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
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 $\text{H}_2\text{O}$

1. **Closure** → $c_2 \sigma_{v1} = \sigma_{v2}$
   
2. **Identity** → $E$

3. **Inverse** → each element is its own inverse

4. **Associativity** → $c_2(\sigma_{v1} \sigma_{v2}) = E$
   
   $(c_2 \sigma_{v1}) \sigma_{v2} = E$

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

Bent Geometry Determined from VSPER
Examples

\[ \text{H}_2\text{F} \quad \text{Cl} \quad \text{F} \quad \text{H} \quad \text{Br} \quad \text{Cl} \quad \text{Br} \quad I_h \]

\[ C_1 \]

\[ \text{H}_2\text{O} \]

\[ C_{2v} \]

\[ \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad C_{4v} \]

\[ D_{\infty h} \]

https://en.wikipedia.org/wiki/Molecular_symmetry
Representations of Molecular Point Groups

A representation is a group homomorphism $\phi: G \rightarrow GL(V,F)$. 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

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

\[ \downarrow \]

\[ \text{GL}(V) := \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} \]
Matrix Representations of Group Operations

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

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

\[ G := \{ E, C_2, \sigma_{v1}, \sigma_{v2} \} \]
A linear representation, $\phi: G \to \text{GL}(V,F)$, is *irreducible* if the vectorspace, $V$, is non-zero and contains no invariant subspaces under $\phi$.

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.
\[ \sum d_r^2 = d_1^2 + d_2^2 + \ldots = |G| \]

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

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

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

\[ \{E\}\{C_2\}\{\sigma_{v1}\}\{\sigma_{v2}\} \]

\[ C_2 E C_2^{-1} = E \quad \sigma_{v1} E \sigma_{v1}^{-1} = E \]
\[ C_2 C_2 C_2^{-1} = C_2 \quad \sigma_{v1} C_2 \sigma_{v1}^{-1} = C_2 \]
\[ C_2 \sigma_{v1} C_2^{-1} = \sigma_{v1} \quad \sigma_{v1} \sigma_{v1} \sigma_{v1}^{-1} = \sigma_{v1} \]
\[ C_2 \sigma_{v2} C_2^{-1} = \sigma_{v2} \quad \sigma_{v1} \sigma_{v2} \sigma_{v1}^{-1} = \sigma_{v2} \]

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:

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>$C_{2v}$</th>
<th>$\sigma_{v1}$</th>
<th>$\sigma_{v2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>1</td>
<td>1</td>
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</tbody>
</table>

The following irreps. must follow character orthogonality:

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

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>$\Gamma_2$</td>
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<tr>
<td>$\Gamma_3$</td>
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<tr>
<td>$\Gamma_4$</td>
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</table>
## Character Table of $C_{2v}$ with Mulliken Symbols

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_{2v}$</th>
<th>$\sigma_{v1}$</th>
<th>$\sigma_{v2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1 \rightarrow A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2 \rightarrow A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3 \rightarrow B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_4 \rightarrow B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

A $\rightarrow$ 1-D, symmetric to $C_n$

B $\rightarrow$ 1-D, anti-symmetry to $C_n$

sub. 1 $\rightarrow$ symmetric to $\sigma$

sub. 2 $\rightarrow$ anti-symmetric to $\sigma$

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.
Let $\Psi_{i_1}, \Psi_{i_2}, \ldots \Psi_{i_k}$ be a set of orthonormal eigenfunctions. $G$ is a symmetry group and $R \in G$.

**Case 1:** Eigenvalue is non-degenerate

\[ \mathcal{H} R \Psi_{i_1} = R \mathcal{H} \Psi_{i_1} = RE_{i_1} \Psi_{i_1} = E_{i_1} R \Psi_{i_1} \]

$\Rightarrow$ $R \Psi_{i_1}$ is an eigenfunction of $\mathcal{H}$

Since $\Psi_{i_1}$ is normalized, then $R \Psi_{i_1}$ must also be normalized.

$\Rightarrow$ $R \Psi_{i_1} = \pm 1 \Psi_{i_1}$

Therefore, application of symmetry operation on $\Psi_{i_1}$ produces a representation of the group where each matrix is $\pm 1$

$\Rightarrow$ Representations are irreducible.
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

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

Suppose $S \in G$ acts on $\Psi$

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

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

\[ T = SR \]

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

\[ \Rightarrow t_{ml} = \sum_{j=1}^{k} s_{mj} r_{jl} \]

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

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 orthonormal eigenfunctions with the same energy be broken up into two subsets as follows
\[(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{ik}) \rightarrow (\Psi_{i1}, \Psi_{i2}, ..., \Psi_{im}) (\Psi_{im+1}, ..., \Psi_{ik})\]

Applying \(R^{(i)}\), an irreducible representation of \(R \in G\), to each of these subsets
\[R^{(i)}(\Psi_{i1}, \Psi_{i2}, ..., \Psi_{im}) = \sum_{j=1}^{m} r_{ij} \Psi_{ij}\]
\[R^{(i)}(\Psi_{im+1}, ..., \Psi_{ik}) = \sum_{j=m+1}^{k} r_{ij} \Psi_{ij}\]

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

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>( C_{2v} )</th>
<th>( \sigma_{v1} )</th>
<th>( \sigma_{v2} )</th>
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<tbody>
<tr>
<td>( A_{1} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>( A_{2} )</td>
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</tr>
<tr>
<td>( B_{1} )</td>
<td>1</td>
<td>-1</td>
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<td>-1</td>
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<tr>
<td>( B_{2} )</td>
<td>1</td>
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<td>1</td>
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</tbody>
</table>

Eigenfunctions are bases for the irreducible representations of a molecule’s symmetry group.
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:

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

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

\[ < \Psi_{el.i} \psi_{vib.I} | \hat{\mu} | \Psi_{el.i} \psi_{vib.F} > \neq 0 \]
Consider the case where the radiation is polarized in the z-direction. Evaluation of the matrix element is as follows:

\[
\langle \Psi_{el.\ i} \psi_{vib.\ I} | \hat{\mu}_z | \Psi_{el.\ i} \psi_{vib.\ F} \rangle = \sum_j \left( \frac{\partial M_z}{\partial Q_j} \right)_0 \int dQ \psi^*_{vib.\ F}(Q)(Q_j - Q_{j0})\psi_{vib.\ I}(Q)
\]

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

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

\[\Downarrow\]

Symmetries will be the same as translations

<table>
<thead>
<tr>
<th></th>
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<th>\sigma_{v1}</th>
<th>\sigma_{v2}</th>
<th></th>
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</thead>
<tbody>
<tr>
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<td>1</td>
<td>z</td>
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<tr>
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<td>-1</td>
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</tr>
<tr>
<td>B_1</td>
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<td>1</td>
<td>-1</td>
<td>x</td>
</tr>
<tr>
<td>B_2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>y</td>
</tr>
</tbody>
</table>

Translations in the X-direction

For polyatomic molecules, a natural 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:

\[ \psi_{vib}(Q_1, Q_2, Q_3, \ldots) = \psi_{v_1}(Q_1)\psi_{v_2}(Q_2)\psi_{v_3}(Q_3) \]
Symmetry of Normal Modes

\[ \begin{align*}
\nu_1 & \rightarrow A_1 \\
\nu_2 & \rightarrow A_1 \\
\nu_3 & \rightarrow B_1
\end{align*} \]

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<td>A_1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A_2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B_1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B_2</td>
<td>1</td>
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</table>
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, $A_1$.

\[
\int \psi^*_\text{vib.}_I \hat{\mu} \psi_{\text{vib.}_F} d\tau \neq 0
\]

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

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<tbody>
<tr>
<td>$A_1$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>$\psi_{v1} \rightarrow A_1$</td>
</tr>
<tr>
<td>$A_2$</td>
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<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$\psi_{v2} \rightarrow A_1$</td>
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<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$\psi_{v3} \rightarrow B_1$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>1</td>
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</tbody>
</table>

All modes are IR active

\[
\begin{align*}
\psi_{1\mu_x}\psi_0 & \Rightarrow A_1 \times B_1 \times A_1 = B_1 \\
\psi_{1\mu_y}\psi_0 & \Rightarrow A_1 \times B_2 \times A_1 = B_2 \\
\psi_{1\mu_z}\psi_0 & \Rightarrow A_1 \times A_1 \times A_1 = A_1 \\
\psi_{1\mu_x}\psi_0 & \Rightarrow B_2 \times B_1 \times A_1 = A_2 \\
\psi_{1\mu_y}\psi_0 & \Rightarrow B_2 \times B_2 \times A_1 = A_1 \\
\psi_{1\mu_z}\psi_0 & \Rightarrow B_2 \times A_1 \times A_1 = B_2 \\
\end{align*}
\]
Infrared Spectrum of Water

Infrared vibrations of Water

- Symmetric stretch
- Asymmetric stretch
- Scissors bend
Infrared Spectrum of Water

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


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) $\rightarrow$ 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) $\rightarrow$ $C_n$ 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

- $C_{ni}$ $\rightarrow$ object has a center of inversion

- $S_n$ $\rightarrow$ improper rotation, i.e. rotation followed by a reflection (Note $S_1 = \sigma$, $S_2 = i$)

- $I,O,T$ $\rightarrow$ icosahedral, octahedral, and tetrahedral
Appendix II - Mulliken Symbols

A ⇒ one dimensional irrep. symmetric rotation about principle axis
B ⇒ one dimensional irrep. anti-symmetric rotation about principle axis.
E ⇒ 2-dimensional irrep.
T ⇒ 3-dimensional irrep.
Subscript 1 or 2 (on A and B) ⇒
symmetric or antisymmetric, respectively, to $C_2 \perp C_n$, or if no $C_2$ then
subscript w.r.t. $\sigma_v$.
Subscripts g or u ⇒
applied to groups with a center of inversion. g (gerade) is symmetric, u (ungerade) antisymmetric w.r.t. center of inversion.
prime ⇒ symmetric w.r.t. reflection in horizontal plane
double prime ⇒ anti-symmetric w.r.t. reflection in horizontal plane