Group Theory and Vibrational Spectroscopy

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Physics 251

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Outline

- Molecular Symmetry
- Representations of Molecular Point Groups
- Group Theory and Quantum Mechanics
- Vibrational Spectroscopy

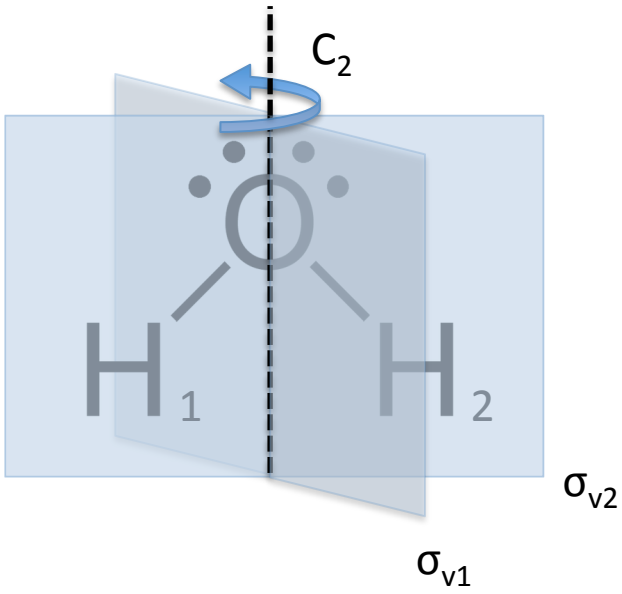
Molecular Symmetry

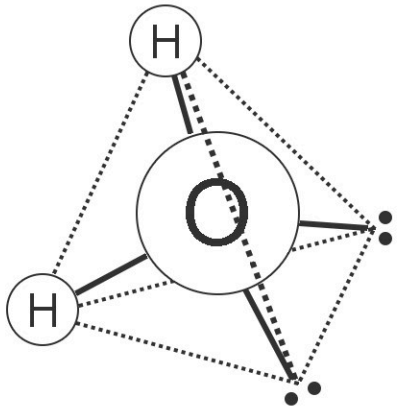
Point Group- is a discrete finite symmetry group whose operation keeps at least one point stays fixed.

Symmetry Group- Group of isomorphisms that map an object onto itself (automorphisms)

Typical mappings include rotations, reflections, and inversions.

Symmetry of H_2O



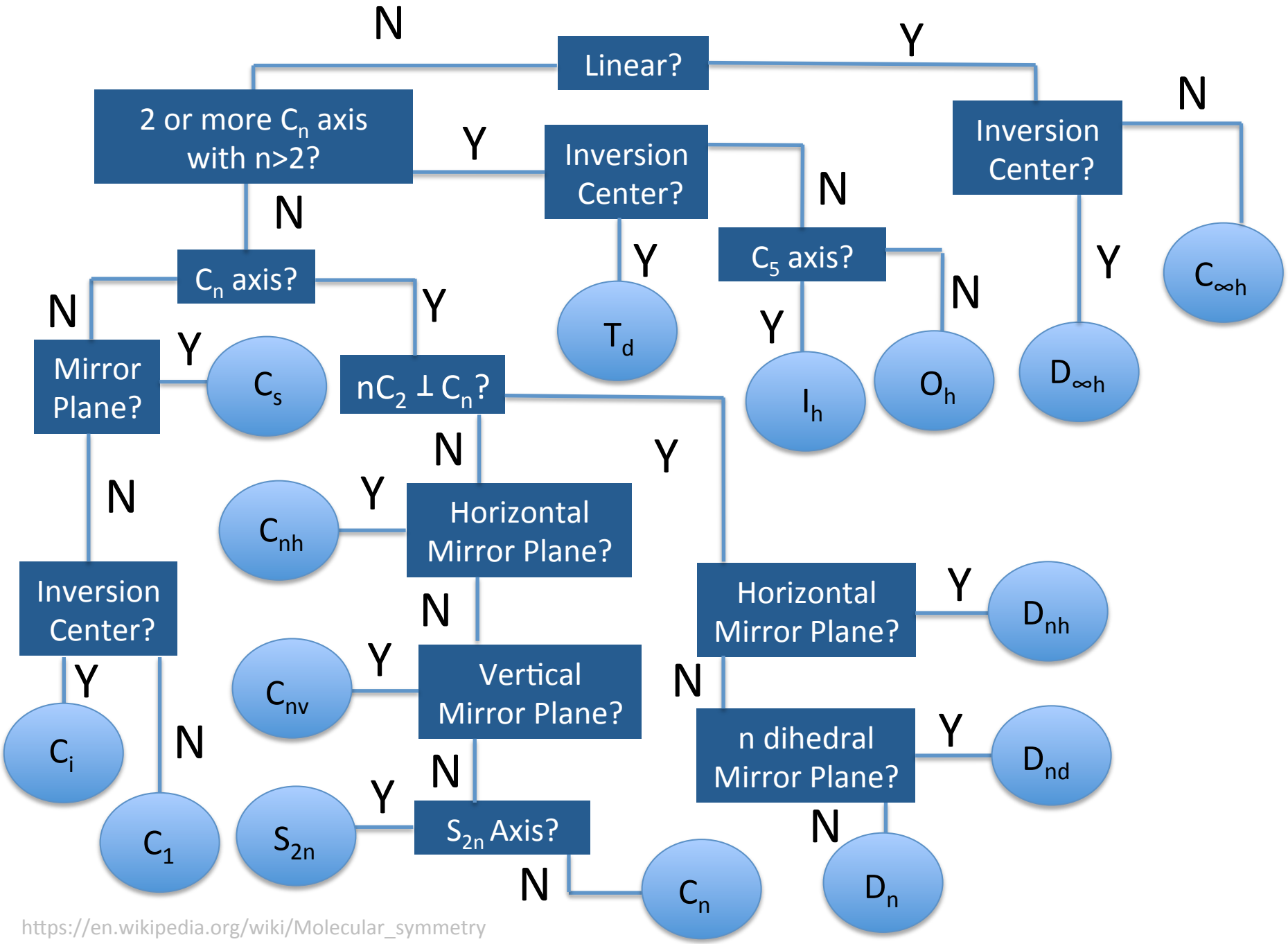


Bent Geometry Determined from VSPER

$G:=\{E, C_2, \sigma_{v1}, \sigma_{v2}\}$

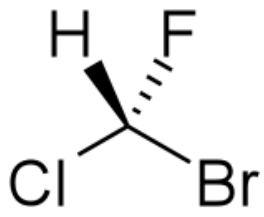
1. Closure → $C_2\sigma_{v1}=\sigma_{v2}$
   $\sigma_{v1}\sigma_{v2}=C_2$
2. Identity → E
3. Inverse → each element is its own inverse
4. Associativity → $C_2(\sigma_{v1}\sigma_{v2})=E$
   $(C_2\sigma_{v1})\sigma_{v2}=E$

https://plus.maths.org/content/os/latestnews/may-aug10/ice/index

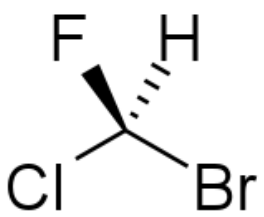


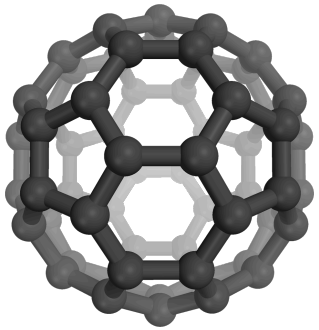
https://en.wikipedia.org/wiki/Molecular_symmetry

Examples

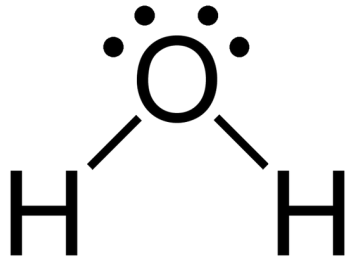


C_1

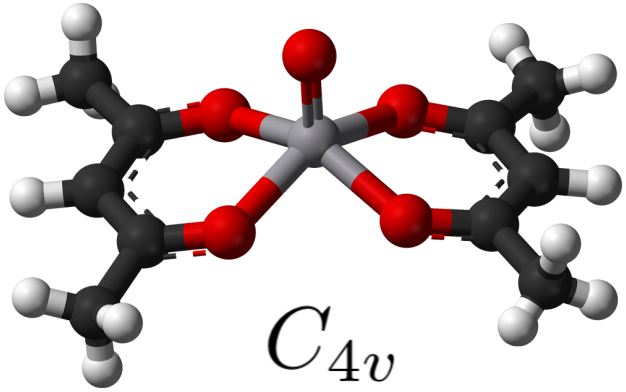




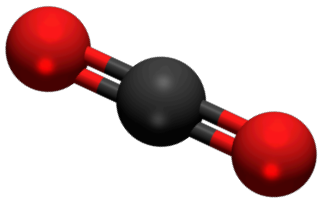
I_h



C_{2v}



C_{4v}



$D_{\infty h}$

https://en.wikipedia.org/wiki/Molecular_symmetry

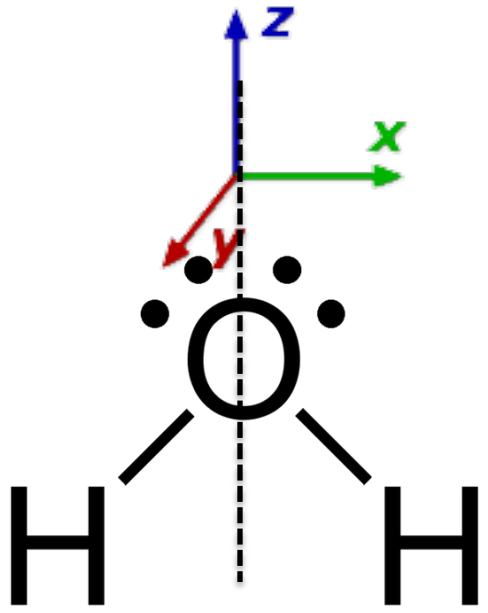
Representations of Molecular Point Groups

A representation is a group homomorphism ϕ: G → GL(V,F). Where V is a vector space and F is a field.

Construction of a representation requires first defining your representation space

Matrix Representations of Group Operations

$$G := \{E, C_2, \sigma_{v1}, \sigma_{v2}\}$$

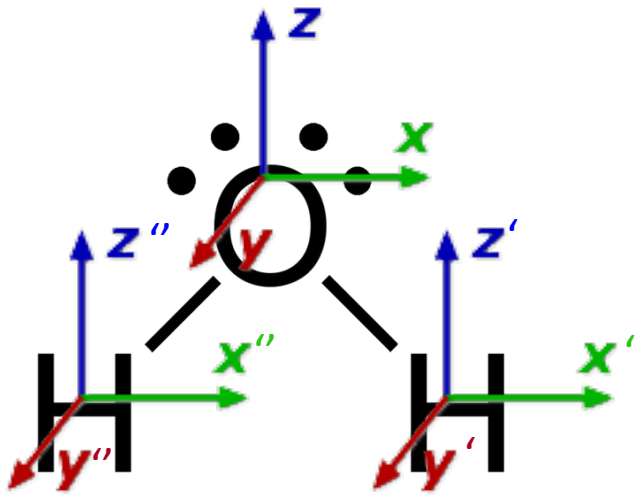


$$\Downarrow$$

$$\mathrm{GL(V)}:= \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}$$

Matrix Representations of Group Operations

$$\sigma_{v1} \begin{bmatrix} x \\ y \\ z \\ x' \\ y' \\ z' \\ x'' \\ y'' \\ z'' \end{bmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} x \\ y \\ z \\ x' \\ y' \\ z' \\ x'' \\ y'' \\ z'' \end{bmatrix}$$



$$C_2 \begin{bmatrix} x \\ y \\ z \\ x' \\ y' \\ z' \\ x'' \\ y'' \\ z'' \end{bmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} x \\ y \\ z \\ x' \\ y' \\ z' \\ x'' \\ y'' \\ z'' \end{bmatrix}$$

$$G := \{E, C_2, \sigma_{v1}, \sigma_{v2}\}$$

Irreducible Representations of Group Elements

A linear representation, ϕ: G → GL(V,F), is *irreducible* if the vectorspace, V, is non-zero and contains no invariant subspaces under ϕ.

Alternatively, if a representation is not block diagonalizable using similarity transformations, then the representation is *irreducible*

- To find irreducible representations, first find the irreducible characters.

Schur Orthogonality Relations

$$\sum_g \Gamma^{(r)^*}(g)_{mn}\Gamma^{(s)}(g)_{m'n'} = \frac{|G|}{\sqrt{d_r d_s}}\delta_{rs}\delta_{mn}\delta_{m'n'}$$

i.e.)

$$\sum_g \Gamma^{(r)^*}(g)_{mn}\Gamma^{(s)}(g)_{mn} = 0$$

$$\sum_g \Gamma^{(r)^*}(g)_{mn}\Gamma^{(r)}(g)_{m'n'} = 0$$

$$\sum_g \Gamma^{(r)^*}(g)_{mn}\Gamma^{(r)}(g)_{mn} = \frac{|G|}{\sqrt{d_r d_s}}$$

By selecting one matrix element from each matrix in an irreducible representations set of matrices we can form a vector that is the same dimension as the order of the group and is orthogonal and normalized by the dimension of the irreducible representations

5 Rules for Irreps. and Characters

1. The sum of the squares of the dimensions of the irreps. of a group is equal to the order of the group.
   $\sum d_r^2 = d_1^2 + d_2^2 + ... = |G|$

2. The sum of the squares of the characters in any irrep. equals the order of the group.
   $\sum_g [\chi_i(g)]^2 = |G|$

   Character $\rightarrow$ Trace of a matrix χ=TrA

3. The vectors whose components are the characters of two different irreps. are orthogonal.
   $\sum_g \chi_i(g)\chi_j(g) = 0$

4. In a given rep. the characters of all matrices belonging to operations in the same class are identical.

5. The number of irreps. of a group is equal to the number of classes in the group.

Irreducible Representations of C_{2v}

The number of irreps. is equal to the number of classes

$$G := \{E, C_2, \sigma_{v1}, \sigma_{v2}\}$$

$$\{E\}\{C_2\}\{\sigma_{v1}\}\{\sigma_{v2}\}$$

$$C_2 E C_2^{-1} = E \qquad \sigma_{v1} E \sigma_{v1}^{-1} = E$$
$$C_2 C_2 C_2^{-1} = C_2 \qquad \sigma_{v1} C_2 \sigma_{v1}^{-1} = C_2$$
$$C_2 \sigma_{v1} C_2^{-1} = \sigma_{v1} \qquad \sigma_{v1} \sigma_{v1} \sigma_{v1}^{-1} = \sigma_{v1}$$
$$C_2 \sigma_{v2} C_2^{-1} = \sigma_{v2} \qquad \sigma_{v1} \sigma_{v2} \sigma_{v1}^{-1} = \sigma_{v2}$$

The sum of the squares of the dimensions of the irreps. of a group is equal to the order of the group.

$$\sum d_r^2 = d_1^2 + d_2^2 + d_3^2 + d_4^2 = 4$$

$$d_1 = d_2 = d_3 = d_4 = 1$$

Character Table of C_{2v}

The trivial representation is always given

	E	C_{2v}	σ_{v1}	σ_{v2}
Γ_1	1	1	1	1

The following irreps. must follow character orthogonality

$$\sum_g \chi_1(g)\chi_j(g) = 0 \ \forall j \neq 1$$

	E	C_{2v}	σ_{v1}	σ_{v2}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Character Table of C_{2v} with Mulliken Symbols

	E	C_{2v}	σ_{v1}	σ_{v2}
$\Gamma_1 \rightarrow A_1$	1	1	1	1
$\Gamma_2 \rightarrow A_2$	1	1	-1	-1
$\Gamma_3 \rightarrow B_1$	1	-1	1	-1
$\Gamma_4 \rightarrow B_2$	1	-1	-1	1

A → 1-D, symmetric to Cn
B→ 1-D, anti-symmetry to C_n

sub. **1** → symmetric to **σ**
sub. **2** →anti- symmetric to **σ**

See Appendix II for details on notation.

Group Theory and Quantum Mechanics

Invariance of the Hamiltonian

A symmetry operation on a molecule leaves the molecule unchanged. This implies the Hamiltonian must also remain unchanged under the symmetry operation.

$$[R, \mathcal{H}]=0$$

Eigenfunctions are bases for the irreducible representation of the symmetry group

Wave Functions as Bases for Irreps.

Let $\Psi_{i1}, \Psi_{i2}, ...\Psi_{ik}$ be a set of orthonormal eigenfunctions.
G is a symmetry group and R $\in$ **G**.

Case 1: Eigenvalue is non-degenerate

$\mathcal{H}R\Psi_{i1} = R\mathcal{H}\Psi_{i1} = RE_{i1}\Psi_{i1} = E_{i1}R\Psi_{i1}$
$\Rightarrow R\Psi_{i1}$ is an eigenfunction of $\mathcal{H}$
Since Ψ_{i1} is normalized, then RΨ_{i1} must also be normalized.
$\Rightarrow R\Psi_{i1}=\pm 1\Psi_{i1}$

Therefore, application of symmetry operation on Ψ_{i1}
produces a representation of the group where each matrix is ± 1
$\Rightarrow$ Representations are irreducible.

Proof

Case 2: Eigenvalue is degenerate. Suppose degeneracy is k-fold.

$\mathcal{H}R\Psi_i = E_i R\Psi_i$

Since E_i is degenerate, any linear combination of its eigenfunctions is also a solution to the wave equation with the same eigenvalue.

Let $\Psi_{il} = \sum_{j=1}^{k} \Psi_{ij}$

Then application of a symmetry operation produces

$\mathrm{R}\Psi_{il} = \sum_{j=1}^{k} r_{jl}\Psi_{ij}$

Suppose $\mathrm{S} \in \mathbf{G}$ acts on Ψ

$\mathrm{S}\Psi_{ij} = \sum_{m=1}^{k} s_{mj}\Psi_{im}$

Since S,R are elements in **G**, then there must exist an element T, such that $T = SR$

Proof

$$T = SR$$

$$SR\Psi_{il} = T\Psi_{il} = \sum_{m=1}^{k} t_{ml}\Psi_{im} = S\sum_{j=1}^{k} r_{jl}\Psi_{ij} = \sum_{j=1}^{k}\sum_{m=1}^{k} s_{mj}r_{jl}\Psi_{im}$$

$$\Rightarrow \mathrm{t}_{ml} = \sum_{j=1}^{k} s_{mj}r_{jl}$$

$$\Rightarrow \begin{pmatrix} t_{11} & \cdots \\ \vdots & \ddots \end{pmatrix} = \begin{pmatrix} s_{11} & \cdots \\ \vdots & \ddots \end{pmatrix} \begin{pmatrix} r_{11} & \cdots \\ \vdots & \ddots \end{pmatrix}$$

Therefore transformations of k-eigenfunctions corresponding to a k-fold eigenvalue are a k-dimensional representation.

Proof

Are these representations irreducible?
Suppose not.

Then these representations can be reduced and $(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{ik})$
the set of othornormal eigenfunctions with the same energy be
broken up into two subsets as follows
$(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{ik}) \longrightarrow (\Psi_{i1}, \Psi_{i2}, ..., \Psi_{im})\ (\Psi_{im+1}, ..., \Psi_{ik})$
Applying $R^{(i)}$, an irreducible representation of R$\in$**G**, to each of these subsets
$R^{(i)}(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{im}) = \sum_{j=1}^{m} r_{jl}\Psi ij$
$R^{(i)}(\Psi_{im+1}, ..., \Psi_{ik}) = \sum_{j=m+1}^{k} r_{jl}\Psi ij$
But these subsets of eigenfunctions when summed together could have different eigenvalues. $\Rightarrow\!\!\!\!\!\!\Leftarrow$$(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{ik})$ being degenerate eigenfunctions.

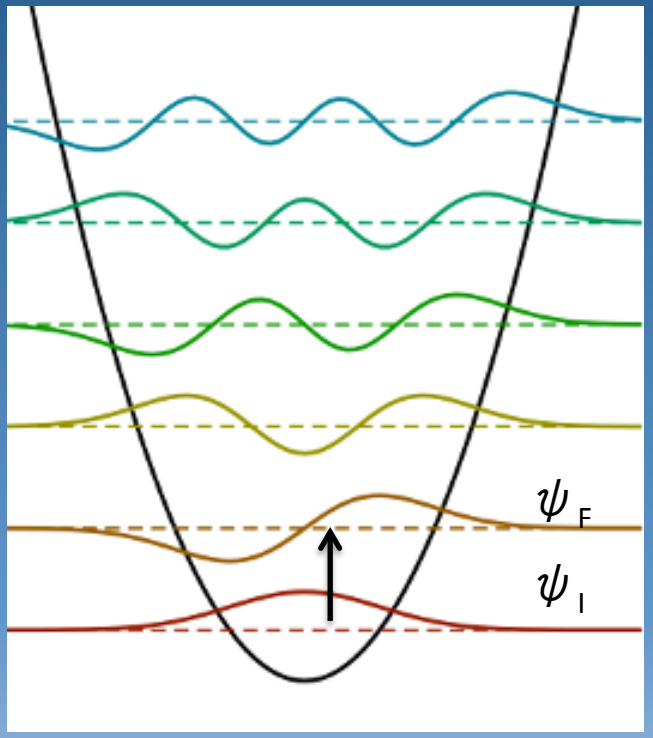
Eigenfunctions are bases for the irreducible representations of a molecule's symmetry group

Eigenfunctions are bases for the irreducible representations of a molecule's symmetry group

Corollary: The dimension of the irreducible representations, n, is equal to the degeneracy of an n-fold degenerate eigenvalue.

	E	C_{2v}	σ_{v1}	σ_{v2}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Group Theory in Vibrational Spectroscopy



Vibrational Transitions

Vibrational spectroscopy is a linear optical process. We can model the transition rate with Fermi's Golden Rule

$$R_{IF}^{(1)}(\omega) = \frac{\pi}{2\hbar^2} E_0^2 | < \psi_F | \hat{H}' | \psi_I > |^2 \rho(E_F - E_I - \hbar\omega)$$

Using the electric dipole approximation for the electric field, the time-independent perturbing Hamiltonian is defined as:

$$\hat{H}' = \frac{E_0}{2} \cdot \hat{\mu}$$

$$\boxed{R_{IF}^{(1)}(\omega) = \frac{\pi}{2\hbar^2} E_0 | < \psi_F | \hat{\mu} | \psi_I > |^2 \rho(E_F - E_I - \hbar\omega)}$$

http://www.iue.tuwien.ac.at/phd/goes/dissse8.html

Vibrational Transitions

Vibrational spectroscopy is a linear optical process. We can model the transition rate with Fermi's Golden Rule

$$R_{IF}^{(1)}(\omega) = \frac{\pi}{2\hbar^2} E_0 | < \Psi_{el._i} \psi_F | \hat{\mu} | \Psi_{el._i} \psi_I > |^2 \rho(E_F - E_I - \hbar\omega)$$

Where for an allowed transition the following must hold:

$$< \Psi_{el._i} \psi_{vib._I} | \hat{\mu} | \Psi_{el._i} \psi_{vib._F} > \neq 0$$

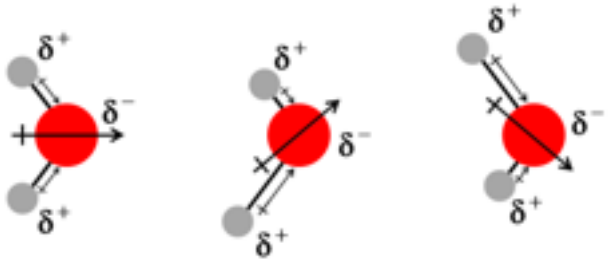
Allowed Transitions

Consider the case where the radiation is polarized in the z-direction. Evaluation of the matrix element is as follows:

$$< \Psi_{el._i}\psi_{vib._I}|\hat{\mu}_z|\Psi_{el._i}\psi_{vib._F} >$$

$$= \sum_j (\frac{\partial M_z}{\partial Q_j})_0 \int dQ \psi^*_{vib._F}(Q)(Q_j - Q_{j_0})\psi_{vib._I}(Q)$$

For a transition, there must be a change in the dipole w.r.t. the bond length



http://nptel.ac.in/courses/102103044/module2/lec3/images/8.png

Symmetry of the Operator

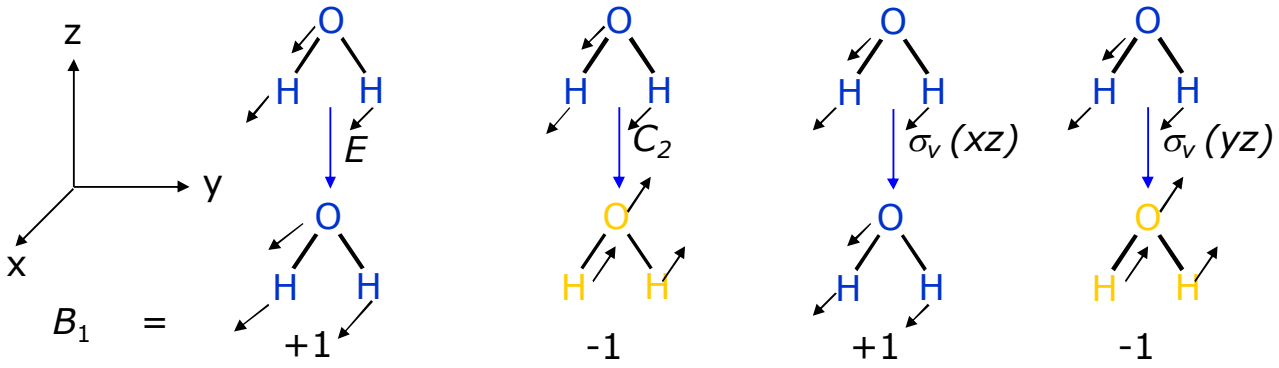
$$\hat{\mu}_x \propto (\frac{\partial M_x}{\partial Q_j})(Q_j - Q_{j_0})$$
$$\hat{\mu}_y \propto (\frac{\partial M_y}{\partial Q_j})(Q_j - Q_{j_0})$$
$$\hat{\mu}_z \propto (\frac{\partial M_z}{\partial Q_j})(Q_j - Q_{j_0})$$

$\Downarrow$

Symmetries will be the same as translations

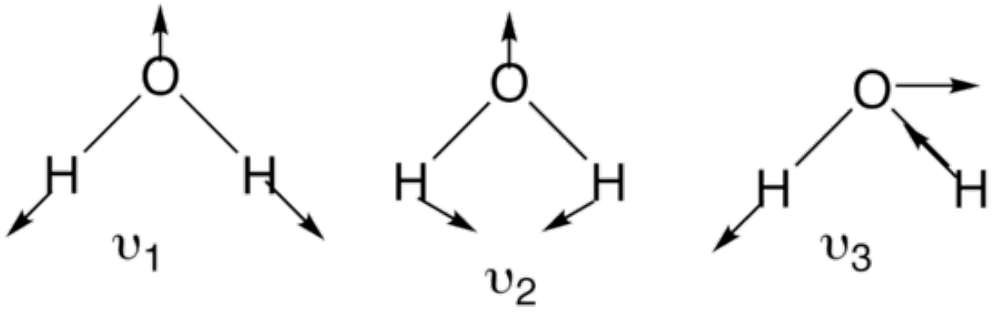
	E	C_{2v}	σ_{v1}	σ_{v2}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Translations in the X-direction



Normal Modes as Bases of Irreps.

For polyatomic molecules, a natural choice of choice for the bases are the normal modes of vibration.

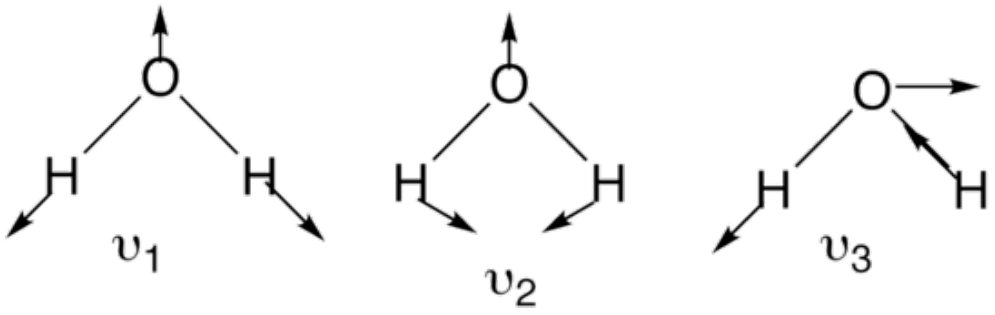


This simplifies the problem to a one-dimensional harmonic oscillator, wherein the Hamiltonian is separable and the wavefunction can be written as the following:

$$\psi_{vib}(Q_1, Q_2, Q_3, ...) = \psi_{v1}(Q1)\psi_{v2}(Q2)\psi_{v3}(Q3)$$

https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Normal_Modes

Symmetry of Normal Modes



$$v1 \rightarrow A_1$$
$$v2 \rightarrow A_1$$
$$v3 \rightarrow B_1$$

	E	C_{2v}	σ_{v1}	σ_{v2}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Normal_Modes

Integrals of Product Functions

Integrand must be invariant to all symmetry operations for it to be non-zero. Implying the product forms a basis containing the totally symmetric representation, A_1.

$$\int \psi^*_{vib.I} \hat{\mu} \psi_{vib.F} d\tau \neq 0$$

We know the functions form a basis for an irreducible representation

$$\psi_A \rightarrow \Gamma_A$$

If the irreducible representation whose basis is the individual functions is known, then the direct product of the irreducible representations can be used to determine the symmetry of the integrand.

$$\Gamma_A \times \Gamma_B \times \Gamma_\mu \subseteq A_1$$

Active Vibrational Transitions

	E	C_{2v}	σ_{v1}	σ_{v2}	
A_1	1	1	1	1	z
A_2	1	-1	-1	1	
B_1	1	-1	1	-1	x
B_2	1	1	-1	-1	y

$$\psi_{v1} \rightarrow A_1$$

$$\psi_{v2} \rightarrow A_1$$

$$\psi_{v3} \rightarrow B_1$$

$$\psi_1 \mu_x \psi_0 \Rightarrow A_1 \times B_1 \times A_1 = B_1$$

$$\psi_1 \mu_y \psi_0 \Rightarrow A_1 \times B_2 \times A_1 = B_2$$

$$\psi_1 \mu_z \psi_0 \Rightarrow A_1 \times A_1 \times A_1 = A_1$$

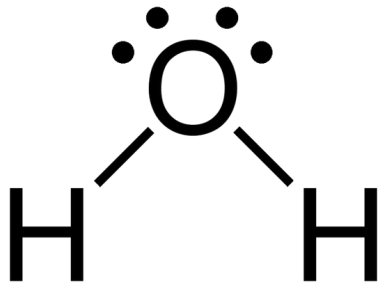
$$\psi_1 \mu_x \psi_0 \Rightarrow B_2 \times B_1 \times A_1 = A_2$$

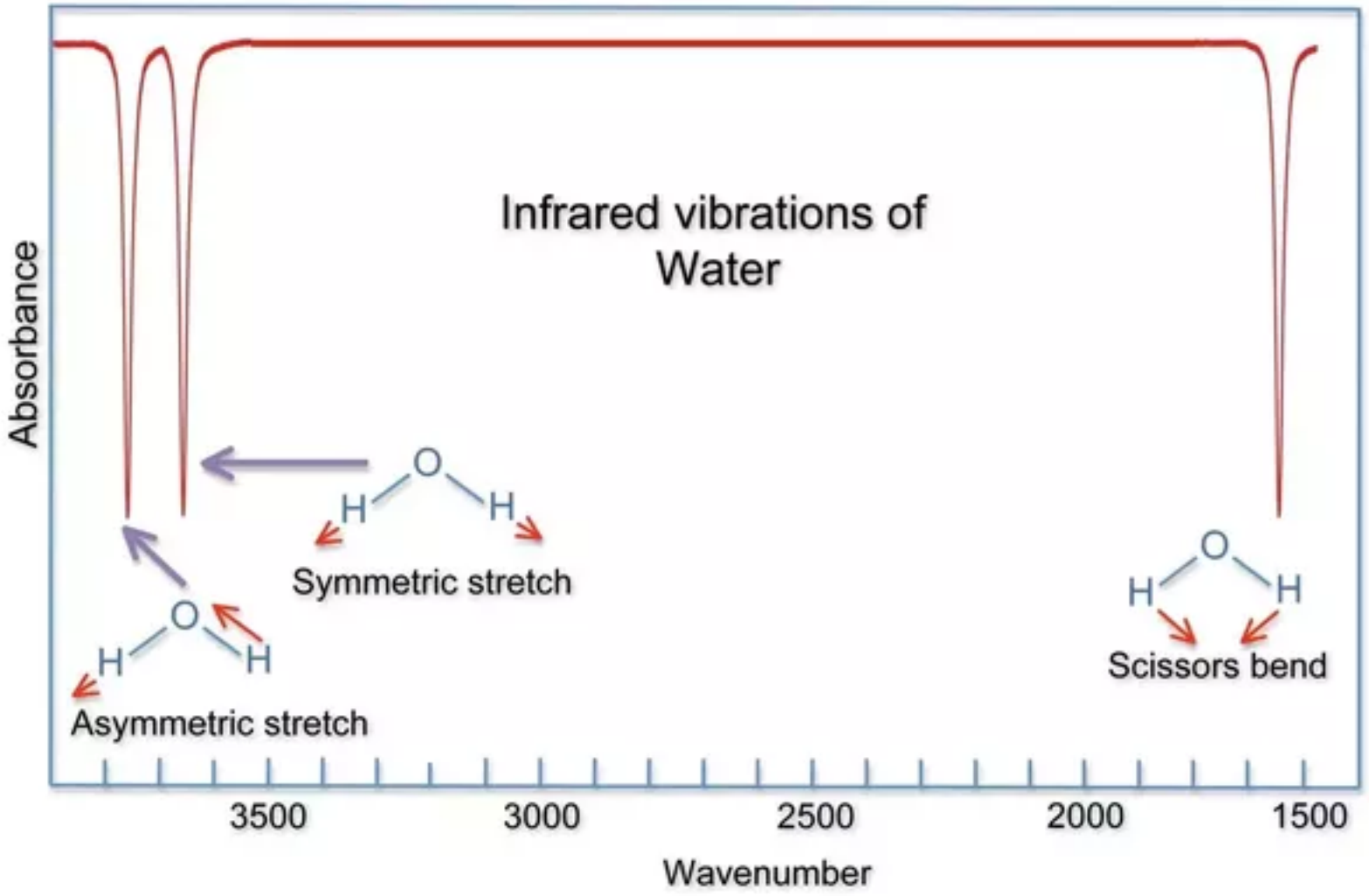
$$\psi_1 \mu_y \psi_0 \Rightarrow B_2 \times B_2 \times A_1 = A_1$$

$$\psi_1 \mu_z \psi_0 \Rightarrow B_2 \times A_1 \times A_1 = B_2$$

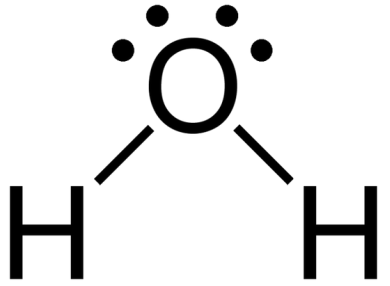
All modes are IR active

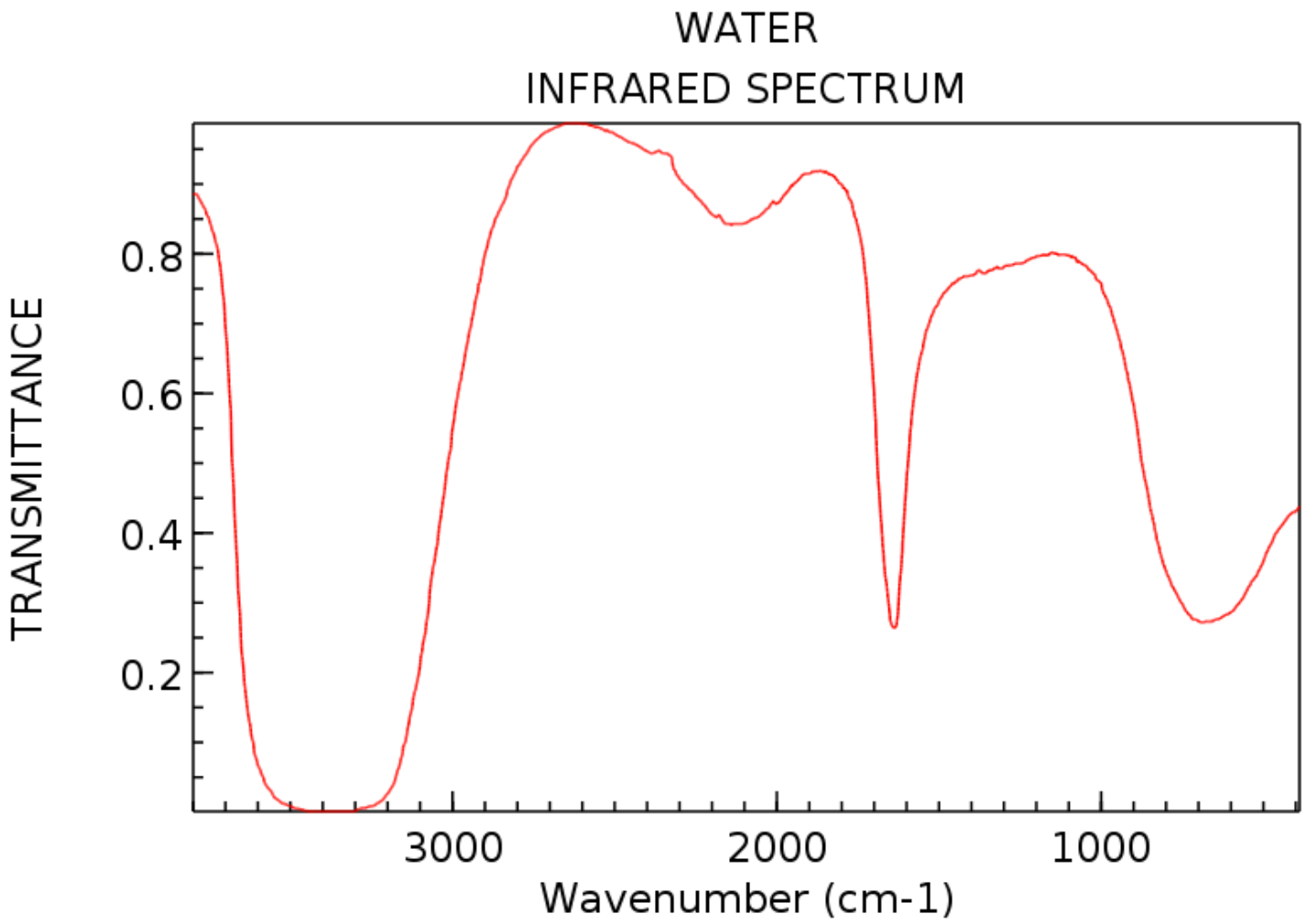
Infrared Spectrum of Water





Infrared Spectrum of Water





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

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https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Group_Theory

If the structure is known then the symmetry is known and vice versa

Thank you.

Questions?

Appendix I-Schönflies Notation

- C_n (cyclic) $\longrightarrow$ object has n-fold rotation axis
  - $C_{nh} \rightarrow$ plane of reflection perpendicular to axis of rotation
  - $C_{nv} \rightarrow$ "n" mirror planes containing the axis of rotation
- D_n (dihedral) $\longrightarrow$ C_n and $nC_2 \perp$ to C_n
  - D_{nh} has a horizontal mirror plane and n vertical mirror planes containing the rotation axis
  - D_{nd} has n diagonal mirror planes
- $C_{ni} \longrightarrow$ object has a center of inversion
- $S_n \longrightarrow$ improper rotation, i.e. rotation followed by a reflection (**Note** $S1 = \sigma$, $S_2 = i$
- I,O,$T \longrightarrow$ icosahedral, octahedral, and tetrahedral

Appendix II - Mulliken Symbols

A $\Rightarrow$ one dimensional irrep. symmetric rotation about principle axis

B $\Rightarrow$ one dimensional irrep. anti-symmetric rotation about principle axis.

E $\Rightarrow$ 2-dimensional irrep.

T $\Rightarrow$ 3-dimensional irrep.

Subscript 1 or 2 (on A and B) $\Rightarrow$
symmetric or antisymetric, respectively, to $C_2 \perp C_n$, or if no C_2 then subscript w.r.t. σ_v.

Subscripts g or u $\Rightarrow$
applied to groups with a center of inversion. g (gerade) is symmetric, u (ungerade) antisymetric w.r.t. center of inversion.

prime $\Rightarrow$ symmetric w.r.t. reflection in horizontal plane

double prime $\Rightarrow$ anti-symmetric w.r.t. reflection in horizontal plane