5.04 Principles of Inorganic Chemistry II
Fall 2008

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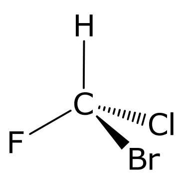
Lecture 4: Molecular Point Groups 1

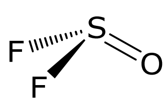
The symmetry properties of molecules (i.e. the atoms of a molecule form a basis set) are described by ***point groups***, since all the symmetry elements in a molecule will intersect at a common point, which is not shifted by any of the symmetry operations. There are also symmetry groups, called ***space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

The point groups are listed below along with their distinguishing symmetry elements

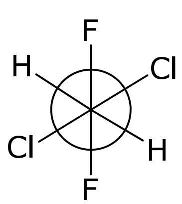
C_1 : E (h = 1) → no symmetry



C_s : σ (h = 2) → only a mirror plane

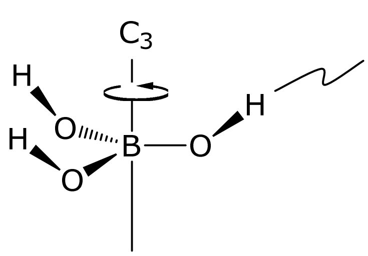


C_i : i (h = 2) → only an inversion center (rare point group)

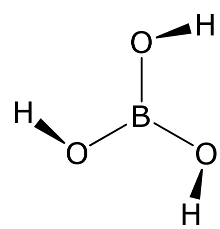


isomer of dichloro(difluoro)ethane

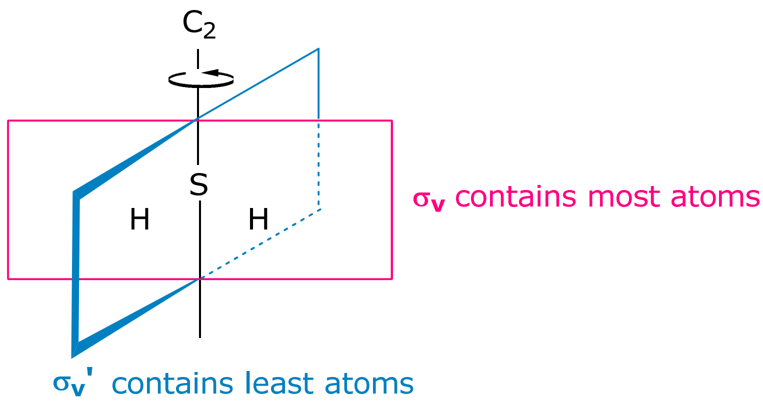
C_n : C_n and all powers up to C_n^n = E (h = 2) → a cyclic point group



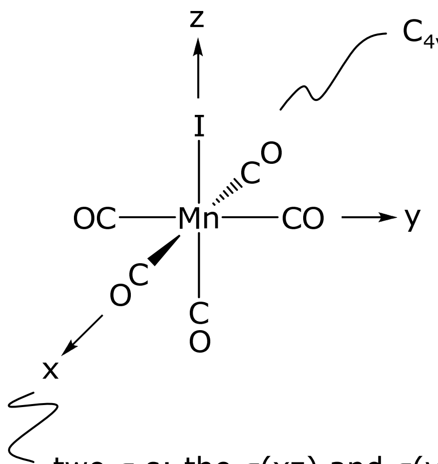
the H's canted out of the BO_3 plane lead to a C_3 point group



C_{nv} : C_n and $n\sigma_v$ (h = 2n) … by convention a σ_v contains C_n (as opposed to σ_h 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_vs containing the least atoms



Consider a second example:

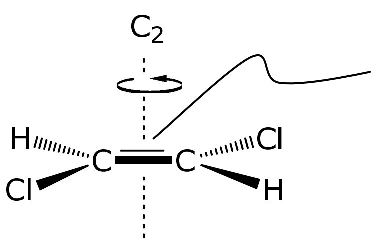


C_{4v} : $C_4, C_2(=C_4^{\,2}), C_4^{\,3}, 2\sigma_v, 2\sigma_d$

a dihedral mirror plane … the σ_ds bisect the σ_vs (and σ_v'); the σ_d designation is more common in D point groups (see below)

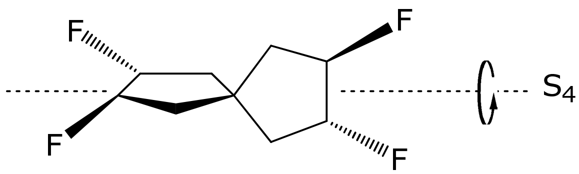
two σ_vs: the σ(xz) and σ(yz) mirror planes
two σ_ds bisect the σ(xz) and σ(yz) planes

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



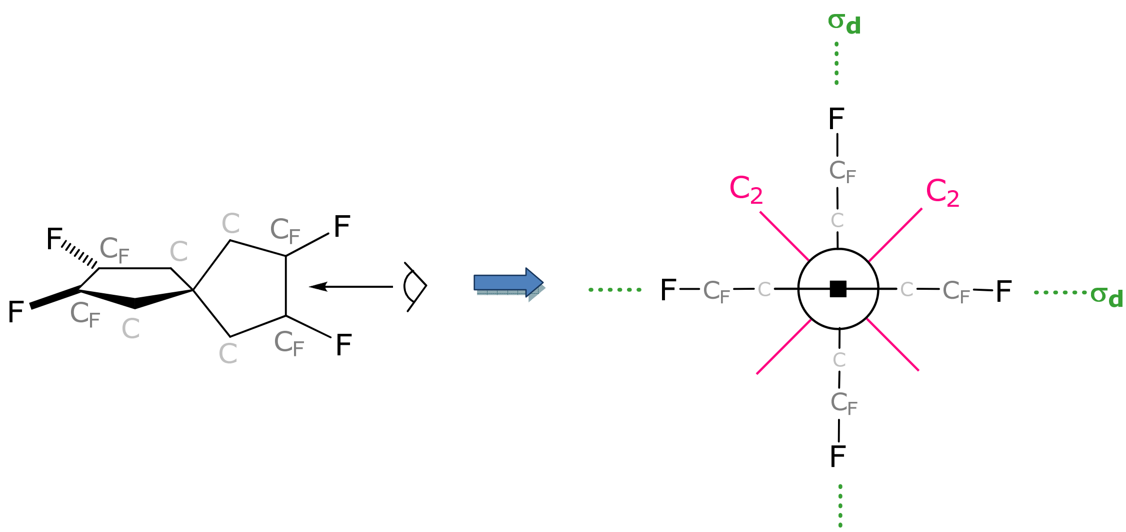
Note the inversion center;
generated from $C_2 \cdot \sigma_h = S_2 = i$

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



S_{2n} is a generator; for this example, the generator S_4 gives rise to C_2 (= S_4^2), S_4^3, E(= S_4^4)

The F's do not lie in the plane of the cyclopentane rings. If they did, then other symmetry operations arise; these are easiest to see by looking down the line indicated below:



Note S_n, where n is 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.