Molecular Symmetry

• Symmetry impacts
  - Physical properties
  - Reactions
  - Molecular orbitals
  - Electronic structure
  - Molecular vibrations

• Group theory
  - Behavior of molecule based on symmetry

• Symmetry analysis
• Applications of symmetry
• Orbital symmetry
• Vibrational symmetry
Introduction to symmetry analysis

- Symmetry operation
  - Action which molecular symmetry unchanged
    - Rotation through an angle
    - Reflection

- Symmetry element
  - Location of symmetry operation
    - Point
    - Line
    - Plane
  - Operation leaves at least one point in molecule unchanged
    - Point group symmetry
Symmetry analysis

- Identity operation (E)
  - Leaves entire molecule unchanged
  - All molecules have at least this operation
- n fold symmetry axis (Cₙ)
  - 360°/n rotation
  - H₂O
    - * 180°, n=2
    - * C₂
  - NH₃
    - * 120°, n=3
    - * C₃
Symmetry analysis

• Mirror plane ($\sigma$)
  ✍️ Vertical ($\sigma_v$), horizontal ($\sigma_h$) or dihedral ($\sigma_d$) to rotation of fold symmetry axis
  ➤ Molecule can have different levels of mirror plane
Symmetry analysis

- Inversion operation (i)
  - Projection through a center point in the molecule
    - Center of an octahedron
    - No AB₄ tetrahedron has a center of inversion
  - Need to differentiate between C₂ and i
Symmetry analysis

- Improper rotation ($S_n$)
  - consist of two separate operations:
    - n-fold rotation (rotation by $360\degree/n$) about an axis followed by
    - reflection in a plane perpendicular to that axis.
  - Each operation is needed to achieve the proper reflection
    - Individual operation does not result in proper reflection
  - Improper axes are often the most difficult symmetry elements to spot
  - $S_1$
    - $C_1$ and $\sigma_h$ is $\sigma_h$
  - $S_2$
    - $C_2$ and $\sigma_h$ is $i$
Symmetry analysis summary

- Molecule can have a number of symmetry operations
- Each operation has associated element

<table>
<thead>
<tr>
<th>Symmetry element</th>
<th>Symmetry operation</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Fold symmetry axis</td>
<td>Identity*</td>
<td>$E$</td>
</tr>
<tr>
<td>Mirror plane</td>
<td>Rotation by $2\pi/n$</td>
<td>$C_n$</td>
</tr>
<tr>
<td>Center of inversion</td>
<td>Reflection</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>$n$-Fold axis of</td>
<td>Inversion</td>
<td>$i$</td>
</tr>
<tr>
<td>improper rotation†</td>
<td>Rotation by $2\pi/n$ followed by reflection</td>
<td>$S_n$</td>
</tr>
<tr>
<td></td>
<td>perpendicular to rotation axis</td>
<td></td>
</tr>
</tbody>
</table>

*The symmetry element can be thought of as the whole of space.
†Note the equivalences $S_1 = \sigma$ and $S_2 = i$.  

4-7
Point Groups

- Point group can be assigned to each element
  - Based on symmetry elements possessed by molecule and compare to element that define group
  - Strong relationship between molecule geometry and point group

  ➤ Linear with center $D_{\infty h}$
  ➤ Linear no center $C_{\infty v}$

* See previous lecture for more information
Point Groups

- \( T_d \)

- \( O_h \)

- \( I_h \)
<table>
<thead>
<tr>
<th>Point group</th>
<th>Symmetry elements</th>
<th>Shape</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>$E$</td>
<td></td>
<td>SiBrClF</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$E, C_2$</td>
<td></td>
<td>$H_2O_2$</td>
</tr>
<tr>
<td>$C_s$</td>
<td>$E, \sigma$</td>
<td></td>
<td>NHF$_3$</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$E, C_2, \sigma_v, \sigma$</td>
<td></td>
<td>$H_2O$, SO$_2$Cl$_2$</td>
</tr>
<tr>
<td>$C_{3v}$</td>
<td>$E, 3\sigma_v$</td>
<td></td>
<td>NH$_3$, PCl$_3$, POCl$_3$</td>
</tr>
<tr>
<td>$C_{nv}$</td>
<td>$E, C_{nv}, 2\sigma_v, \cdots \infty \sigma_v$</td>
<td></td>
<td>CO, HCl, OCS</td>
</tr>
<tr>
<td>$D_{2h}$</td>
<td>$E, C_2(x, y, z), \sigma(xy, yz, zx), i$</td>
<td></td>
<td>N$_2$O$_4$, B$_2$H$_6$</td>
</tr>
<tr>
<td>$D_{3h}$</td>
<td>$E, C_3, 3\sigma_v, \sigma_h, S_3$</td>
<td></td>
<td>BF$_3$, PCl$_3$</td>
</tr>
<tr>
<td>$D_{4h}$</td>
<td>$E, C_4, C_2, 2\sigma_v, 2\sigma_d, i, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$</td>
<td></td>
<td>XeF$_4$, trans-MA$_2$B$_2$</td>
</tr>
<tr>
<td>$D_{5h}$</td>
<td>$E, 5\sigma_v, \infty \sigma_v, \sigma_h, 5\sigma_d, \cdots \infty C_2$</td>
<td></td>
<td>H$_2$, CO$_2$, C$_4$H$_6$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>$E, 3C_2, 4S_4, 6\sigma_d, 4S_4$</td>
<td></td>
<td>CH$_4$, SiCl$_4$</td>
</tr>
<tr>
<td>$O_h$</td>
<td>$E, 6C_2, 4S_4, 3C_4, 4S_6, 3S_6, i, 3\sigma_d, 6\sigma_d$</td>
<td></td>
<td>SF$_6$</td>
</tr>
</tbody>
</table>

*Not all the elements of each group are listed, but enough are listed for unambiguous assignments to be made.
Point Groups

- **H₂O point group**
  - Know it is C₂ᵥ from table
  - Symmetry elements
    - E, C₂ (180° rotation), 2 vertical mirror planes (σᵥ)
      * E, C₂, σᵥ, σᵥ'

- **NH₃ point group**
  - C₃ᵥ point group
  - Elements
    - E, C₃ (each N-H), three vertical mirror plane through each N-H (3σᵥ)
      * E, C₃, 3σᵥ

- Apply to identification tree
Application of symmetry

• Construction and labeling of molecular orbitals
• Molecular properties
  ➕ Polarity
  ➕ Chirality
• Polar
  ➕ Permanent dipole
  ➕ Cannot set up dipole on molecule with symmetry elements that exchange dipole over molecule
    ➕ Cannot have dipole with following symmetry elements
      * Center of inversion
      * Perpendicular to mirror plane or axis of rotation
    ➕ D point groups, T_d, O_h, I_h do not have dipoles
Polar molecules

- Consider Ruthenocene
  - Is point group D or cubic?
  - What is the point group?
    - $C_5, C_2$ perpendicular with $C_5$, $\sigma_h$ mirror plane
    - $D_{5h}$
    - Molecule is non-polar
Chiral Molecules

- **Chirality**
  - Cannot be superimposed on mirror image
    - Enantiomers
  - Optically active
    - Rotate light
  - Chiral molecules do not have $S_n$ symmetry element
    - $D_{nd}$, $D_{nh}$, $T_d$, $O_h$
Orbitals and symmetry

• Correlate symmetry with orbital characteristics

• Character tables

   ✄ Sigma
   ➤ No sign change with rotation
   * 1 on table

   ✄ Pi
   ➤ Sign change with rotation
   * -1 on table

   ✄ p\textsubscript{z} has sigma symmetry
Orbital Symmetry

- Symmetry adapted linear combination
  - SALC
  - Combination of orbitals with symmetry considerations
  - HN₃
    \[ \phi 1s_a + \phi 1s_b + \phi 1s_c \]
Character table

Table 4.3 The $C_{3v}$ character table*

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

$z$, $x^2 + y^2, z^2$, $(x, y)$, $(x^2 - y^2, xy)$, $(zx, yz)$, $R_z$, $(R_x, R_y)$

*$(a, b)$ denotes a degenerate pair of orbitals, the characters in the table refer to the symmetry of the pair jointly. The symbol $R_q$ denotes a rotation around the axis $q$.

- Orbitals are symmetry types
- Symmetry based on center point of molecule
- Angular variation of orbitals represented by directions
- Element operation
  - $E$ gives degeneracy $(a, b; e; t)$
  - 1, -1 symmetry
    - Only symmetry similar orbitals can overlap
    - Evaluate $D_{3h}$ of $BF_3$
Character tables

- E and T are sum
  - Can be 0
- Consider H₂O
  - What is the pₗ orbital on O?
  - C₂ changes sign
    - -1
  - σᵥ does not change sign
    - B₁

<table>
<thead>
<tr>
<th>Group</th>
<th>E</th>
<th>C₂</th>
<th>σᵥ(xz)</th>
<th>σᵥ(yz)</th>
<th>h = 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂ᵥ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2mm)</td>
</tr>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>Rz</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x, R₁</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>y, R₂</td>
</tr>
</tbody>
</table>
Molecular orbitals

- Based on SALC of atomic orbitals of same symmetry
  - σ and p\textsubscript{z} can combine to form molecular orbital
- Consider H on H\textsubscript{2}O
  - What are the symmetry labels for H1s and which O orbitals overlap?
    - \( \phi_+ = \phi A1s^+ + \phi B1s; \phi_- = \phi A1s^- + \phi B1s \) for H orbitals
    - \( \phi_+ \) for E, C\textsubscript{2}, \( \sigma_v, \sigma_{v'} = 1 \); \( \phi_- \) for C\textsubscript{2}, \( \sigma_v = -1 \), E and \( \sigma_{v'} = 1 \)
    - A\textsubscript{1} and B\textsubscript{2} from table
      - * O\textsubscript{s} and O\textsubscript{pz} orbitals with H \( \phi_+ \) form \( \psi_{a1} \)
      - * O\textsubscript{py} with H \( \phi_- \) form \( \psi_{b2} \)
Construction Molecular orbitals

- Assign point group to molecule
- Look up shapes from SALC
- Arrange SALCs based on energy and number of nodes
  - $s < p < d$
- Combine N SALC into N molecular orbitals
- Estimate energy and compare with data
Molecular Vibration

- **Polar molecules IR active**
  - $\text{H}_2\text{O}$, $\text{HCl}$, $\text{NO}$
  - Most molecules will absorb IR
- **Homonuclear species IR inactive**
  - $\text{O}_2$, $\text{N}_2$, $\text{Cl}_2$

- **Vibrations**
  - **Stretching**
    - Symmetric and asymmetric
  - **Bending**
    - Rocking
    - Scissoring
    - Wagging
    - Twisting
Theory

- Only some modes IR active
- Model based on Hooke’s law
  \[ F = -ky \]
  - \( F \)= force, \( k \)= constant, \( y \)= displacement distance
  - Change in energy related to \( F \)

\[
\begin{align*}
\text{dE} &= -F\text{dy} \\
\text{dE} &= ky\text{dy} \\
\int_0^y \text{dE} &= k \int_0^y y\text{dy} \\
E &= \frac{1}{2}ky^2
\end{align*}
\]
Theory

- Harmonic oscillator derived
  \[ E = \frac{1}{2} ky^2 \]

- Vibrational Frequency
  - F = ma
  - a = d²y/dt²
  - md²y/dt² = -ky
  - Substitute
    \[ y = A\cos2\pi\nu_m t \]
  - \( \nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \)
  - m goes to reduced mass
    \[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]
Theory

- **Quantum treatment**
  - \( h \) is Planck constant
  - \( \nu \) is vibrational quantum number
  - Integer \( \geq 0 \)

\[
E = \left( \nu + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = (\nu + \frac{1}{2}) h \nu_m
\]

\[
E_0 = \left( \frac{1}{2} \right) h \nu_m, \quad E_1 = \left( \frac{3}{2} \right) h \nu_m, \quad \Delta E = h \nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}
\]

- **Solve for \( \nu \)**
  \[
  \nu = \nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
  \]

- **Express in wavenumbers**
  - In cm\(^{-1}\), \( k \) in N/m, \( c \) in m/s, \( \mu \) in kg
  - \( K \) 3-8E2 for single bonds
  - 1e3 double, 1.5e3 triple
Theory

• Calculate stretching frequency of C=O
  ➤ Calculate mass in kg
    ➤ $m_c = 2e-26 \text{ kg}$
    ➤ $m_o = 2.7e-26 \text{ kg}$
    ➤ $\mu = 2.7 \times 2 \times 1e-26/(2.7+2) = 1.1E-26 \text{ kg}$

  \[ \bar{\nu} = 5.3E - 12 \sqrt{\frac{1E3}{1.1E - 26}} = 1.6E3 \text{ cm}^{-1} \]

  ➤ Experimental value 1600 cm$^{-1}$ to 1800 cm$^{-1}$

• Actual system is anharmonic
  ➤ Selection rules $\Delta \nu \pm 2$ and 3 are observed
Theory

- Electron repulsion
- Bond breaking
- Vibrational modes
  - Depends upon number of atoms and degrees of freedom
    - 3N total
    - N number to atoms
- Constraints due to
  - Translational and rotational motion of molecule
  - Motion of atoms relative to each other
    - Non linear 3N-6
    - Linear 3N-5
- CO₂, 4 modes
  - 2 bend, symmetric stretch, asymmetric stretch
- H₂O, 3 modes
- SF₆, 15 modes

\[ \nu_1 \, (3652 \, \text{cm}^{-1}) \]
\[ \nu_2 \, (1595 \, \text{cm}^{-1}) \]
\[ \nu_3 \, (3756 \, \text{cm}^{-1}) \]
Raman Theory

- **Excitation**
  - From ground or 1st vibrationally excited state
    - Population of excited state from Boltzmann’s equation
      * Molecule populates virtual states with energy from photon
      * Can be effected by temperature
  - Elastic scattering is Rayleigh
    - Energy scattered=energy incident
  - Energy difference due to $\Delta$ ground and 1st excited state
    - $h\nu-\Delta E$ is Stokes scattering
    - $H\nu+\Delta E$ is anti-Stokes scattering
Theory

- 3 types of scattered radiation
  - **Stokes**
    - Lower energy than Anti-Stokes
      * Named from fluorescence behavior
    - More intense
    - Used for Raman measurements
  - **Anti-Stokes**
    - No fluorescence interference
  - **Rayleigh**
    - Most intense
    - Same as incident radiation

- Shift patterns independent of incident radiation wavelength
Figure 18-2  Origin of Rayleigh and Raman scattering.
Theory

- Variation in polarizability of bond with length
- Electric field ($E$) due to excitation frequency with $E_0$
  \[ E = E_0 \cos(2\pi \nu_{ext} t) \]
- Dipole moment ($m$) based on polarizability of bond ($\alpha$)
  \[ m = \alpha E = \alpha E_0 \cos(2\pi \nu_{ext} t) \]
- For Raman activity $\alpha$ must vary with distance along bond
  \[ \alpha = \alpha_0 + (r - r_{eq}) \left( \frac{\partial \alpha}{\partial r} \right) \]

\( \alpha_0 \) is polarizability at \( r_{eq} \)

\[ r - r_{eq} = r_{max} \cos(2\pi \nu v t) \]
Theory

\[ m = \alpha_0 E_0 \cos(2\pi \nu_{ex} t) + \frac{E_0}{2} r_m \left( \frac{\partial \alpha}{\partial r} \right) \cos(2\pi (\nu_{ex} - \nu_\nu) t) + \]

\[ \frac{E_0}{2} r_m \left( \frac{\partial \alpha}{\partial r} \right) \cos(2\pi (\nu_{ex} + \nu_\nu) t) \]

- Equation has Rayleigh, Stokes, and Anti-Stokes component
- Complementary to IR absorbance
  - Overlap not complete
Figure 18-3  Comparison of Raman and infrared spectra.  (Courtesy Perkin-Elmer Corp., Norwalk, CT.)
Vibrational spectroscopy and group

• Molecules with inversion cannot be both IR and Raman active
  ➡️ For CO$_2$, symmetric stretch is IR inactive
    ➩ No net change of dipole
    ➩ Raman active

• A vibrational mode is IR active if it is symmetric with electric dipole vector
  ➡️ Causes change in dipole

• Mode is Raman active if it has component of molecular polarizability
Vibrational spectroscopy

- Consider cis ($C_{2v}$) and trans ($D_{2h}$) $\text{PdCl}_2(\text{NH}_3)_2$
  - Both have Pd-Cl stretch
  - For $C_{2v}$, all 1 is symmetric
    - $A_1$
  - Asymmetric mode
    - $C_2$ and $\sigma_v$ are -1
      - $B_2$ group
- Same information can be used to assign symmetry
### Symmetry and vibration

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>C₂</th>
<th>σ_v (xz)</th>
<th>σ_v (yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>z</th>
<th>x², y², z²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>R_z</td>
<td>xy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x, R_y</td>
<td>xz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>y, Rₓ</td>
<td>yz</td>
</tr>
</tbody>
</table>

- a₁ vibration generates a changing dipole moment in the z-direction
- b₁ vibration generates a changing dipole moment in the x-direction
- b₂ vibration generates a changing dipole moment in the y-direction
- a₂ vibration does not generate a changing dipole moment in any direction (no ‘x’, ‘y’ or ‘z’ in the a₂ row).
- **Thus, a₁, b₁ and b₂ vibrations give rise to changing dipole moments and are IR active**
- However, a₂ vibrations do not give rise to changing dipole moments and are IR inactive
Symmetry and vibration

• Which bonds are IR active in CCl$_4$?
  ➢ Symmetry is T$_d$
  ➢ From table, which bonds are dipole active in x, y, or z
    ➢ t$_2$ is active in x, y, and z
    ➢ What do these bonds look like?
  ➢ xz, yz, xy, x$^2$, y$^2$, z$^2$ are Raman active
    ➢ From table, a$_1$ and t$_2$ are Raman active