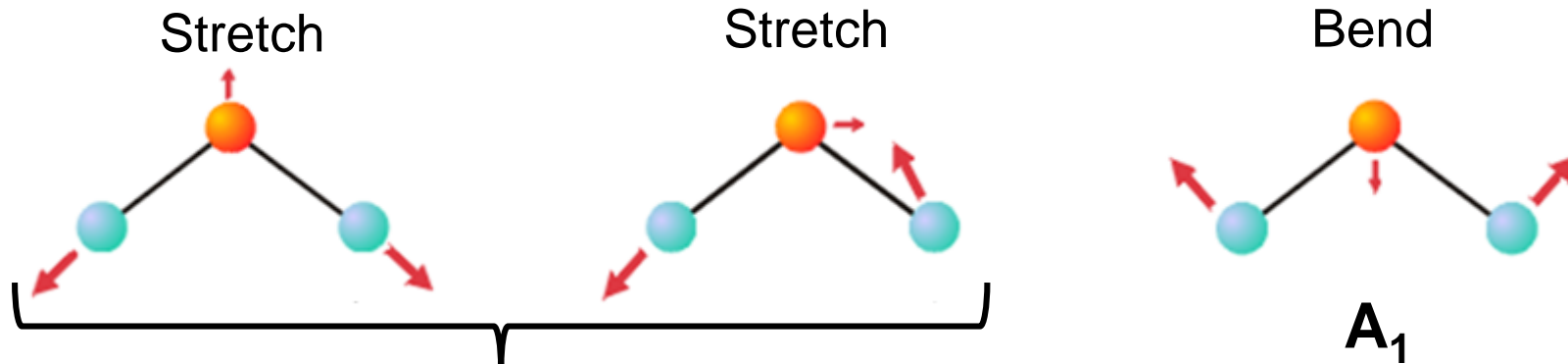| C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
Γ	2	0	0	2

$$a_{A1} = \frac{1}{4} \left[(1)(2)(1) + (1)(0)(1) + (1)(0)(1) + (1)(2)(1)\right] = \frac{4}{4} = \mathbf{1}$$

$$a_{B2} = \frac{1}{4} \left[(1)(2)(1) + (1)(0)(-1) + (1)(0)(-1) + (1)(2)(1)\right] = \frac{4}{4} = \mathbf{1}$$

$$\Gamma = \mathbf{A_1} + \mathbf{B_2}$$

2) Assign the Symmetry of a Known Vibrations

Stretch   Stretch   Bend

A$_1$

Vibrations = A$_1$ + B$_2$

3) What does the vibration look like?

By Inspection

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

By Projection Operator

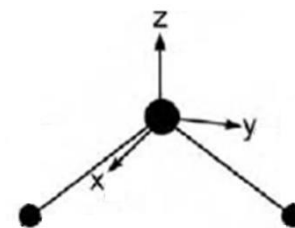Δr_1 Δr_2

Vibrations and Group Theory

1. Find number/symmetry of vibrational modes.

2. Assign the symmetry of known vibrations.

3. **What does the vibration look like?**

4. Find if a vibrational mode is IR or Raman Active.

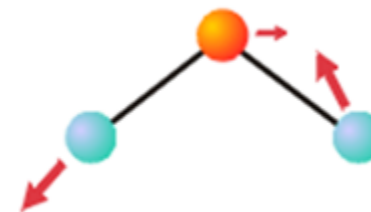# 3) What does the vibration look like?

- **By Inspection**

$\Gamma = A_1 + B_2$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ	1	1	1	1

A_1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ	1	-1	-1	1

B_2

3) What does the vibration look like?

Bend

ν_2 (1595 cm^{-1})

A$_1$

Symmetric Stretch

ν_1 (3652 cm^{-1})

A$_1$

Asymmetric Stretch

ν_3 (3756 cm^{-1})

B$_2$
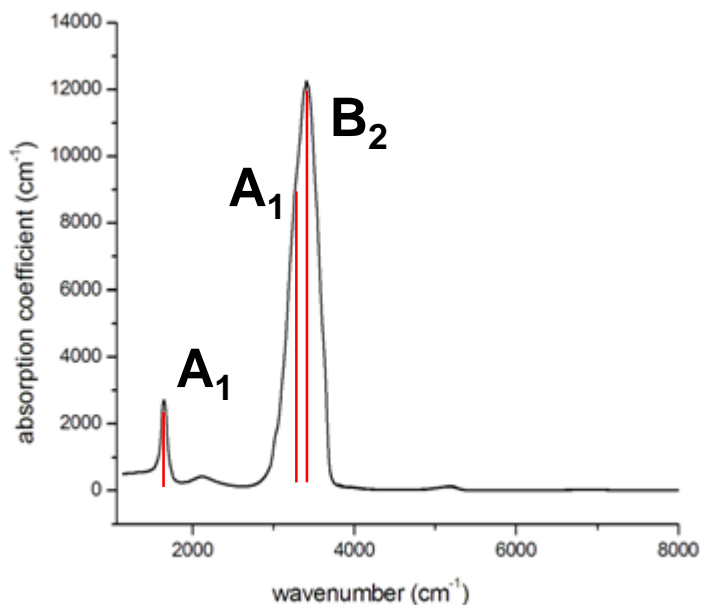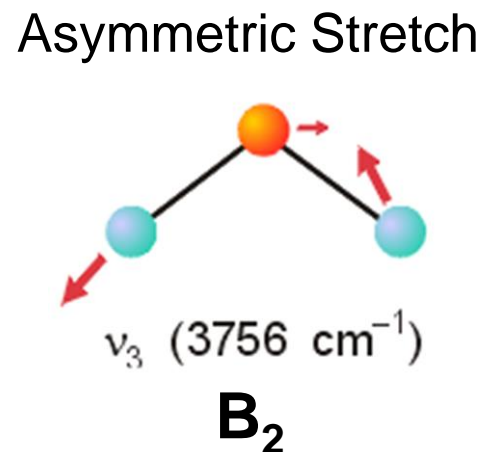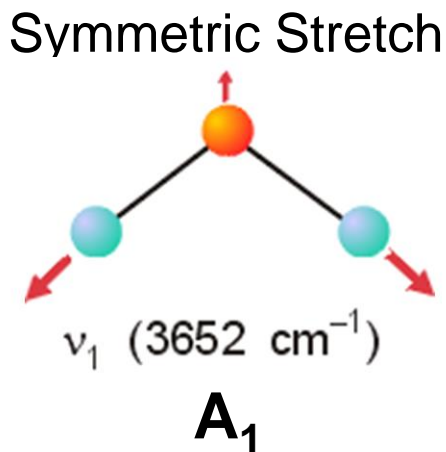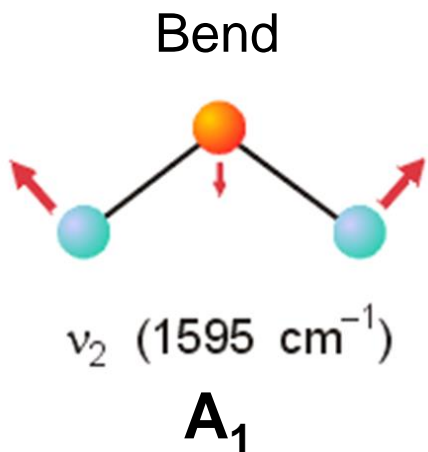
Molecular Structure
+
**Point Group**

=

Find/draw the vibrational modes of the molecule

Does not tell us the energy!

Does not tell us IR or Raman active!

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- One important condition is that only those vibrations that produce a change in the electric dipole moment of the molecule will be observed in the infrared spectrum.

- For example: carbon monoxide, water, ammonia, iodine chloride and hydrogen chloride are IR active because after adoration IR radiation their dipole moments are changed.

- On the other hand, hydrogen, nitrogen, and chlorine are IR inactive. In general, larger the dipole change, stronger the intensity of the band in an IR spectrum.
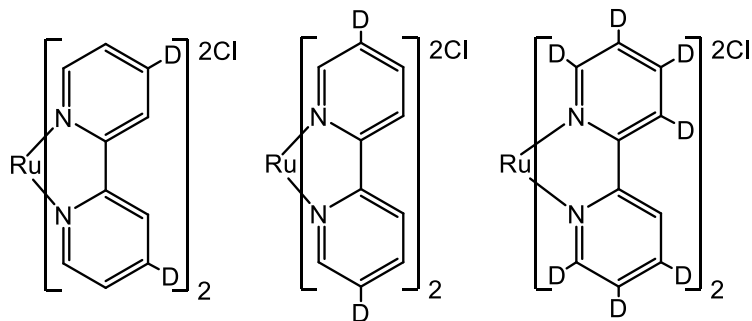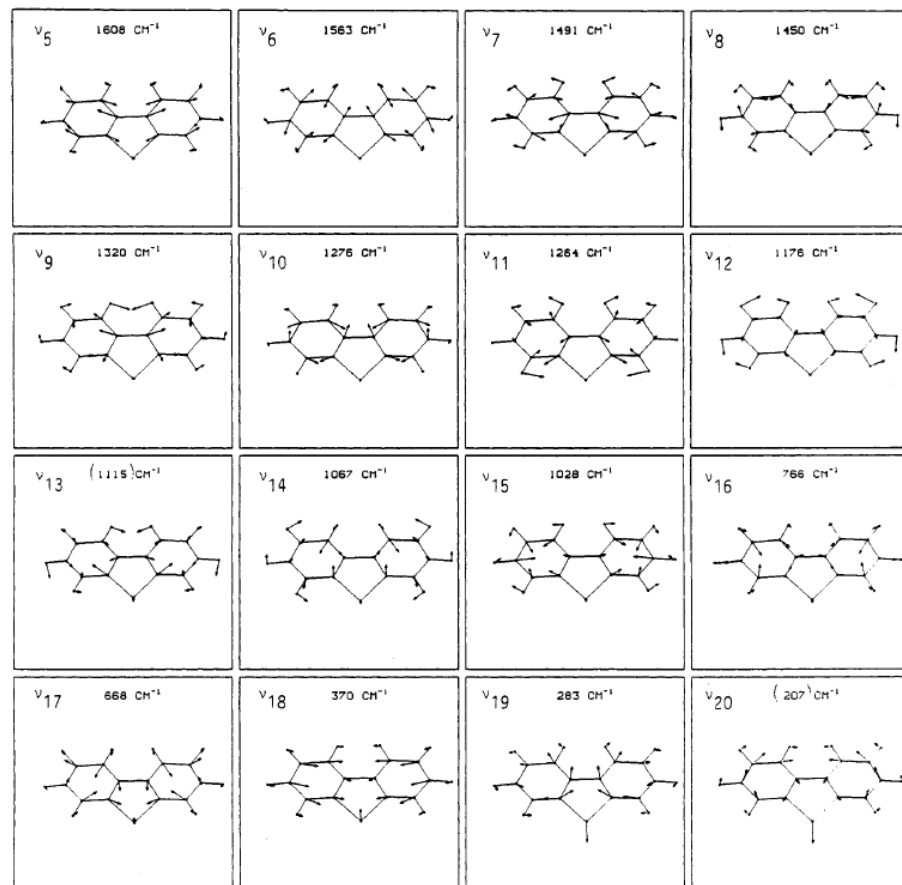
$$H \overset{\delta+}{-} Cl \overset{\delta-}{}$$

$\longmapsto$

$O - O$

No dipole
moment
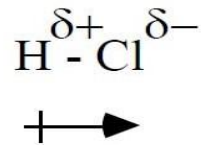
HCl, H$_2$O, NO

IR active

Atoms, O$_2$, H$_2$, Cl$_2$

IR inactive
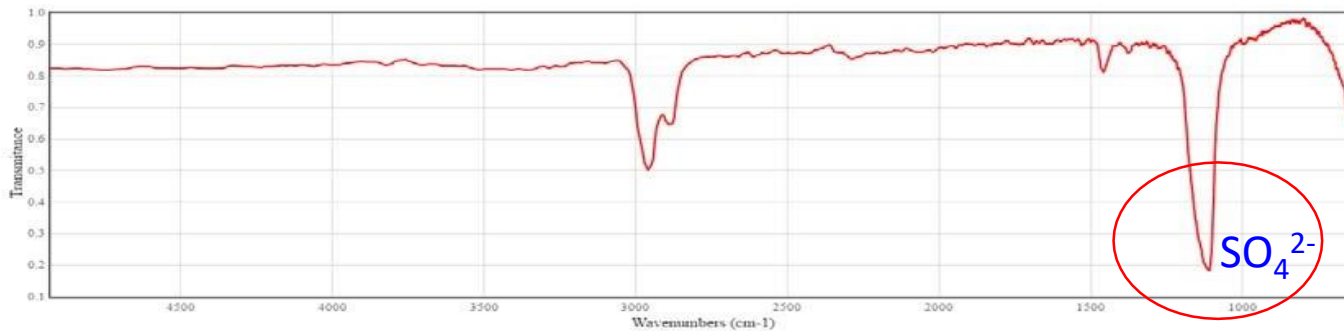
Side note: A Heroic Feat in IR Spectroscopy

2Cl
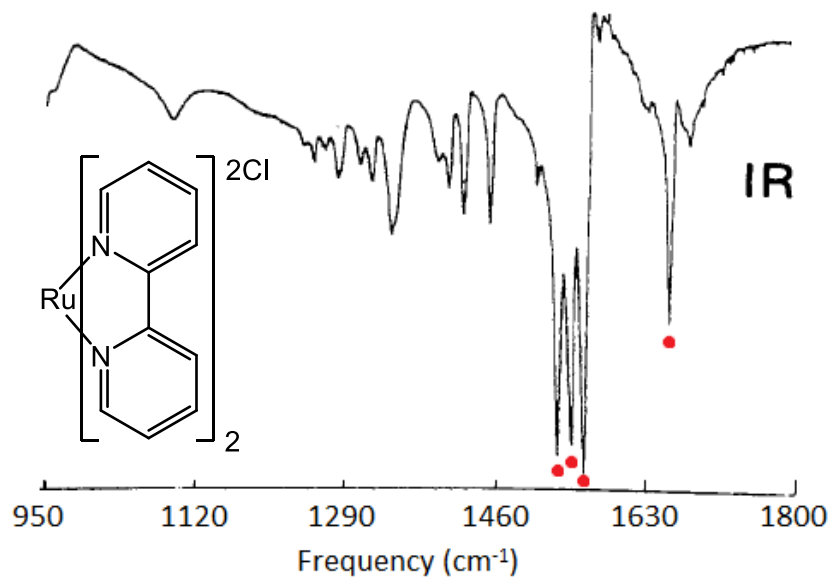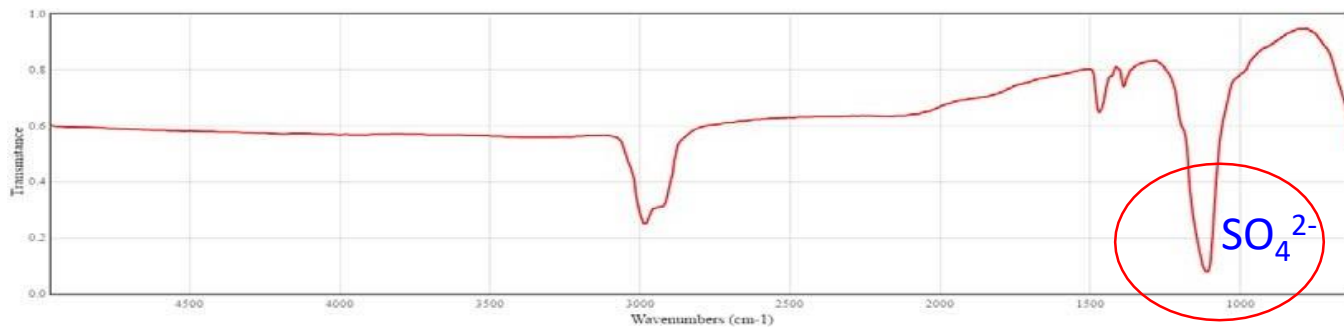
Kincaid et al. *J . Phys. Chem.* **1988**, 92, 5628.
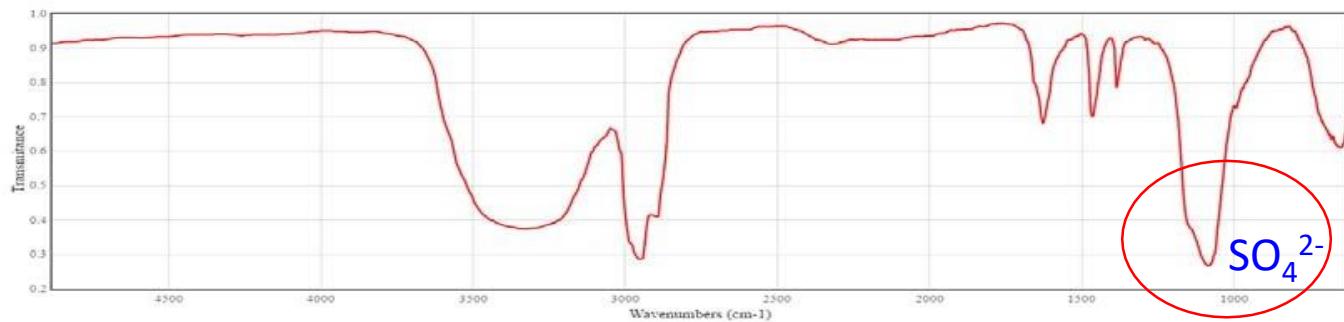

C_{2v}: 20A_1 + 19B_2 + 9B_1

SO_4^{2-} (1130-1080, 680-610 cm^{-1}):
The SO_4^{2-} may be seen extending between 1130-1080, 680-610 cm^{-1}

FTIR Spectra of **Sodium Sulfate**

FTIR Spectra of **Potassium Sulfate**

FTIR Spectra of **CaSO$_4$**

Zn-O and Fe-O
FTIR spectra of metal oxide:
The metal oxide may be seen extending between 580-710 cm^{-1}.

ZINC OXIDE (FRENCH PROCESS)
INFRARED SPECTRUM

Zn-O

YELLOW IRON OXIDE
INFRARED SPECTRUM

Fe-O