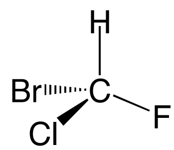
5.04, Principles of Inorganic Chemistry II

MIT Department of Chemistry

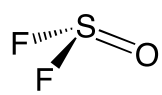
Lecture 5: Molecular Point Groups I

The symmetry properties of molecules (i.e. atoms of a molecule form a basis set) are described by point groups, since all the symmetry elements in a molecule will intersect at a common point, which is not shifted by any of the symmetry operations. There are also symmetry groups, called space groups, which contain operators involving translational motion. The point groups are listed below along with their distinguishing symmetry elements.

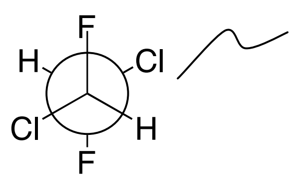
C_1 : E (h=1) … no symmetry



C_s : σ (h=2) … only a mirror plane

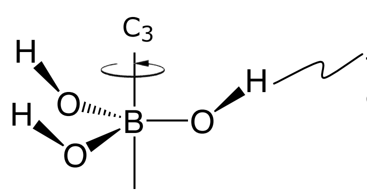


C_i : i (h=2) … only an inversion center (rare point group)



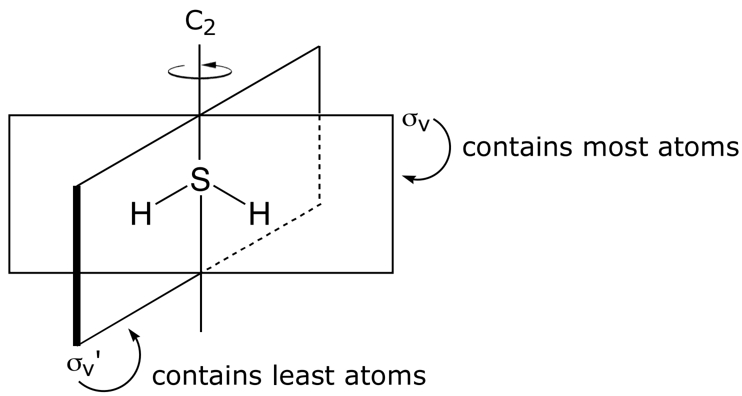
this isomer of dichloro difluoroethane

C_n : C_n and all powers up to C_n^n = E (h=2)… a cyclic point group

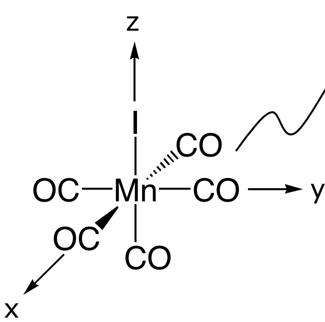


the H's canted out of the BO_3 plane lead to a C_3 point group.

C_{nv} : C_n and $n\sigma_v$ ($h=2n$) … by convention a σ_v contains C_n (as opposed to σ_n, which is normal to C_n). For n even, there are $\frac{n}{2}\sigma_v$ and $\frac{n}{2}\sigma_v{}'$ with the σ_v containing the most atoms and the σ_v's containing the least atoms.



Consider a second example:

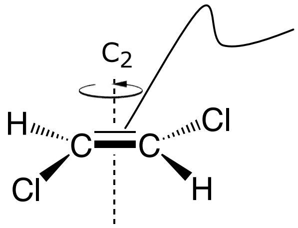


$C_{4v}: C_4, C_2(=C_4^{\,2}), C_4^{\,3}, 2\sigma_v, 2\sigma_d$

a dihedral mirror plane
… in place of $\sigma_v{}'$ and σ_ds which bisect the σ_vs . The σ_d designation is more common in D point groups (see below)

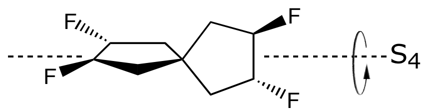
two σ_vs: the $\sigma(xz)$ and $\sigma(yz)$ mirror planes
the σ_ds bisect the $\sigma(xz)$ and $\sigma(yz)$ planes

C_{nh} : C_n and σ_h (normal to C_n) are generators of S_n operations as well (h=2n)



Note the inversion center… generated from $C_2 \bullet \sigma_h = S_2 = i$

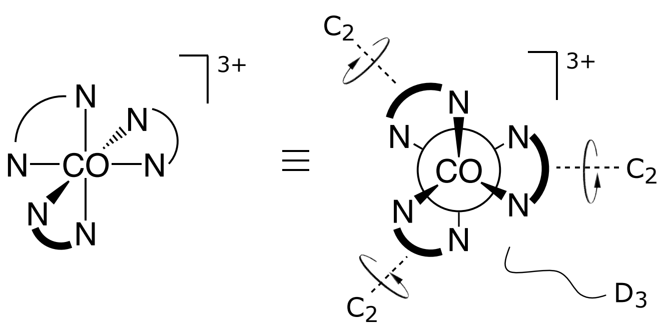
S_{2n} : S_{2n} and all powers up to S_{2n}^{2n} = E (h=2n).

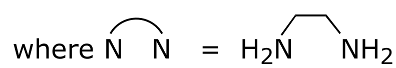


… generator for C_2 (=S_4^2), S_4^3, E(=S_4^4)

Note S_n odd is redundant with C_{nh} because $S_n^n = \sigma_h$ for n odd. As an example consider a "S_3" point group… S_3 is the generator for S_3, S_3^2(=C_3^2) S_3^3(=σ_h), S_3^4(=C_3), S_3^5, S_3^6(=E). The C_3's and σ_h are the distinguishing elements of the C_{3h} point group.

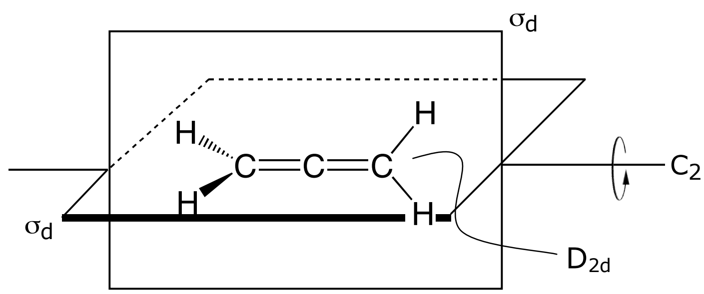
D_n : C_n and n⊥C_2 (h=2n).



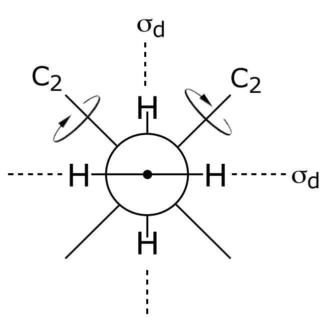


In identifying molecules belonging to this point group… if a C_n present and one ⊥C_2 axis is identified … necessarily (n-1) ⊥C_2s generated by rotation about C_n.

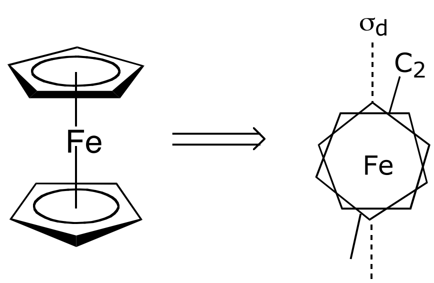
D_{nd} : C_n, $n\perp C_2$, $n\sigma_d$ — bisect the $\perp C_2$s



The C_2s bisect σ_ds. As is often the case, easier to see symmetry operations of D_{nd} point groups with a Newman projection



Note: D_{nd} point groups will contain i, when n is odd.



S_{10}^{2} S_{10}^{4} S_{10}^{6} S_{10}^{8}

$\equiv$ $\equiv$ $\equiv$ $\equiv$

E C_5 C_5^{2} C_5^{3} C_5^{4}

$5\sigma_d$ (generate with C_5 axis)

$5\perp C_2$ (generate with C_5 axis)

S_{10}, S_{10}^{3}, S_{10}^{5}, S_{10}^{7}, S_{10}^{9}

$\equiv$

i