MOLECULAR SYMMETRY

Know intuitively what "symmetry" means - how to make it quantitative?

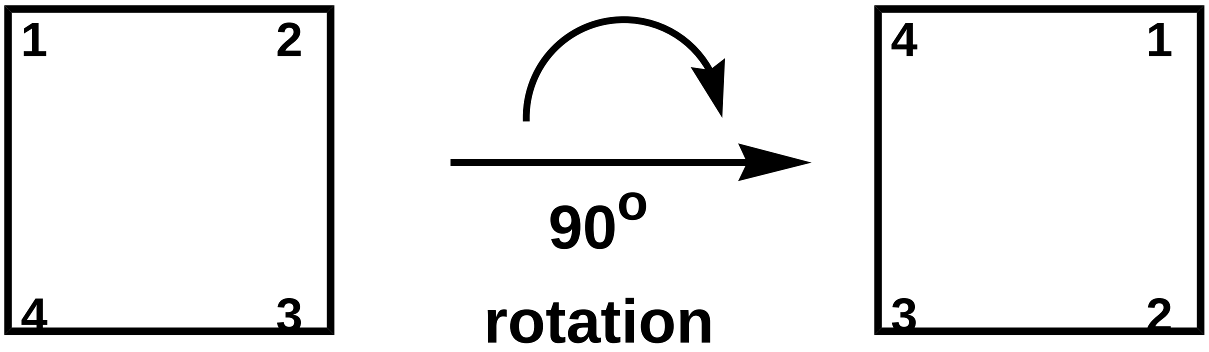
Will stick to isolated, finite molecules (not crystals).

SYMMETRY OPERATION

Carry out some operation on a molecule (or other object) - e.g. rotation. If final configuration is INDISTINGUISHABLE from the initial one - then the operation is a SYMMETRY OPERATION for that object. The line, point, or plane about which the operation occurs is a SYMMETRY ELEMENT

N.B. “Indistinguishable” does not necessarily mean “identical”.

e.g. for a square piece of card, rotate by 90º as shown below:



i.e. the operation of rotating by 90° is a symmetry operation for this object

Labels show final configuration is NOT identical to original.

Further 90º rotations give other indistinguishable configurations - until after 4 (360º) the result *is* identical.

SYMMETRY OPERATIONS

Motions of molecule (rotations, reflections, inversions etc. - see below) which convert molecule into configuration indistinguishable from original.

SYMMETRY ELEMENTS

Each element is a LINE, PLANE or POINT about which the symmetry operation is performed. Example above - operation was rotation, element was a ROTATION AXIS. Other examples later.

Summary of symmetry elements and operations:

Symmetry element	Symmetry operation(s)
–	E (identity)
C_n (rotation axis)	$C_n^1 ..... C_n^{n-1}$ (rotation about axis)
σ (reflection plane)	σ (reflection in plane)
i (centre of symm.)	i (inversion at centre)
S_n (rot./reflection axis)	$S_n^1 ... S_n^{n-1}$ (n even) (rot./reflection about axis)
	$S_n^1 ... S_n^{2n-1}$ (n odd)

Notes

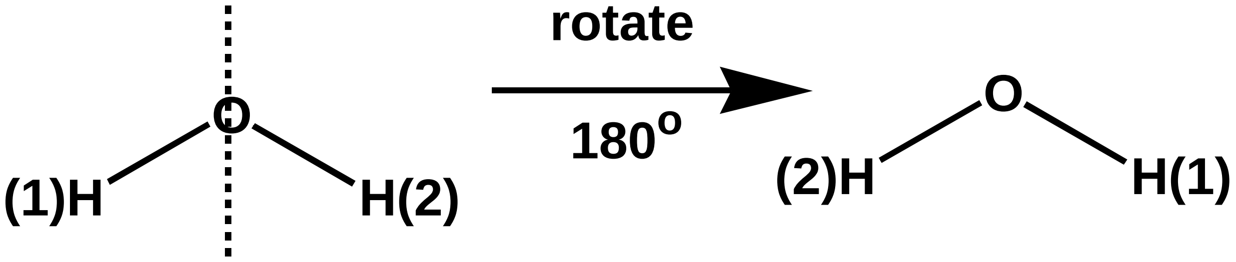
(i) symmetry operations more fundamental, but elements often easier to spot.

(ii) some symmetry elements give rise to more than one operation - especially rotation - as above.

ROTATIONS - AXES OF SYMMETRY

Some examples for different types of molecule: e.g.

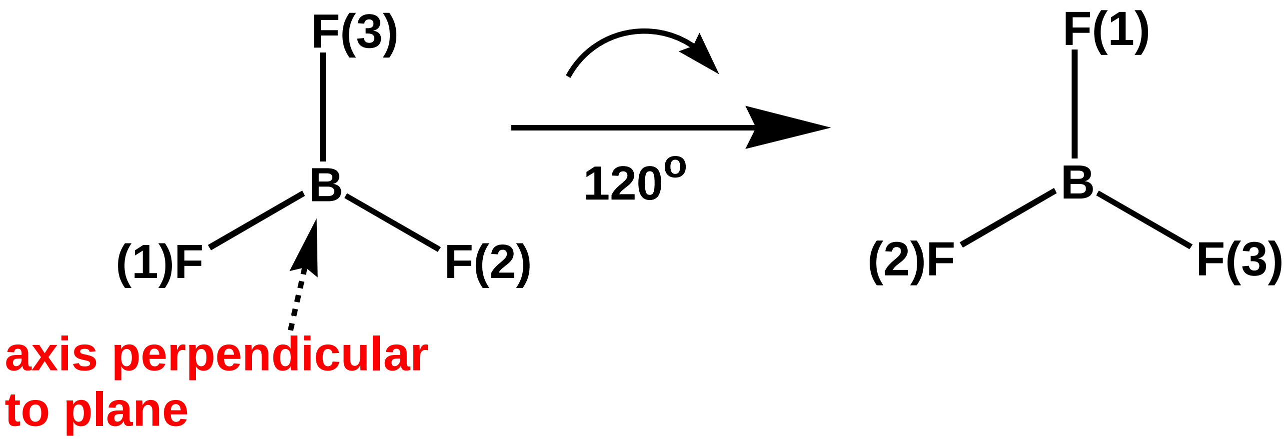
$\boxed{H_2O}$



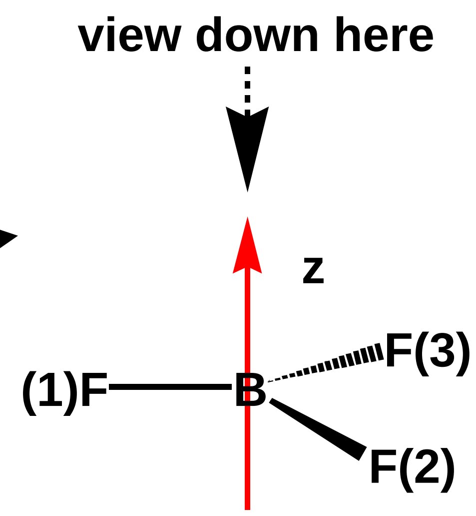
Line in molecular plane, bisecting HOH angle is a rotation axis, giving indistinguishable configuration on rotation by 180°.

BF_3

By VSEPR - trigonal, planar, all bonds equal, all angles 120°. Take as axis a line perpendicular to molecular plane, passing through B atom.



N.B. all rotations CLOCKWISE when viewed along -z direction.

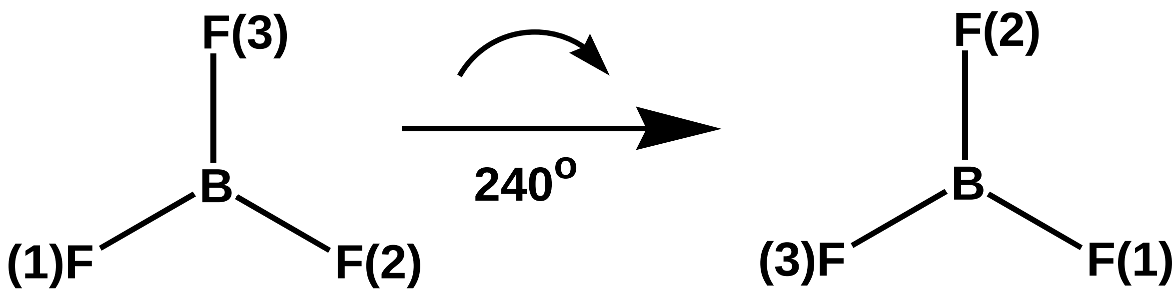


Symbol for axes of symmetry

C_n

where rotation about axis gives indistinguishable configuration every $(360/n)^o$ (i.e. an n-fold axis)

Thus H_2O has a C_2 (two-fold) axis, BF_3 a C_3 (three-fold) axis. One axis can give rise to >1 rotation, e.g. for BF_3, what if we rotate by 240^o?



Must differentiate between two operations.

Rotation by 120^o described as C_3^1,

rotation by 240^o as C_3^2.

In general C_n axis (minimum angle of rotation $(360/n)^o$) gives operations C_n^m, where both m and n are integers.

When m = n we have a special case, which introduces a new type of symmetry operation.....

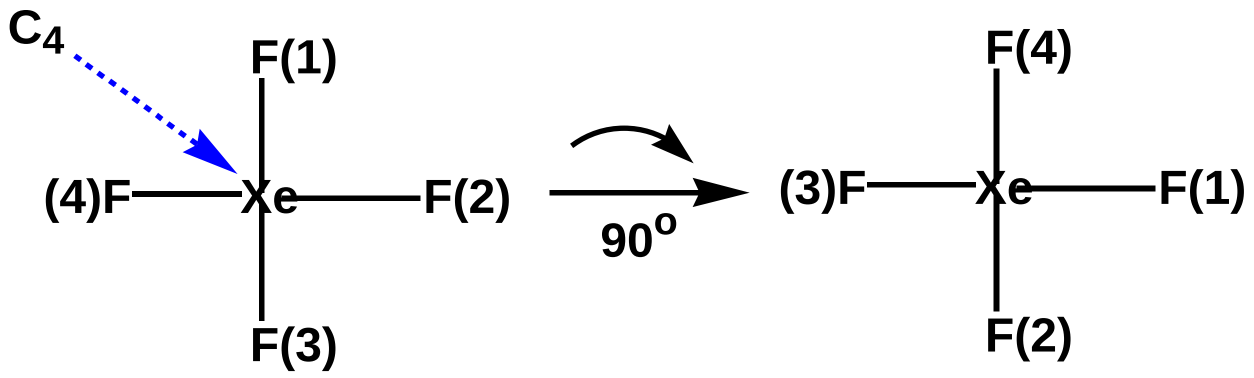
IDENTITY OPERATION

For H_2O, C_2^2 and for BF_3 C_3^3 both bring the molecule to an IDENTICAL arrangement to initial one.

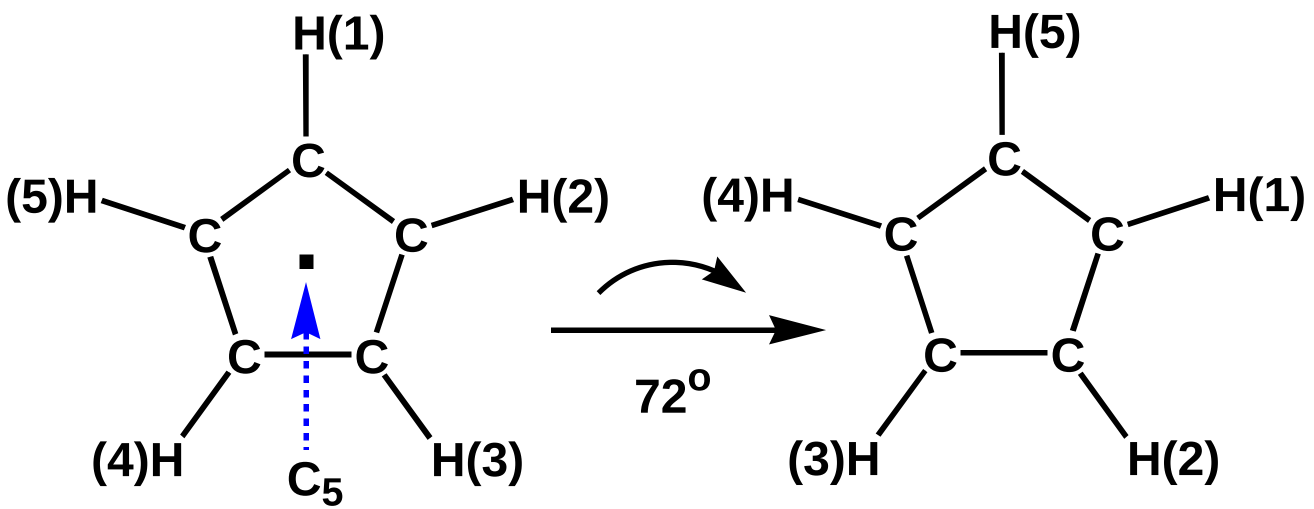
Rotation by 360^o is exactly equivalent to rotation by 0^o, i.e. the operation of doing NOTHING to the molecule.

MORE ROTATION AXES

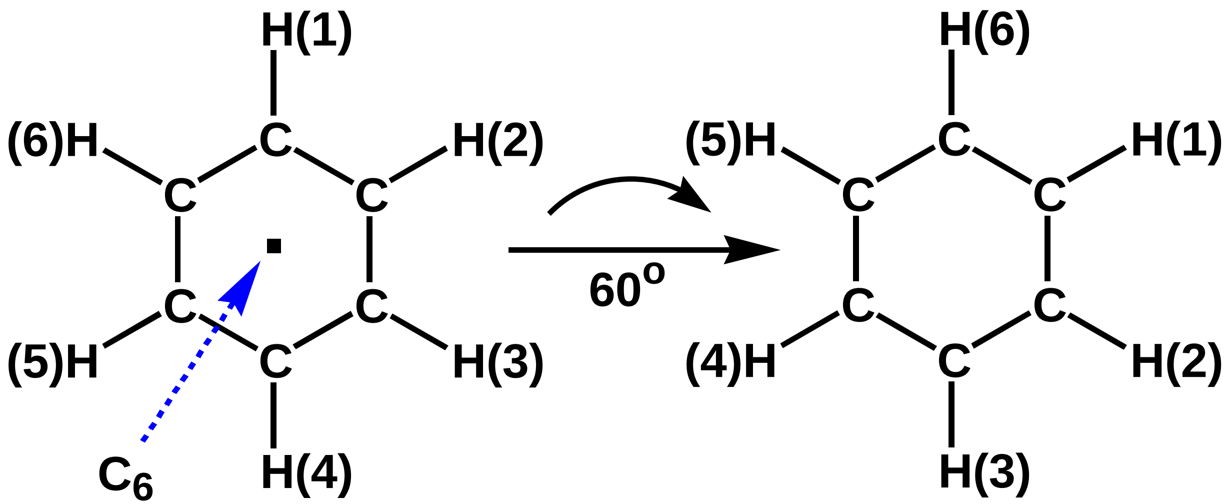
xenon tetrafluoride, XeF_4



cyclopentadienide ion, $C_5H_5^-$

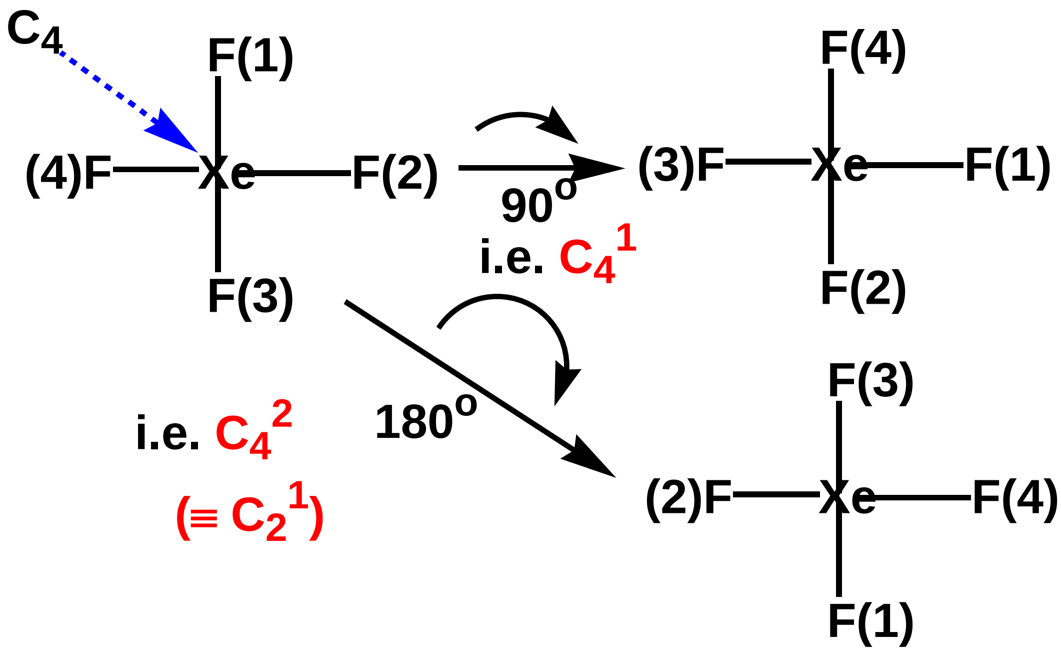


benzene, C_6H_6



Examples also known of C_7 and C_8 axes.

If a C_{2n} axis (i.e. even order) present, then C_n must also be present:



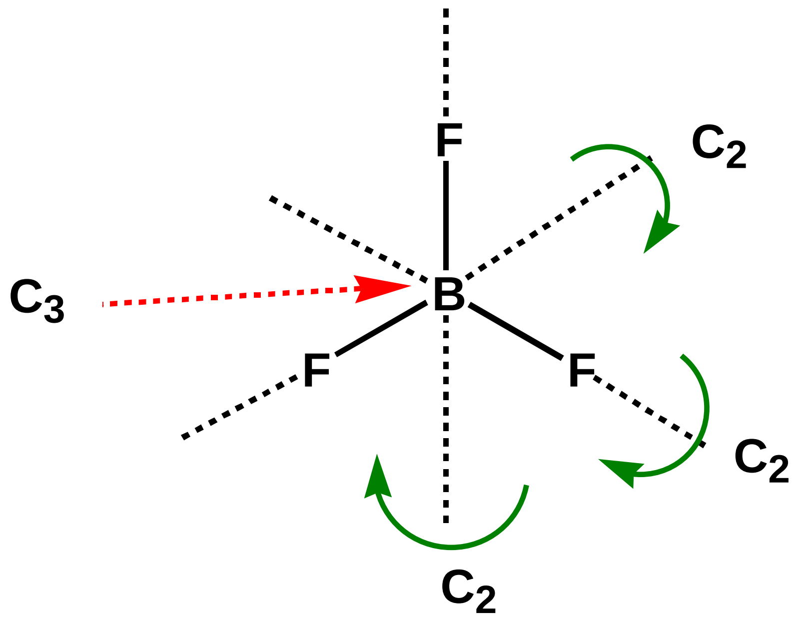
Therefore there must be a C_2 axis coincident with C_4, and the operations generated by C_4 can be written:

$\boxed{C_4^1,\ C_4^2\ (C_2^1),\ C_4^3,\ C_4^4\ (E)}$

Similarly, a C_6 axis is accompanied by C_3 and C_2, and the operations generated by C_6 are:

$\boxed{C_6^1,\ C_6^2\ (C_3^1),\ C_6^3\ (C_2^1),\ C_6^4\ (C_3^2),\ C_6^5,\ C_6^6\ (E)}$

Molecules can possess several distinct axes, e.g. BF_3:



Three C_2 axes, one along each B-F bond, perpendicular to C_3

Operation = reflection

Element = plane of symmetry

symbol $\boxed{\sigma}$

Greek letter ‘sigma’

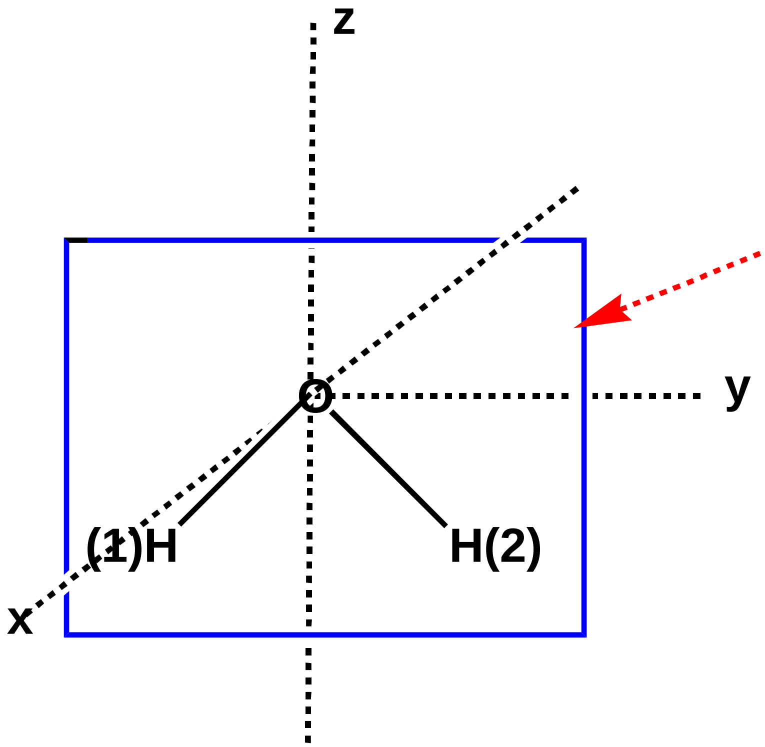
Several different types of symmetry plane -
different orientations with respect to symmetry axes.

By convention - highest order rotation axis drawn VERTICAL.

Therefore any plane containing this axis is a VERTICAL PLANE, σ_v.

e.g. H_2O plane above (often also called $\sigma(xz)$)

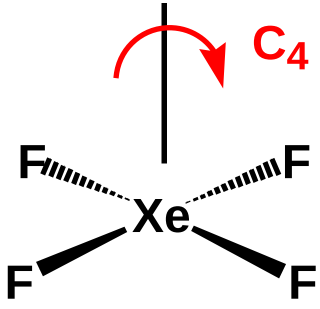
Can be >1 vertical plane, e.g. for H_2O there is also:



$\sigma(yz)$ - reflection leaves all atoms unshifted, therefore symmetry plane

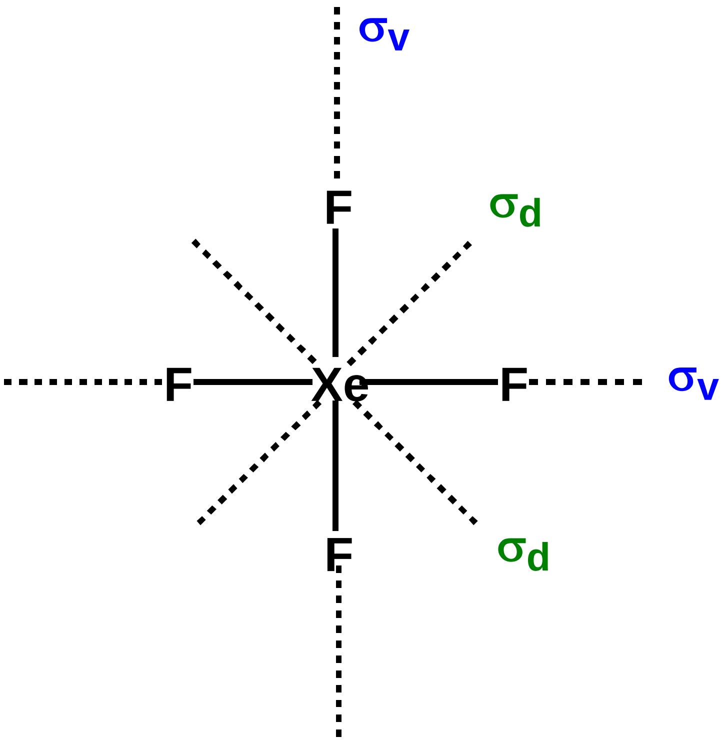
This is also a vertical plane, but symmetrically different from other, could be labelled σ_v'.

Any symmetry plane PERPENDICULAR to main axis is a HORIZONTAL PLANE, σ_h. e.g. for XeF_4:



Plane of molecule (perp. to C_4) is a symmetry plane, i.e. σ_h)

Some molecules possess additional planes, as well as σ_v and σ_h, which need a separate label. e.g. XeF4



Four "vertical" planes - but two different from others.Those along bonds called σ_v, but those bisecting bonds σ_d - i.e. DIHEDRAL PLANES

Usually, but not always, σ_v and σ_d differentiated in same way.

Two final points about planes of symmetry:

(i) if no C_n axis, plane just called σ;

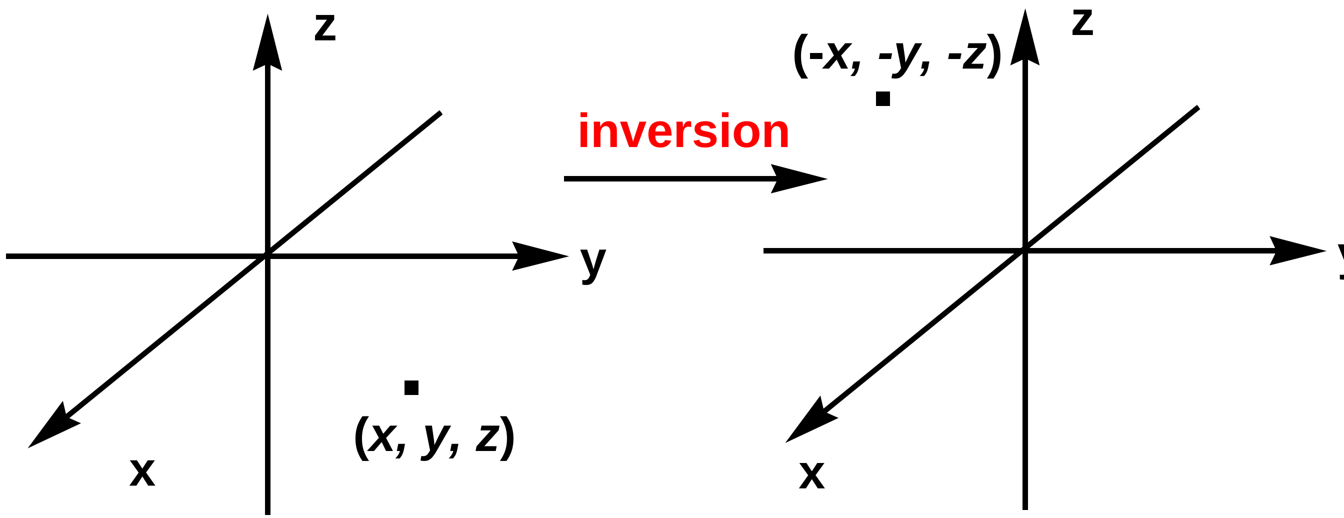
(ii) unlike rotations, only ONE operation per plane. A second reflection returns you to original state,

i.e. $(\sigma)(\sigma) = \sigma^2 = E$

INVERSION : CENTRES OF SYMMETRY

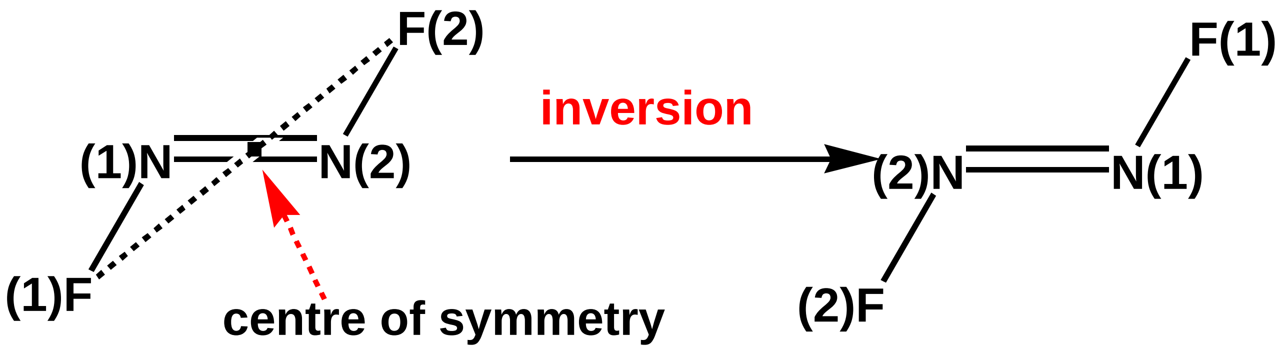
Involves BOTH rotation AND reflection.
OPERATION : INVERSION
ELEMENT : a POINT - CENTRE OF SYMMETRY or INVERSION CENTRE.

Best described in terms of cartesian axes:



The origin, (0, 0, 0) is the centre of inversion. If the coordinates of every point are changed from (x,y,z) to (-x, -y, -z), and the resulting arrangement is indistinguishable from original - the INVERSION is a symmetry operation, and the molecule possesses a CENTRE OF SYMMETRY (INVERSION) (i.e. CENTROSYMMETRIC)

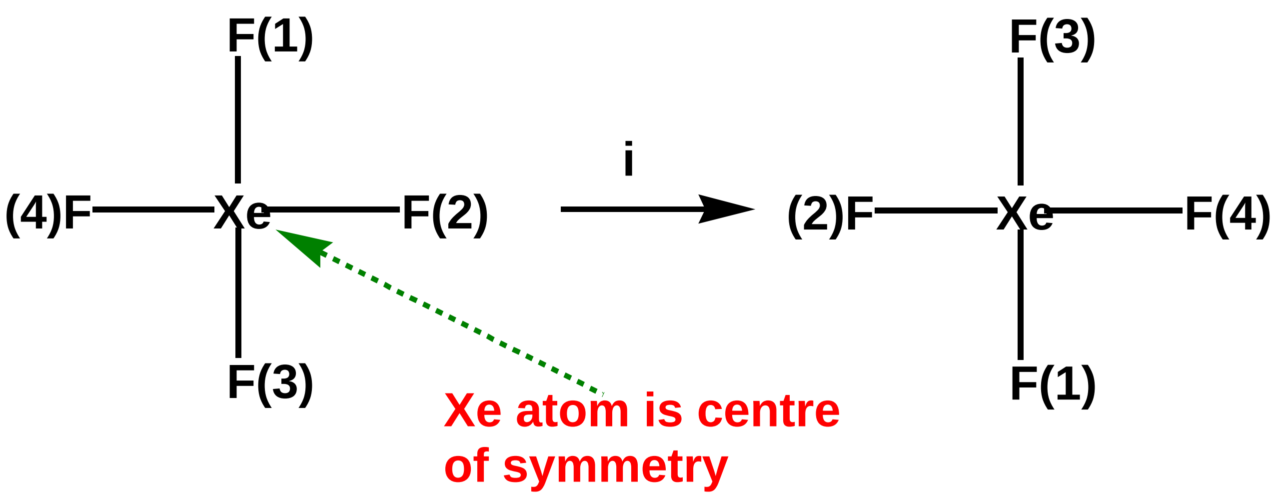
e.g. trans-N_2F_2



In practice, **inversion involves taking every atom to the centre - and out the same distance in the same direction on the other side.**

Symbol - same for operation (inversion) and element (centre): $\boxed{i}$

Another example: XeF_4



As for reflections, the presence of a centre of symmetry only generates one new operation, since carrying out inversion twice returns everything back to start.

$$(x, y, z) \xrightarrow{i} (-x, -y, -z) \xrightarrow{i} (x, y, z) \qquad \text{i.e. } (i)(i) = i^2 = E$$

Inversion is a COMPOSITE operation, with both rotation and reflection components. Consider a rotation by 180^o about the z axis:

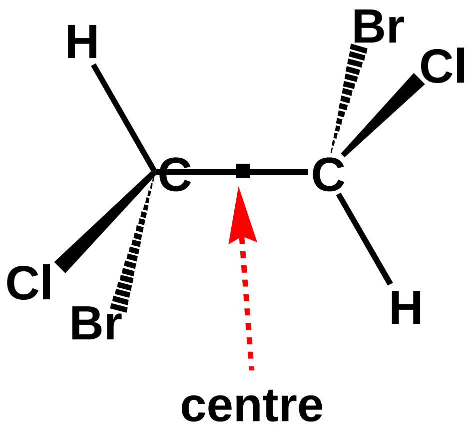
$$(x, y, z) \longrightarrow (-x, -y, z)$$

Follow this by reflection in the xy plane

$$(-x, -y, z) \longrightarrow (-x, -y, -z)$$

BUT individual components need not be symmetry operations themselves............

e.g. staggered conformation of CHClBr-CHClBr



Inversion at centre gives indistinguishable configuration.

The components, of rotation by 180^{o} or reflection in a plane perpendicular to the axis, do not.

If, however, a molecule does possess a C_2 axis and a σ_h (perpendicular) plane as symmetry operations, then inversion (i) must also be a symmetry operation.

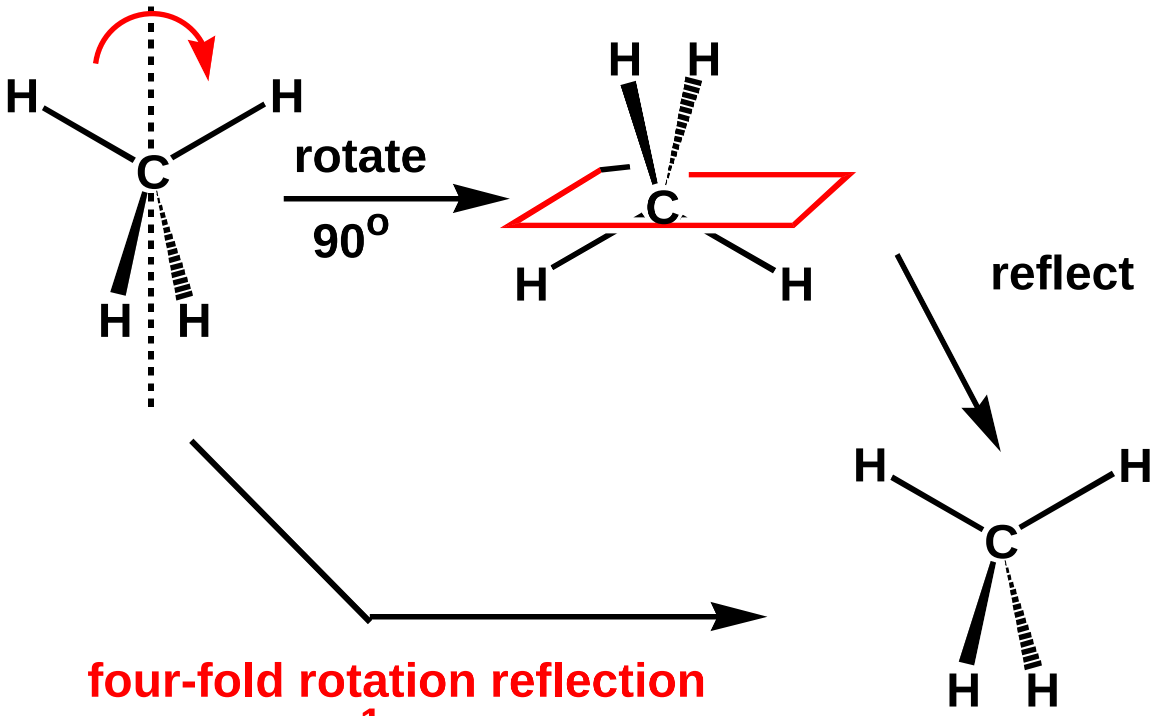
IMPROPER ROTATIONS : ROTATION-REFLECTION AXES

Operation: clockwise rotation (viewed along -z direction) followed by reflection in a plane perpendicular to that axis.

Element: rotation-reflection axis (sometimes known as "alternating axis of symmetry")

As for inversion - components need not be themselves symmetry operations for the molecule.

e.g. a regular tetrahedral molecule, such as CH_4



four-fold rotation reflection
S_4^1

Symbols: rotation-reflection axis S_n (element)

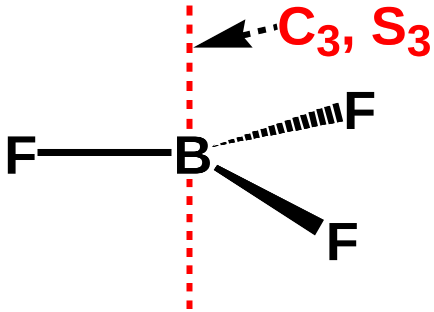
rotation-reflection S_n^m (operations)

where rotation is through $(360/n)^o$

S_4 axis requires presence of coincident C_2 axis

If C_n and σ_h are both present individually - there must also be an S_n axis :

e.g. BF_3 - trigonal planar



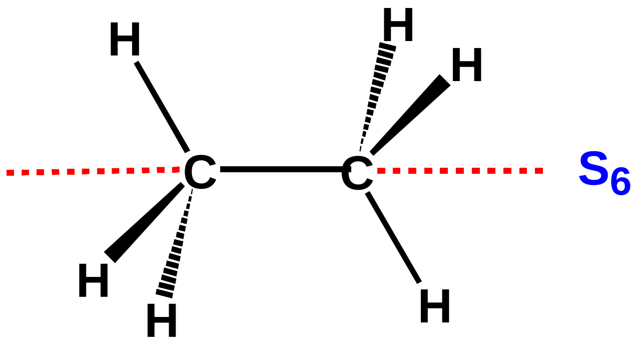
σ_h in plane of molecule.

C_3^1 + σ_h individually,

therefore S_3^1 must also be a symmetry operation

Other S_n examples: IF_7, pentagonal bipyramid, has C_5 and σ_h, therefore S_5 also.

Ethane in staggered conformation



i.e. rotate by 60^o and reflect in perp. plane.

Note NO C_6, σ_h separately.

POINT GROUPS

A collection of symmetry operations all of which pass through a single point

A point group for a molecule is a quantitative measure of the symmetry of that molecule

ASSIGNMENT OF MOLECULES TO POINT GROUPS

STEP 1 : LOOK FOR AN AXIS OF SYMMETRY

If one is found - go to STEP 2

If not: look for

(a) plane of symmetry - if one is found, molecule belongs to point group C_s

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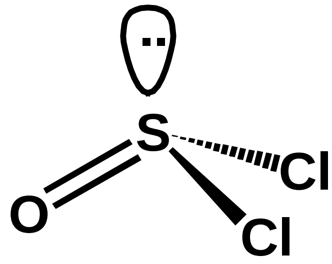
e.g. $SOCl_2$

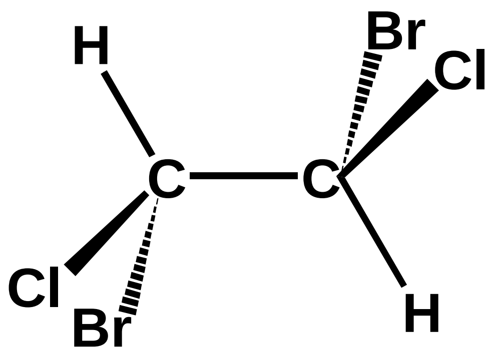


No axis, but plane containing S, O, bisecting ClSCl angle, is a symmetry plane. Hence C_s point group.

If no plane is found, look for

(b) centre of symmetry - if one is found, molecule belongs to point group C_i.

e.g. CHClBrCHClBr (staggered conformation):



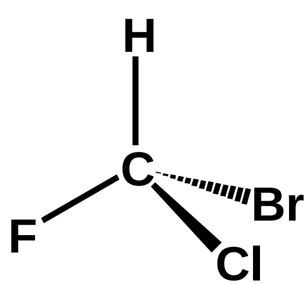
No axis, no planes, but mid-point of C-C bond is centre of symmetry. Therefore C_i point group.

No axes, plane or centre, therefore

(c) no symmetry except E : point group C_1

(so called because E = C_1, rotation through 360^o)

e.g. CHFClBr



No symmetry except E, therefore point group C_1.

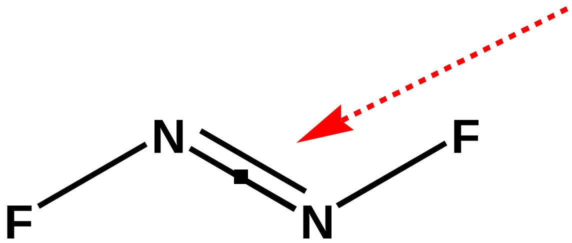
STEP 2 : LOOK FOR C_2 AXES PERPENDICULAR TO C_n

If found, go to STEP 3. If not, look for

(a) a HORIZONTAL PLANE OF SYMMETRY, if found - point group is C_{nh}

(C_n = highest order axis)

e.g. *trans*-N_2F_2:



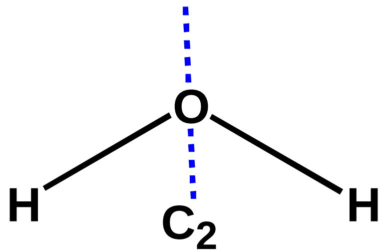
Highest order axis is C_2 (perp. to plane, through mid-pt. of N=N bond).

No C_2 axes perp. to this, but molecular plane is plane of symmetry (perp. to C_2, i.e. σ_h). Point group C_{2h}.

If there is no horizontal plane, look for

(b) n VERTICAL PLANES OF SYMMETRY. If found, molecule belongs to point group C_{nv}

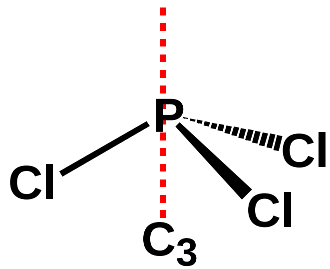
Many examples, e.g. H_2O



C_2 axis as shown. No other C_2's, no σ_h, but two sv's, one in plane, one perp. to plane, bisecting HOH angle.

Point group C_{2v}

PCl_3



C_3 highest order axis

No C_2's perp. to C_3

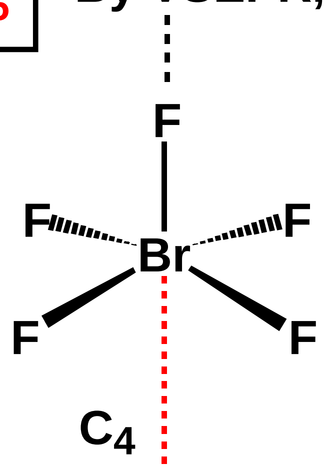
No σ_h, but

3 σ_v's, each contains P, one Cl

Therefore C_{3v}

BrF_5

By VSEPR, square pyramidal



Highest order axis : C_4

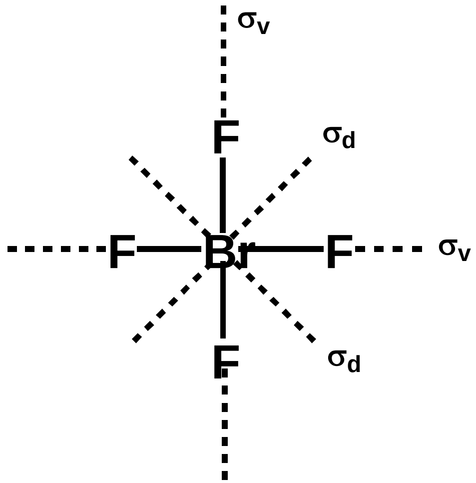
No C_2's perp. to C_4

No σ_h, but

4 vertical planes.

Therefore C_{4v}

N.B. of 4 vertical planes, two are σ_v's, two σ_d's



(looking down C_4 axis)

If no planes at all, could have

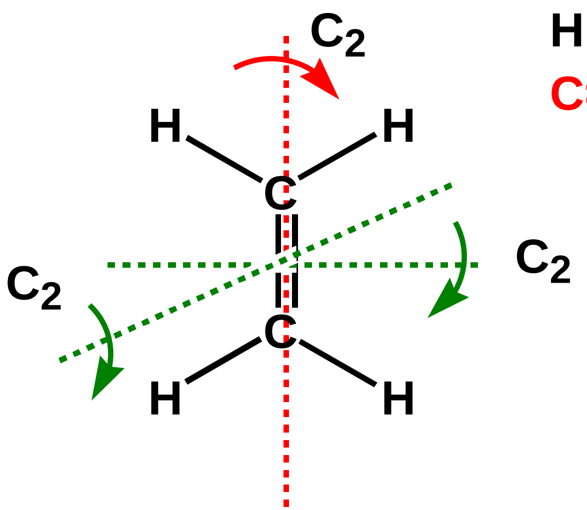
(c) no other symmetry elements: point group C_n , or

(d) an S_{2n} axis coincident with C_n: point group S_{2n}

STEP 3 If there are nC_2's perp. to C_n, look for:

(a) horizontal plane of symmetry. If present, point group is $\boxed{D_{nh}}$

e.g. **ethene (ethylene), C_2H_4**



Highest order axis C_2 - along C=C bond

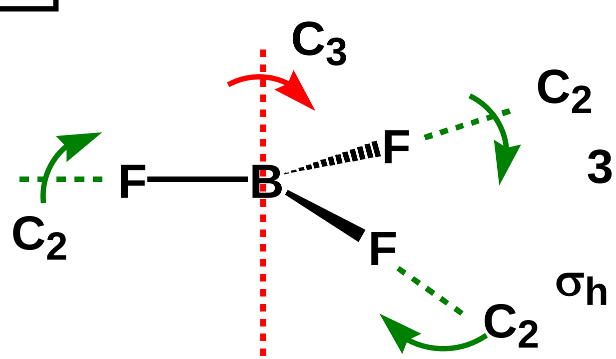
Two additional C_2's as shown.

σ_h in plane defined by the last two C_2's

Point group D_{2h}

BF_3

Planar trigonal molecule by VSEPR



Main axis C_3

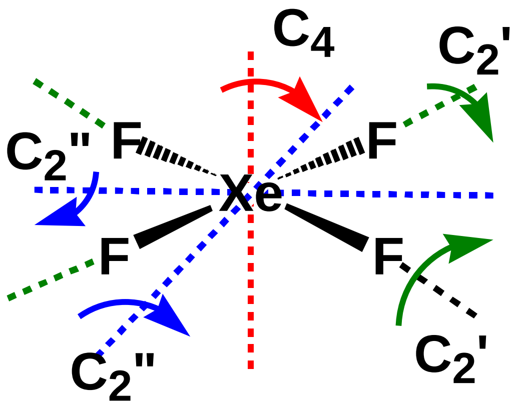
3 C_2's perp. to C_3

σ_h - plane of molecule

Point group D_{3h}

XeF_4

Square planar by VSEPR



Main axis C_4

4 C_2's perp. to C_4 (2 along XeF bonds (C_2'), 2 bisecting, (C_2"))

σ_h - plane of molecule

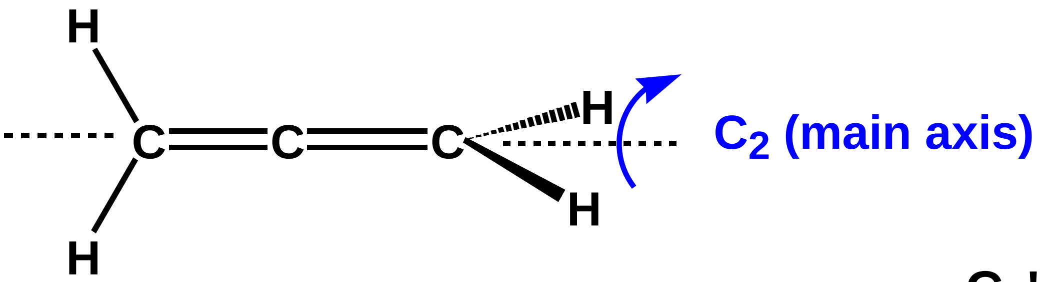
Point group D_{4h}

If no σ_h, look for:

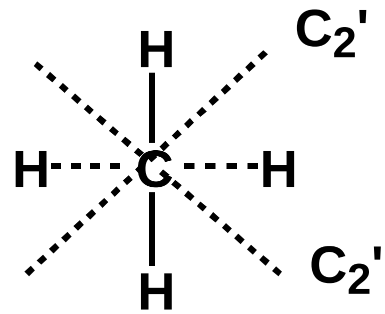
(b) n vertical planes of symmetry (σ_v/σ_d).

If these are present, molecule belongs to point group D_{nd}

e.g. allene, $H_2C{=}C{=}CH_2$.



Looking down
C=C=C bond



Main axis C_2 - along C=C=C

Two C_2's as shown

Two vertical planes (σ_d) - each containing one CH_2 unit

$\boxed{\text{Point group} \quad D_{2d}}$

A few molecules do not appear to fit into this general scheme..........

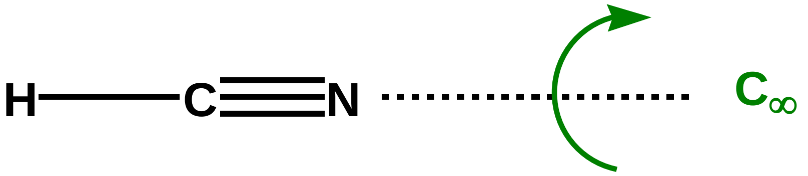
LINEAR MOLECULES

Do in fact fit into scheme - but they have an infinite number of symmetry operations.

Molecular axis is C_∞ - rotation by any arbitrary angle $(360/\infty)^o$, so infinite number of rotations. Also any plane containing axis is symmetry plane, so infinite number of planes of symmetry.

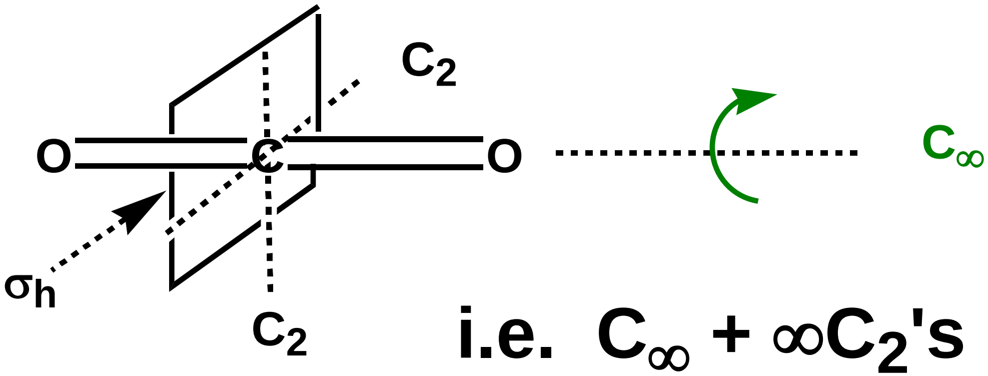
Divide linear molecules into two groups:

(i) No centre of symmetry, e.g.:



No C_2's perp. to main axis, but ∞ σ_v's containing main axis: point group $C_{\infty v}$

(ii) Centre of symmetry, e.g.:



i.e. $C_\infty + \infty C_2\text{'s} + \sigma_h$

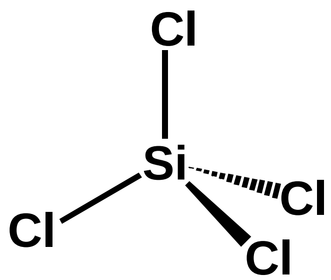
Point group $D_{\infty h}$

Highly symmetrical molecules

A few geometries have several, equivalent, highest order axes. Two geometries most important:

Regular tetrahedron

e.g.



4 C_3 axes (one along each bond)

3 C_2 axes (bisecting pairs of bonds)

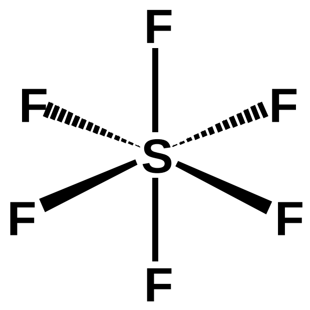
3 S_4 axes (coincident with C_2's)

6 σ_d's (each containing Si and 2 Cl's)

Point group: T_d

Regular octahedron

e.g.



3C_4's (along F-S-F axes)
also 4 C_3's. 6 C_2's, several planes, S_4, S_6 axes, and a centre of symmetry (at S atom)

Point group O_h

These molecules can be identified without going through the usual steps.

Note: many of the more symmetrical molecules possess many more symmetry operations than are needed to assign the point group.