Linear Molecules with a Centre of Symmetry: CO$_2$, C$_2$H$_2$, H$_2$

- Linear? – YES
- ↓
- $\Rightarrow D_{\infty h} \leftarrow \sigma_h$ plane
- $i$?– YES
- ↑
- infinite order rotational axis

Linear Molecules with No Centre of Symmetry: HCl, OCS, NNO

- NO $\perp C_2$ axes
- Linear? – YES
- ↓
- $\Rightarrow C_{\infty v} \leftarrow$ infinite number of $\sigma_v$ planes, but NO $\sigma_h$ plane
- $i$?– NO
- ↑
- infinite order rotational axis
Tetrahedral Molecules $T_d$ and Octahedral Molecules $O_h$

**HOMEWORK:** Using the Decision Tree, prove to yourself that CH$_4$ belongs to the $T_d$ point group and that SF$_6$ belongs to the $O_h$ point group.

**HOMEWORK** (try before the next tutorial class): Use CH$_4$ to find all the symmetry elements (listed below) in a $T_d$ molecule. Use SF$_6$ to find all the symmetry elements (listed below) in an $O_h$ molecule.

**(NOTE:** Some of these are very difficult to find!)

$T_d$ point group has: $E$, 8 $C_3$ (note that this includes $C_3^2$), 3 $C_2$, 6 $S_4$ (includes $S_4^3$), 6 $\sigma_d$

$O_h$ point group has: $E$, 8 $C_3$, 6 $C_2$, 6 $C_4$, 3 $C_2(=C_4^2)$, $i$, 6 $S_4$, 8 $S_6$, 3 $\sigma_h$, 6 $\sigma_d$

Here are a couple of perspectives of $T_d$ and $O_h$ molecules which might help. A molecular modeling kit will also help. If you have one, bring it to the tutorial.
Important CHEM 2060 Course Goal = **Finding The Point Group!**

***You must become adept at assigning point groups to molecules in this part of the course. You can use a truth/decision table if you wish. Ultimately, you should strive to learn, understand and be able to apply the method below because you will not always be given a truth/decision table in upper year courses or in “real life”!***

***Once you have decided that the point group is not “special” (see below), the following method is easy to remember.***

**STEP 1.** Find the highest order rotational axis, $C_n$. What is $n$? (This is achieved by inspecting the molecule and becomes easier with practice.)

**STEP 2.** Is there a $C_2$ axis at right angles to the highest order axis?

Perpendicular $C_2$ axis = $D$  
No perpendicular $C_2$ axes = $C$

(DIFFERENCE BETWEEN $D$ & $C$)
STEP 3. (If the answer is C, go to step 4.) If the answer is D then:

\[ D + \sigma_h \Rightarrow D_{nh} \]

\[ D + \text{no } \sigma_h + \sigma_d \Rightarrow D_{nd} \quad (\sigma_d \text{ planes bisect } C_2 \text{ axes}) \]

\[ D + \text{no } \sigma \Rightarrow D_n \]

NOTE: Some \( D_{nh} \) point groups have all three types of mirror planes (\( \sigma_h \), \( \sigma_v \) and \( \sigma_d \)) and some only have two of the three, but \( \sigma_h \) must be present.

NOTE: In the \( D \) point groups, it is not possible to have only \( \sigma_v \) mirror planes. This is a function of the definition of \( \sigma_v \) and \( \sigma_d \) mirror planes and with practice this will become clear to you.
STEP 4. If the answer is $C$ then:

$$C + \text{ no other axes of symmetry } \Rightarrow C_n$$

$$C + \sigma_h \Rightarrow C_{nh}$$

$$C + \text{ no } \sigma_h + \sigma_v \Rightarrow C_{nv}$$

Hydrogen peroxide, $\text{H}_2\text{O}_2$: rotation about the O-O single bond gives 3 different conformations with 3 different point groups.

*Question:* Which is the lowest energy conformer?
Now let’s look at the so-called “special groups”

The LINEAR groups ($C_{\infty v}$ and $D_{\infty h}$)…we’ve already looked at these.

The CUBIC groups ($I_h$, $O_h$ and $T_d$)…you are looking at octahedral and tetrahedral groups for homework and these are very important in chemistry.

The icosahedral group is rarely observed because it requires the regular placement of 12 atoms about a central point.

Icosahedron: 12 vertices, 20 faces (all equilateral triangles), 30 sides
The LOW SYMMETRY groups \((S_{2n}, C_s, C_i, C_1)\) are quite common because it is often the case that a molecule’s symmetry is technically lowered from what appears to be a high symmetry group to a low symmetry group by a distortion.

\[\rightarrow\] This is often the case in the solid state (crystal) structure where intermolecular interactions can alter bond lengths/angles from the ideal gas phase structure.

If the only symmetry elements present are \(E, C_n\) and \(S_{2n} \Rightarrow S_{2n}\)
If the only symmetry elements present are \(E\) and \(\sigma \Rightarrow C_s\)
If the only symmetry elements present are \(E\) and \(i \Rightarrow C_i\)
If the only symmetry element present is \(E \Rightarrow C_1\) (essentially, no symmetry)
One last note … **looking at \( \sigma_d \) versus \( \sigma_v \) planes again**

\( \sigma_d \) planes bisect \( C_2 \) axes  
(ethane, \( D_{3d} \) conformation)

\( \sigma_v \) planes are colinear with \( C_2 \) axes  
(ethane, \( D_{3h} \) conformation)

In some species, there are several sets of \( C_2 \) axes.

In \( D_{4h} \) there is \( C_4^2 = C_2, C_2' \) and \( C_2'' \).
The \( \sigma_h \) bisects the \( C_4 \) axis (and \( C_4^2 = C_2 \) also).
The \( \sigma_v \) is colinear with \( C_2' \) (and thus bisects \( C_2'' \)).
The \( \sigma_d \) bisects \( C_2' \) (and is thus colinear with \( C_2'' \)).