Molecular Symmetry

Symmetry is relevant to: spectroscopy, chirality, polarity, Group Theory, Molecular Orbitals

- A molecule has a “symmetry element” if it is unchanged by a particular “symmetry operation”
- Element could be a plane, an axis, a point
- A collection of symmetry elements classifies a molecule in a specific POINT GROUP
- Five general symmetry operations exist

Symmetry operation:
1. Identity “E”
2. Proper Rotation “Cn”
3. Reflection plane “σx”
4. Inversion “i”
5. Improper rotations or “rotation-reflection”
1. Proper Rotation “$C_n$”

$C_1 \rightarrow 360^\circ$ rotation $\rightarrow$ equiv. to E

$C_2 \rightarrow 180^\circ$ rotation

$C_3 \rightarrow 120^\circ$ rotation

- rotations are conducted counterclockwise in convention
- The highest # rotation is the principal axis
3. Reflection plane “$\sigma_x$” $x = v$, vertical; $h$, horizontal; $d$, dihedral 
a $\sigma_v$ reflection is in the plane containing the principal rotation axis 
a $\sigma_h$ – plane perpendicular to the principal axis
4. Inversion “i” \((x, y, z) \rightarrow (-x, -y, -z)\)

- centre of symmetry

5. Improper rotations or “rotation – reflection”
- rotation by \(C_n\) followed by reflection in the plane perpendicular to \(C_n\) axis
Point Group
e.g. $\text{H}_2\text{O}$

e.g. $\text{H}_2\text{O}_2$

Linear molecules:
$\text{A—B}$

$\text{A—A}$ or $\text{A—B—A}$
Special high symmetry:
- octahedron  $MX_6$; $O_h$
- tetrahedron  $MX_4$; $T_d$
- Cube  $MX_8$;

$C_n$ groups have a principal axis $C_n$ and no perpendicular c-axis
$D_n$ groups have a principal axis $C_n$ and $n$-$C_2$ perpendicular axes
$S_n$ groups have no c-axes at all but $S_n$-axes (unusual)

Final label involves $\sigma$-planes:
  a) if no x, no label
  b) if $\sigma_v$ only, then v is used
  c) if $\sigma_h$ is present, then h suffix
Applications:
a) chirality; “optical isomers”
   - non-superimposable mirror images
   - molecules are chiral if they lack an improper rotation axis. (C₁, Cₙ, Dₙ only)

How to detect? Absorption spectroscopy using polarized light
Examples of Circular Dichroism applied to inorganic chemistry
b). dipole moment
   - summation of the bond-moment vectors is non-zero
Character Table
- express each symmetry operation in matrix form using transformation matrix
- z-axis conventionally unique
Character → sum of # on diagonal

\[
\begin{array}{ccccc}
C_{2v} & E & C_2 & \sigma_v^{xz} & \sigma_v^{yz} \\
3 & -1 & 1 & 1 \\
\end{array}
\]

This set is a representation It is a reducible representation \( \Gamma \) as it can be broken into combinations of simpler irreducible representation.

For \( C_{2v} \) matrices, each non-diagonal element is 0, so \( x, y, z \) are independent → Can read along \( x, y, z \) to obtain representation of the symmetry operations on \( xyz \) coordinates
How to use $C_{2v}$ point group symmetry operations:
- consider atomic orbitals on c-atom
- express the result of a symmetry operation on the orbital as a number
  - if unchanged: +1
  - if changes sign: -1
  - other change: 0

e.g. $p_x$ orbital
A character table is a collection of all possible irreducible representation (I. R.)

1. Point group name (Schonflies symbol)

2. Listing of the symmetry elements, starting with E according to their class. Symmetry elements are collected together in the same class
   e.g. \( C_{4v} : E, 2C_4, C_2, 2\sigma_v, 2\sigma_d \)

3. Characters of the matrices, or the I.R.

4. Mulliken symbols for the I. R. (A, B, E, T – except \( D_{\infty h} \))
   - A, B → singly degenerate
   - T → triply degenerate
   - g → “gerade” (symmetric w.r.t. inversion)
   - u → “ungerade” (antisymmetric with w.r.t. inversion)
   - \( t_{2g}, e_g \) come from the \( O_h \) character table

5. Functions of \( x, y, z \) p-orbitals and \( R_x, R_y, R_z \) (rotations about axis) which match or `transforms` the char. of I. R.

6. Functions of \( x^2, y^2, z^2, xy, yz, xz \), which transforms as the indicated I. R. (d-orbitals)
   The first I. R. is always “totally symmetric I. R.” e.g. \( A_1(g) \)
Group Theory, Symmetry and IR
- IR measures molecular vibrations – stretches and bends

From first principles, we can determine # of possible vibrations.
- There are 3N total motions (N = # of atoms) in a molecule (each atom can move in 3 directions)
  - degrees of freedom
  - of these, 3 are translational, 3 are rotational; therefore total vibrational degree of freedom = 3N – 6
  - linear molecule: 3N – 5

So 3N-6 vibrations possible. How many are observed?
Selection rule: For an IR absorption to occur, a vibration must cause a change in the dipole moment of the compound

Related technique – Raman spectroscopy
- measures vibrations
  - selection rule is different → need a change in the polarizability for Raman-active
IR and Raman are both useful for Fingerprinting.

Symmetry dictates which are active in Raman and IR.
Raman spectroscopy
- based on inelastic scattering of a monochromatic excitation source

Raman scattering cross-section is very small → need to use Laser light ( $$$ )
How to tell if IR/Raman active? Symmetry!
Exclusion rule: if a molecule has an inversion centre, none of its modes can be both IR + Raman active. i.e. IR and Raman are complementary for molecules with i symmetry

Raman active = IR inactive

By group theory:
- dipole moment vector transforms as x, y, z.
- Polarizability vector transforms as $x^2$, $y^2$, $z^2$, xy, xz, zy
What is the symmetry of a vibration?
Two methods:
1. Full motion analysis
   a) determine the molecular point group
   b) the motion of each atom is represented by (x, y, z) vectors. Determine $\Gamma$ reducible representations for each atom by applying point group symmetry operation. Assign 1 for no change; 0 for positional change and -1 for reversed (only)
c) find the irreducible representations which make up $\Gamma$
d) This is all motions. For vibrations remove translation + rotation
   - Translation transforms as x, y, z
     \[ x \rightarrow B_1 \quad y \rightarrow B_2 \quad z \rightarrow A_1 \]
   - Rotations \[ R_x \rightarrow B_2, \quad R_y \rightarrow B_1, \quad R_z \rightarrow A_2 \]

Subtracting these leaves:


e) For IR-active, must correspond to x, y, z

All 3 bands will be observed in IR.

Note: use single crystal and x-polarized light will see only the \( B_1 \) band
Raman:
\[ x_2, y_2, z_2 \rightarrow A_1 \]
\[ xz \rightarrow B_1 \]
All 3 bands are also Raman active
Exact same spectra as IR.

No “complementarity” here because no “\text{i}” centre in H\textsubscript{2}O
What is the symmetry of a vibration?
2. Use localized symmetry analysis:
   a) draw a vector for each independent vibrating group
e.g. νCO bands in trans-ML₂(CO)₂

a) Using the appropriate point group, determine $\Gamma$ for the vectors by applying symmetry operations

- translations and rotations are not included here if the vectors chosen are appropriate
$A_g$ – no $x, y, z$ transformation $\rightarrow$ IR-inactive
  - has $x^2, y^2, z^2$ transformation $\rightarrow$ Raman-active

$B_{3u}$ – $x$ transform. $\rightarrow$ IR-active
  - Raman-inactive; no quadratic transformation

Note: exclusion rule applies! i centre $\rightarrow$ complementary

Do cis-$ML_2(CO)_2$
Isotope effects and IR
- for most molecules, isotopic substitution has no significant physical effect
- e.g. $^{15}$NH$_3$, $^{14}$NH$_3$
  - similar vapor pressures, b.p., chemistry
  - mass different is small

But D for H, doubles the mass
- bond strengths are also different

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>D$_2$</th>
<th>H$_2$O</th>
<th>D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p. (°C)</td>
<td>-252.8</td>
<td>-249.7</td>
<td>100.0</td>
<td>101.42</td>
</tr>
<tr>
<td>Bond enthalpy (kJ/mol)</td>
<td>436</td>
<td>443.3</td>
<td>463.5</td>
<td>470.9</td>
</tr>
</tbody>
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Why is there a stronger bond between D-D vs H-H, O-D vs O-H?
Zero-point energy
- energy of a molecule or bond is not determined solely by the electron because bonds vibrate
- molecules always have some vibrational energy, never at the lowest Morse potential
This difference can be detected in an IR spectrum!

Any E-D bond will vibrate at a frequency lower than E-H bond by a $1/\sqrt{2}$ factor. This is due to mass difference, NOT a weaker bond!
e.g. $\text{Me}_2\text{As—H}$

Can do similar isotopic substitutions with other elements, but effect will be much smaller

Standard IR instrument resolution $\sim 1\text{cm}^{-1}$ – limits whether shift is observable