

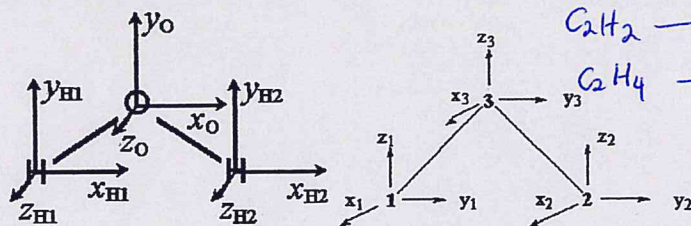
CHEM 481 LAB Report. Vibrational Analysis & FTIR. Name: _____

For a molecule with N atoms, 3N cartesian coordinates are needed to describe its configuration. Another way of describing the motion of the atoms is in terms of the normal modes of the system:

- 3 translations
- 3 rotations and 3N-6 vibrations (nonlinear molecules)
- 2 rotations and 3N-5 vibrations (linear molecules)

1. How many vibration modes are there for:

H₂O: NH₃: C₂H₂: C₂H₄:



Can be symbolised as $\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3$.

$$H_2O \rightarrow 3(3) - 6 = 3 \text{ vibrations}$$

$$NH_3 \rightarrow 3(4) - 6 = 6 \text{ vibrations}$$

$$C_2H_2 \rightarrow 3(4) - 6 = 6 \text{ vibrations}$$

$$C_2H_4 \rightarrow 3(6) - 6 = 12 \text{ vibrations}$$

2) Calculate Reducible Representations (3N) for H₂O: Normal Coordinate Method (NCM)

Carry out the symmetry operations of C_{2v} on this set, we will obtain a transformation matrix for each operation. E.g. C_2 effects the following transformations: $x_1 \rightarrow -x_2, y_1 \rightarrow -y_2, z_1 \rightarrow z_2, x_2 \rightarrow -x_1, y_2 \rightarrow -y_1, z_2 \rightarrow z_1, x_3 \rightarrow -x_3, y_3 \rightarrow -y_3, z_3 \rightarrow z_3$.

$$\begin{matrix} \begin{matrix} x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3 \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{matrix} \end{matrix} \leftarrow E \quad \chi(E) = 9$$

$$\begin{matrix} \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{matrix} \leftarrow C_2 \quad \chi(C_2) = -1$$

$$\begin{matrix} \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{matrix} \leftarrow \sigma_{xz} \quad \chi(\sigma_{xz}) = 1$$

$$\begin{matrix} \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{matrix} \leftarrow \sigma_{yz} \quad \chi(\sigma_{yz}) = 3$$

a) Calculate the χ for each matrix in the operations of E, C_2 , σ_{xz} and σ_{yz}

	χ
E	9
C_2	-1
σ_{xz}	1
σ_{yz}	3

$$\chi(E); \chi(C_2); \chi(\sigma_{xz}); \chi(\sigma_{yz})$$

are equal to the sum of the elements on the diagonal.

b) What are characters of the reducible representation of all modes in water:

	E	C_2	σ_{xz}	σ_{yz}
Γ_{3N}	9	-1	1	3

c) Use Reduction Formula to find the number of each representation

The reduction can always be achieved using the reduction formula.
The number of times an irrep occurs in the reducible

$$n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r$$

h = the order of the group

χ_r = character of reducible representation

χ_i = character of irreducible representation

g_c = no. of symmetry operations in the class

(i.e. the number of equivalent operations, e.g.
for C_2 $g_c = 1$)

C_{2v}	1 E	1 C_2	1 σ_v	1 σ_v	Translations x, y, z, Rotations R
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_x
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_z

Find

$$\Gamma_{3N} =$$

$$A_1 = 1/4 [(2 \times 1 \times 1) + (-1 \times 1 \times 1) + (1 \times 1 \times 1) + (-1 \times 1 \times 1)] = 3 A_1$$

$$A_2 = 1/4 [(2 \times 1 \times 1) + (-1 \times 1 \times 1) + (1 \times -1 \times 1) + (-1 \times -1 \times 1)] = 1$$

$$B_1 = 1/4 [(2 \times 1 \times 1) + (-1 \times -1 \times 1) + (1 \times 1 \times 1) + (-1 \times -1 \times 1)] = 2$$

$$B_2 = 1/4 [(2 \times 1 \times 1) + (-1 \times -1 \times 1) + (1 \times -1 \times 1) + (-1 \times 1 \times 1)] = 3$$

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

Using $3N$ (translation + rotation + vibration) and character table, find Γ_{Rot} , Γ_{Trans} , $\Gamma_{\text{T+R}}$ and Γ_{Vib}

$$\Gamma_{\text{rot}} = A_2 + B_1 + B_2$$

$$\Gamma_{\text{trans}} = A_1 + B_2 + B_1$$

$$\Gamma_{\text{T+R}} = A_1 + A_2 + 2B_1 + 2B_2$$

$$\Gamma_{\text{Vib}} = \Gamma_{3N} - \Gamma_{\text{T+R}} = 3A_1 - A_1 + A_2 - A_2 + 2B_1 - 2B_1 + 3B_2 - 2B_2 = 2A_1 + B_2$$

d) Using the character table below find which of the above normal modes would be IR and Raman active or inactive?

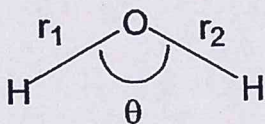
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$				
A_1	1	1	1	1	z	x^2, y^2, z^2	IR	Raman
A_2	1	1	-1	-1	R_z	xy		Raman
B_1	1	-1	1	-1	x, R_y	xz	IR	Raman
B_2	1	-1	-1	1	y, R_x	yz	IR	Raman

$\Gamma_{\text{rot}} \Rightarrow$ IR and Raman Active.

$\Gamma_{\text{trans}} \Rightarrow$ IR and Raman Active

$\Gamma_{\text{vib}} \Rightarrow$ IR and Raman Active

3) Calculate Reducible Representations (Γ) bond vectors r and θ for H_2O : Internal Coordinate Method



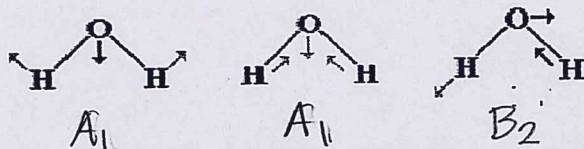
	C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{stretch}$	2	0	0	2	
Γ_{bend}	1	1	1	1	

Transformation matrices for $\Gamma_{stretch}$:

$$E, \sigma_{yz} : \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_2, \sigma_{xz} : \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\begin{aligned} \Gamma &= 2r + 2\theta \\ A_1 &= \frac{1}{4} [(2 \times 1 \times 1) + (0 \times 1 \times 1) + (0 \times 1 \times 1) + (2 \times 1 \times 1)] = 1 \\ A_2 &= \frac{1}{4} [(2 \times 1 \times 1) + (0 \times 1 \times 1) + (0 \times 1 \times 1) + (2 \times 1 \times 1)] = 1 \\ B_1 &= \frac{1}{4} [(2 \times 1 \times 1) + (0 \times 1 \times 1) + (0 \times 1 \times 1) + (2 \times 1 \times 1)] = 1 \\ B_2 &= \frac{1}{4} [(2 \times 1 \times 1) + (0 \times 1 \times 1) + (0 \times 1 \times 1) + (2 \times 1 \times 1)] = 1 \\ \Gamma &= A_1 + A_2 + B_1 + B_2 \end{aligned}$$

Assign the symmetry labels to following vibrations and identify them as stretching or bending. which one would have lower energy bending or stretching vibrations?



4) Use internal coordinate method to get the CO stretching vibrations in the handout given.

Procedure to Run Mattson Instruments Genesis II FT-IR Instrument

Genesis II FT-IR Instrument Description of Instrument

Mattson Instruments Genesis II FTIR spectrometer system designed for routine sample analysis in the QA/QC environment. The Genesis II features 1 cm^{-1} resolution in either near or mid infrared configurations with the choice of **room temperature** detector. For easy access, there is a sample hatch to the sliding sample compartment cover. Genesis II FTIR spectrometer is compatible with all standard sampling techniques for powders, liquids and gases to provide additional flexibility. The First software provides full IQ, OQ and PQ validation for laboratories subject to regulatory review.

Procedure:

1. Sign on the log book.
2. Turn on the computer.
3. Turn on the FTIR Spectrometer switch at the back of the instrument.
4. On the computer screen "Cancel" the login to network option.

TABLE 16-7
NUMBER AND TYPE OF INFRARED
STRETCHING FREQUENCIES EXPECTED
FOR COMMON METAL CARBONYL
COMPLEXES

Molecule	Point Group	Number of ν_{CO} Expected	Symmetry of ν_{CO} Bands
1.  $M(CO)_5L$	C_{4v}	3	$2a_1 + e$
2. <i>cis</i> - $[M(CO)_4L_2]$ 	C_{2v}	4	$2a_1 + b_1 + b_2$
3.  <i>trans</i> - $[M(CO)_4L_2]$	D_{4h}	1	e_u
4. <i>cis</i> - $[M(CO)_3L_3]$ 	C_{3v}	2	$a_1 + e$
5.  <i>trans</i> - $[M(CO)_3L_3]$	C_{2v}	3	$2a_1 + b_2$
6. <i>cis</i> - $[M(CO)_2L_2X_2]$ 	C_{2v}	2	$a_1 + b_2$
7.  <i>trans</i> - $[M(CO)_2L_2X_2]$	D_{2h}	1	b_{1u}
8. $M(CO)_4L$ 	C_{3v}	3	$2a_1 + e$
9.  $M(CO)_4L$	C_{2v}	4	$2a_1 + b_1 + b_2$
10. $M(CO)_3L_2$ 	D_{3h}	1	e'
11.  $M(CO)_3L_2$	C_s	3	$2a' + a''$