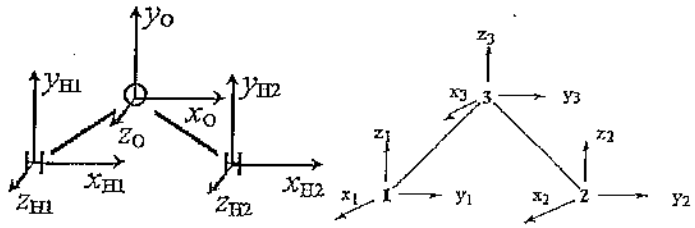
CHEM 481 LAB 4. Vibrational Analysis & FTIR. Name:_____

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:**

H_2O: NH_3: C_2H_2: C_2H_4:



Can be symbolised as Δx_1, Δy_1, Δz_1, Δx_2, Δy_2, Δz_2, Δx_3, Δy_3, Δz_3.

2) Calculate Reducible Representations (3N) for H_2O: Normal Coordinate Method

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: $x_1 \rightarrow -x_2$, $y_1 \rightarrow -y_2$, $z_1 \rightarrow z_2$, $x_2 \rightarrow -x_1$, $y_2 \rightarrow -y_1$, $z_2 \rightarrow z_1$, $x_3 \rightarrow -x_3$, $y_3 \rightarrow -y_3$, $z_3 \rightarrow z_3$.

$$\begin{bmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{bmatrix} \leftarrow E \qquad \chi(E) =$$

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

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

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

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

	χ
E	
C_2	
σ_{xz}	
σ_{yz}	

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

	E	C_2	σ_{xz}	σ_{yz}
Γ_{3N}				

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_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	-1	y, R_x

Find

Γ_{3N} =
$A_1 = 1/4\,[(3 \times 1 \times 1) + (-1 \times 1 \times 1) + (1 \times 1 \times 1) + (3 \times 1 \times 1)] = 3$
A_2 = [ ] =
B_1 = [ ] =
B_2 = [ ] =
$\Gamma_{3N} = 3A_1 +$

Using 3N (translation + rotation + vibration) and <u>character table</u>, find Γ_{Rot} , Γ_{Trans}, Γ_{T+R} and Γ_{Vib}

Γ_{rot} :

Γ_{trans} :

Γ_{T+R} =

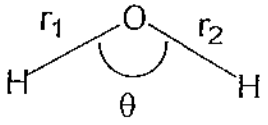
$\Gamma_{Vib} = \Gamma_{3N} - \Gamma_{T+R}$ =

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

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

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



Transformation matrices for $\Gamma_{stretch}$:

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

Γ =

A_1 = [ ]=

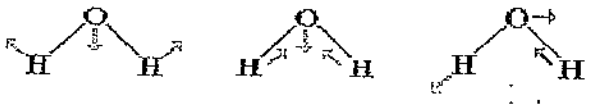
A_2 = [ ]=

B_1 = [ ]=

B_2 = [ ]=

Γ =

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

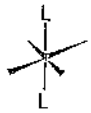
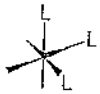
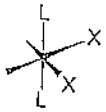
15. Attach your Spectra with spectral assignment to the report.

Sample Preparation Methods

1. Liquid Solution Samples:
2. KBr Pellets:
3. Solid Samples: Diffuse Reflectance:
4. Nujol/Fluorolube Mull:
5. Thin Film Support:
6. Gas Samples

Using Internal coordinate method show that cis-$[M(CO)_4L_2]$ belonging to C_{2v} point group is expected to show 4 ν_{CO} stretching vibrations with symmetry representation 2 a_1, b_1 and b_2, and trans-$[M(CO)_4L_2]$ belonging to D_{4h} point group is expected to show only 1 ν_{CO} stretching vibration with the symmetry representation e_u.

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.	*cis*-$[M(CO)_4L_2]$ 	C_{2v}	4	$2a_1 + b_1 + b_2$
3.	 *trans*-$[M(CO)_4L_2]$	D_{4h}	1	e_u
4.	*cis*-$[M(CO)_3L_3]$ 	C_{3v}	2	$a_1 + e$
5.	 *trans*-$[M(CO)_3L_3]$	C_{2v}	3	$2a_1 + b_2$
6.	*cis*-$[M(CO)_2L_2X_2]$ 	C_{2v}	2	$a_1 + b_2$
7.	 *trans*-$[M(CO)_2L_2X_2]$	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	$2a' + a''$