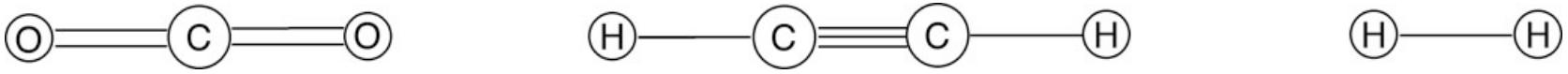
Linear Molecules with a Centre of Symmetry: CO_2, C_2H_2, H_2



$\perp C_2$ axes

Linear ? – *YES* $\downarrow$

$\Rightarrow$ $\boldsymbol{D_{\infty h}} \leftarrow \sigma_h$ plane

i ?– *YES* $\uparrow$

infinite order rotational axis

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

NO $\perp C_2$ axes

Linear ? – *YES* $\downarrow$

$\Rightarrow$ $\boldsymbol{C_{\infty v}} \leftarrow$ infinite number of σ_v planes, but NO σ_h plane

i ?– *NO* $\uparrow$

infinite order rotational axis

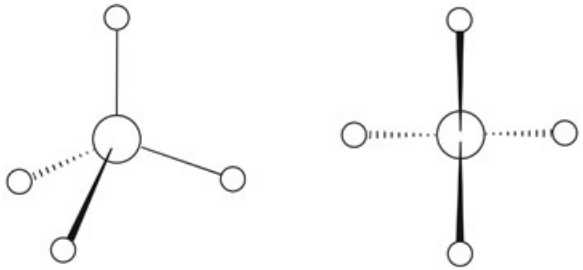
Tetrahedral Molecules T_d and Octahedral Molecules O_h

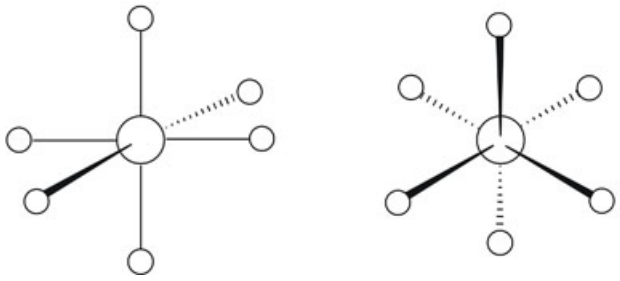
HOMEWORK: Using the Decision Tree, prove to yourself that CH_4 belongs to the T_d point group and that SF_6 belongs to the O_h point group.

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 σ_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 σ_h, 6 σ_d

T_d 

O_h 

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:

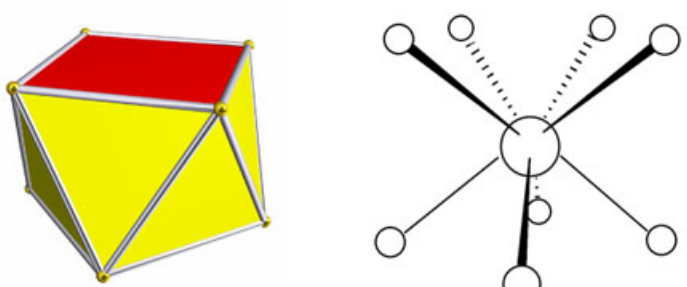
$$\boldsymbol{D} + \boldsymbol{\sigma_h} \Rightarrow \boldsymbol{D_{nh}}$$

$$\boldsymbol{D} + \text{no } \boldsymbol{\sigma_h} + \boldsymbol{\sigma_d} \Rightarrow \boldsymbol{D_{nd}} \qquad (\sigma_d \text{ planes bisect } C_2 \text{ axes})$$

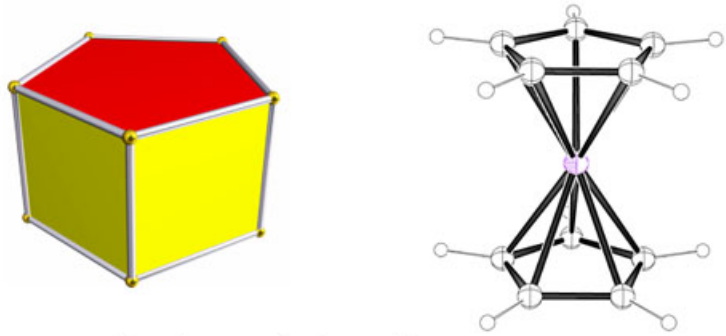
$$\boldsymbol{D} + \text{no } \boldsymbol{\sigma} \Rightarrow \boldsymbol{D_n}$$

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

NOTE: In the *D* point groups, it is not possible to have only σ_v mirror planes. This is a function of the definition of σ_v and σ_d mirror planes and with practice this will become clear to you.



Square antiprismatic D_{4d}
e.g., XeF_8^{2-}



Pentagonal prismatic D_{5h}
e.g., ruthenocene, $RuCp_2$

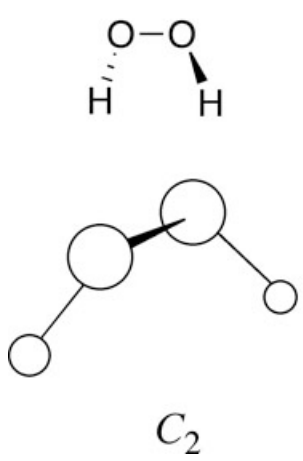
STEP 4. If the answer is *C* then:

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

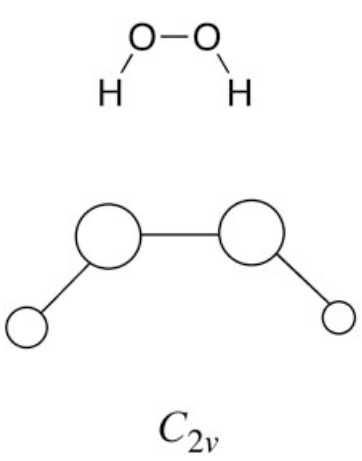
$\boldsymbol{C}$ + $\boldsymbol{\sigma_h}$ $\Rightarrow$ $\boldsymbol{C_{nh}}$

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

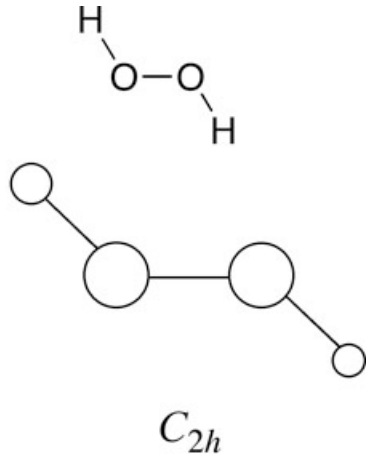
Hydrogen peroxide, H_2O_2 : rotation about the O-O single bond gives 3 different conformations with 3 different point groups.



C_2



C_{2v}



C_{2h}

Question: Which is the lowest energy conformer?

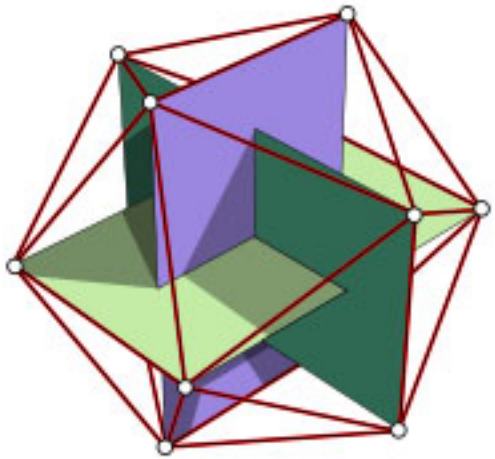
Now let's look at the so-called "special groups"

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.

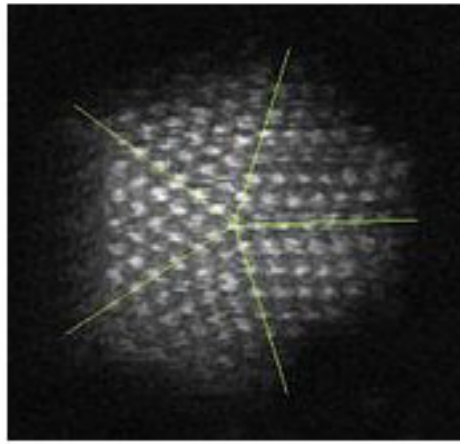
The *icosahedral* group is rarely observed because it requires the regular placement of 12 atoms about a central point.

Icosahedron: 12 vertices, 20 faces (all equilateral triangles), 30 sides



icosahedron
showing "golden rectangles"

a soccer ball is I_c
so is C_{60}

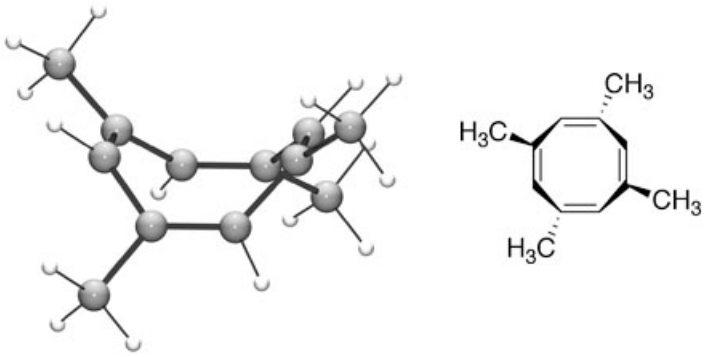


Au nanoparticle
STEM-HAADF image

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.

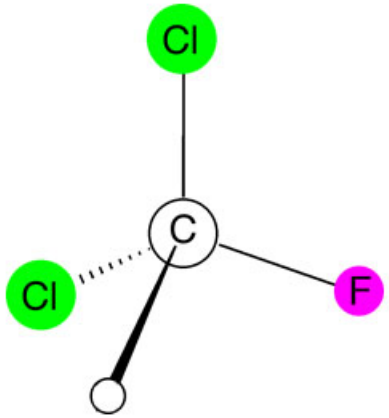
→ This is often the case in the solid state (crystal) structure where intermolecular interactions can alter bond lengths/angles from the ideal gas phase structure.

If the only symmetry elements present are E, C_n and S_{2n} $\Rightarrow$ $\boldsymbol{S_{2n}}$
If the only symmetry elements present are E and σ $\Rightarrow$ $\boldsymbol{C_s}$
If the only symmetry elements present are E and i $\Rightarrow$ $\boldsymbol{C_i}$
If the only symmetry element present is E $\Rightarrow$ $\boldsymbol{C_1}$ (essentially, no symmetry)

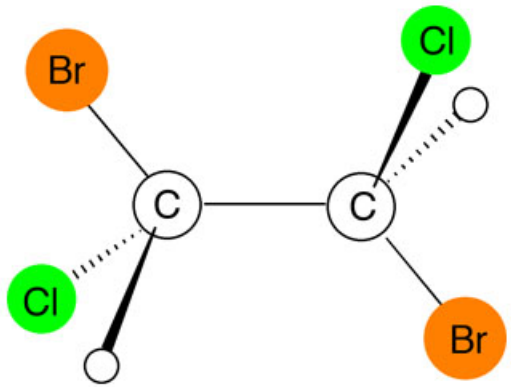


1,3,5,7-tetramethyl-COT

S_4

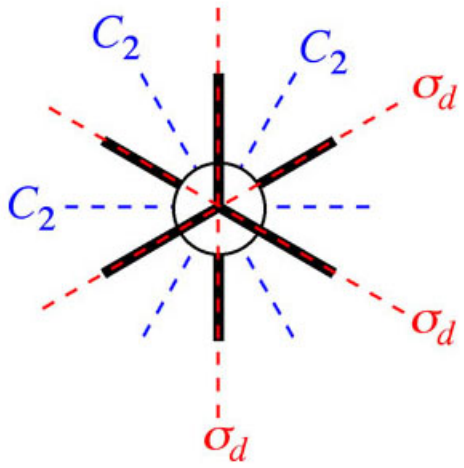


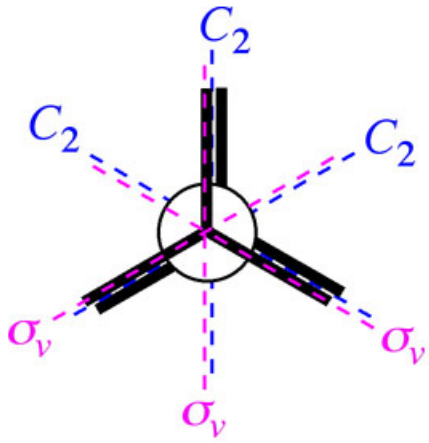
C_s



C_i

One last note … **looking at σ_d versus σ_v planes again**





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

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

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

In $\boldsymbol{D_{4h}}$ there is $C_4^2 = C_2$, C_2' and C_2''.
The σ_h bisects the C_4 axis (and $C_4^2 = C_2$ also).
The σ_v is colinear with C_2' (and thus bisects C_2'').
The σ_d bisects C_2' (and is thus colinear with C_2'').