Molecular symmetry
and
Group theory

Molecular symmetry

- The concept of 'shape' can be sharpen systematically into a precise definition of 'symmetry
- The systematic discussion of symmetry is called group theory
- Any molecule can be classified according to its symmetry and how to use this classification to discuss molecular properties

- The symmetry transformations of orbitals can be used to set up a labeling scheme
- These symmetry labels are used to identify integrals that necessarily vanish
- By considering the symmetry properties of integrals, we see that it is possible to derive the selection rules that govern spectroscopic transitions

Applications of Group Theory

1. Predicting polarity of molecules.
2. Predicting chirality of molecules.
3. Predicting the orbitals used in σ bonds. Group theory can be used to predict which orbitals on a central atom can be mixed to create hybrid orbitals.
4. Predicting the orbitals used in *molecular orbitals*. Molecular orbitals result from the combining or overlap of atomic orbitals, and they encompass the entire molecule.

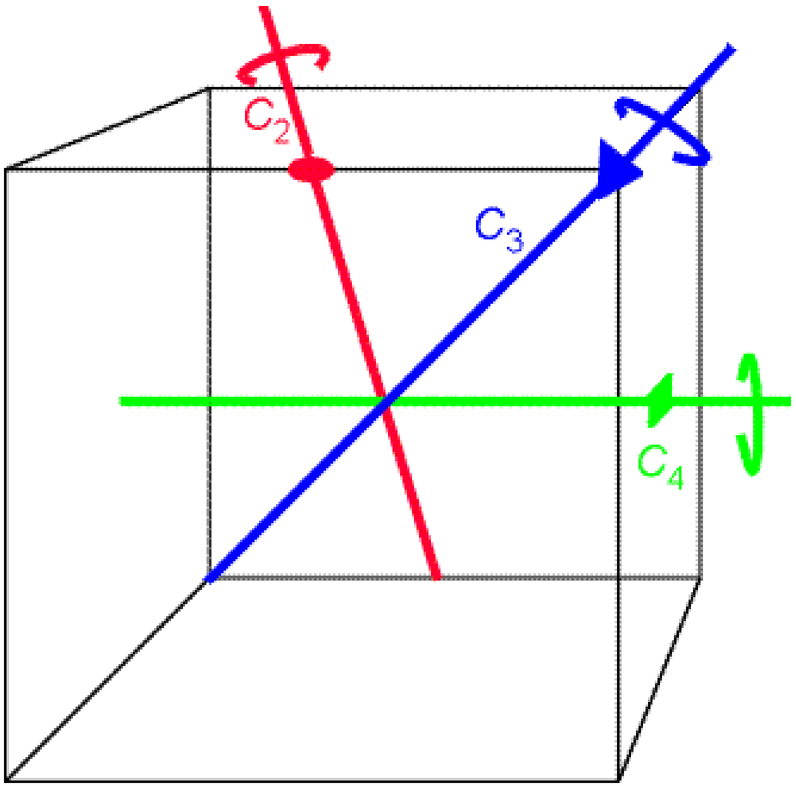
Applications of Group Theory

5. Determining the symmetry properties of all molecular motion (rotations, translations and vibrations). Group theory can be used to predict which molecular vibrations will be seen in the infrared or Raman spectra.

The symmetry elements of objects

- Some objects are 'more symmetrical' than others
- A sphere is more symmetrical than a cube because it looks the same after it has been rotated through any angle about any diameter
- A cube looks the same only if it is rotated through certain angles about specific axes, such as 90°, 180°, or 270°

Some of the symmetry elements of a cube. The twofold, threefold, and four fold axes are labeled with the conventional system



NH_3 molecule is 'more symmetrical' than an H_2O

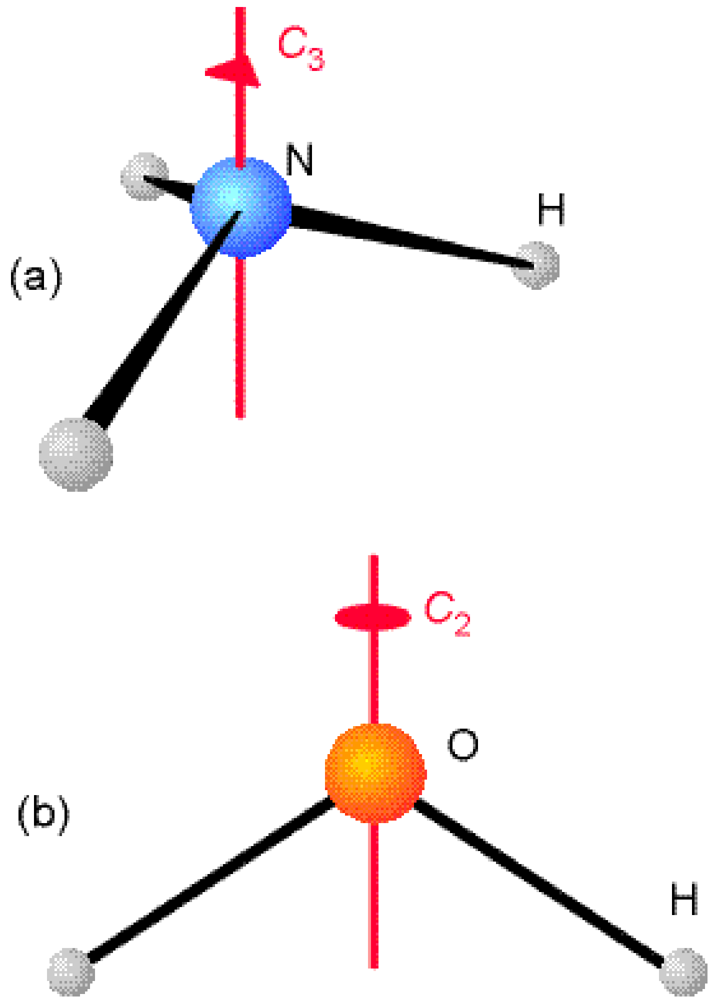


Fig 2: (a) An NH_3 molecule has a threefold (C_3) axis and (b) an H_2O molecule has a twofold (C_2) axis. Both have other symmetry elements too.

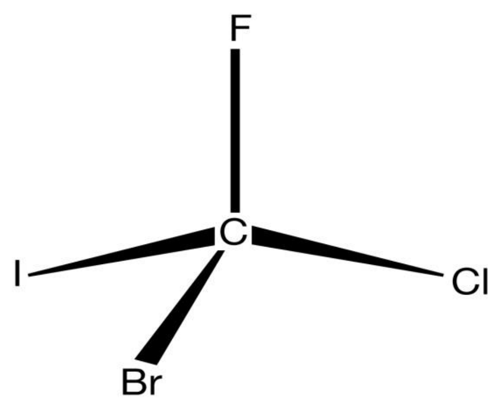
Operations and symmetry elements

- An action that leaves an object looking the same after it has been carried out is called a symmetry operation
- Typical symmetry operations include rotations, reflections, and inversions
- There is a corresponding symmetry element for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed
- A rotation (a symmetry operation) is carried out around an axis (the corresponding symmetry element)

- The classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged gives rise to the **point groups**
- There are five kinds of symmetry operation (and five kinds of symmetry element) of this kind
- Considering crystals; symmetries arising from translation through space are called **space groups**

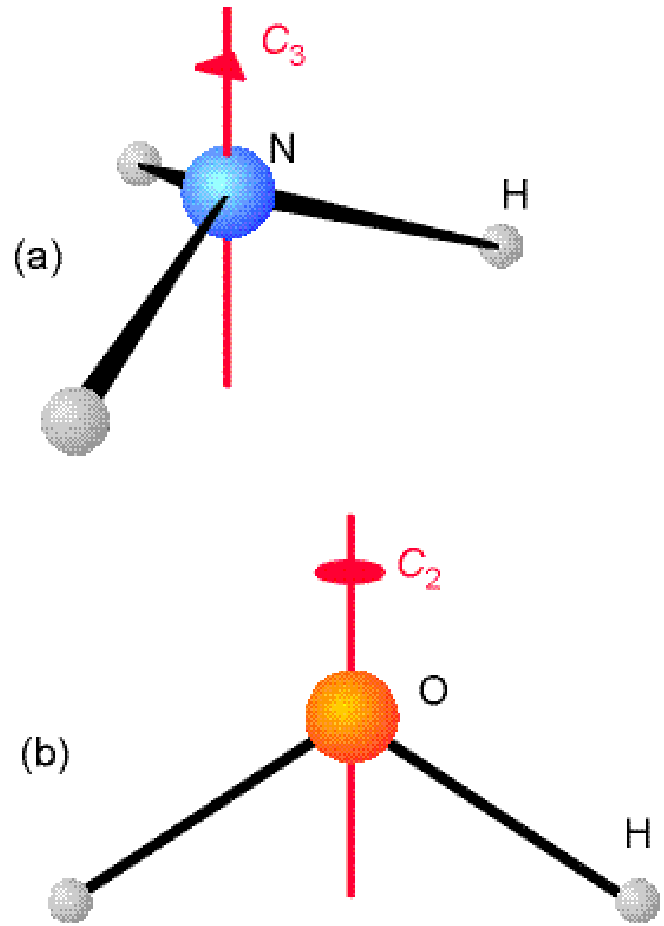
- The **identity**, *E*, consists of doing nothing
- The corresponding symmetry element is the entire object
- Because every molecule is indistinguishable from itself if nothing is done to it, every object possesses at least the identity element.

- One reason for including the identity is that some molecules have only this symmetry element (1); another reason is technical and connected with the detailed formulation of group theory



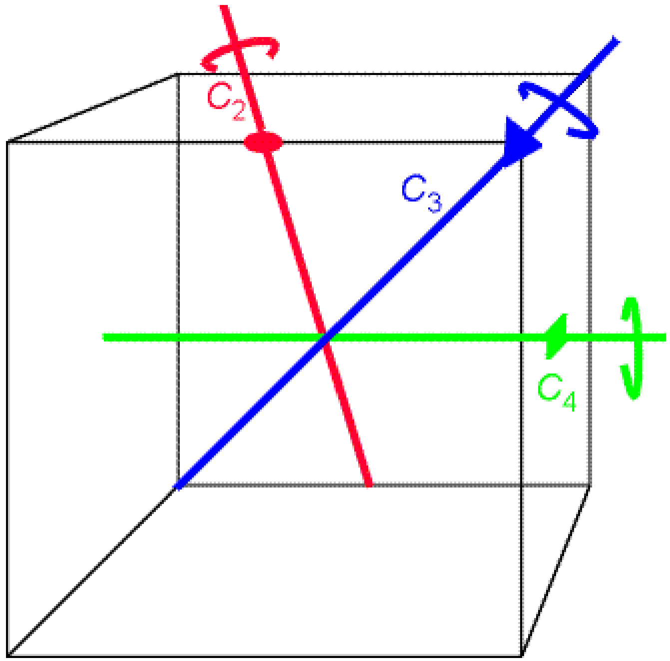
1 CBrClFI

- An **n-fold rotation** (the operation) about an **n-fold axis of** symmetry, C_n (the corresponding element), is a rotation through 360°/n.
- The operation C_1 is a rotation through 360°, and is equivalent to the identity operation *E*
- An H_20 molecule has one twofold axis, C_2
- An NH_3 molecule has one threefold axis, C_3, with which is associated two symmetry operations, one being 120° rotation in a clockwise sense and the other 120° rotation in a counter-clockwise sense.


C_3
N
H
(a)
C_2
O
H
(b)

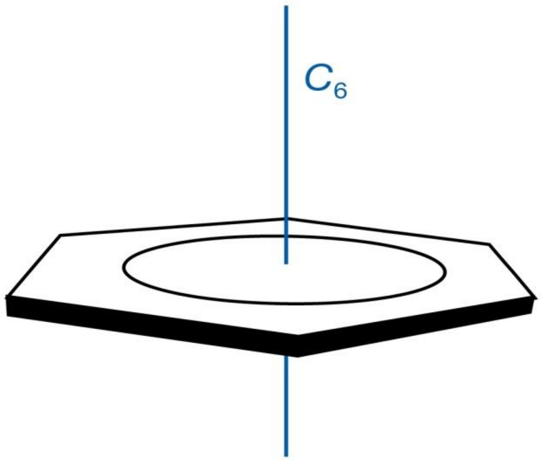
- A pentagon has a C_5 axis, with two (clockwise and counter-clockwise) rotations through 72° associated with it.
- It also has an axis denoted C_5^2, corresponding to two successive C_5 rotations; there are two such operations, one through 144° in a clockwise sense and the other through 144° in a counter-clockwise sense

- A cube has three C_4 axes, four C_3 axes, and six C_2 axes



- However, even this high symmetry is exceeded by a sphere, which possesses an infinite number of symmetry axes (along any diameter) of all possible integral values of n

- If a molecule possesses several rotation axes, then the one (or more) with the greatest value of n is called the **principal axis**
- The principal axis of a benzene molecule is the sixfold axis perpendicular to the hexagonal ring (**2**)

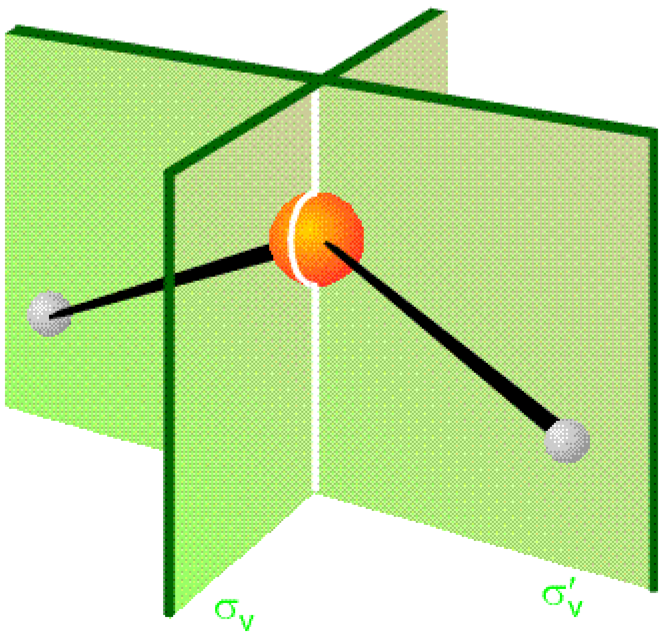


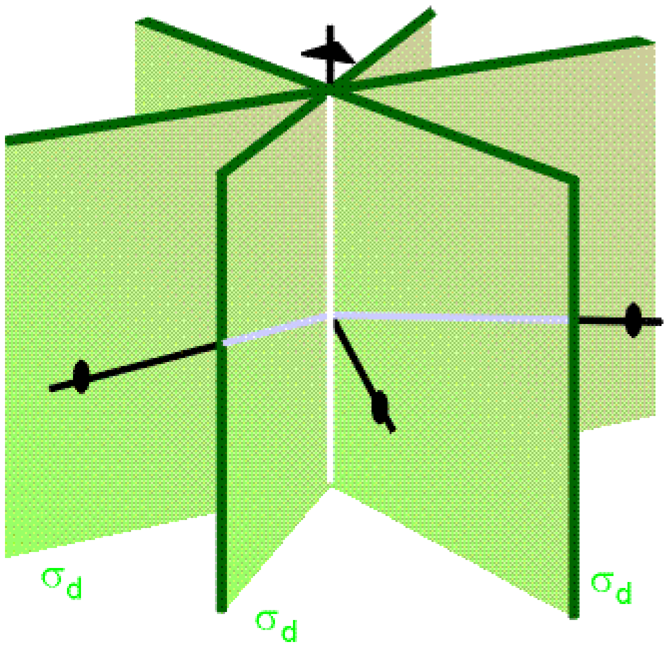
2 Benzene

- A **reflection** (the operation) in a **mirror plane,** σ (the element), may contain the principal axis of a molecule or be perpendicular to it
- If the plane is parallel to the principal axis, it is called 'vertical' and denoted σ_V
- A vertical mirror plane that bisects the angle between two C_2 axes is called a 'dihedral plane' and is denoted σ_d
- When the plane of symmetry is perpendicular to the principal axis it is called 'horizontal' and denoted σ_h

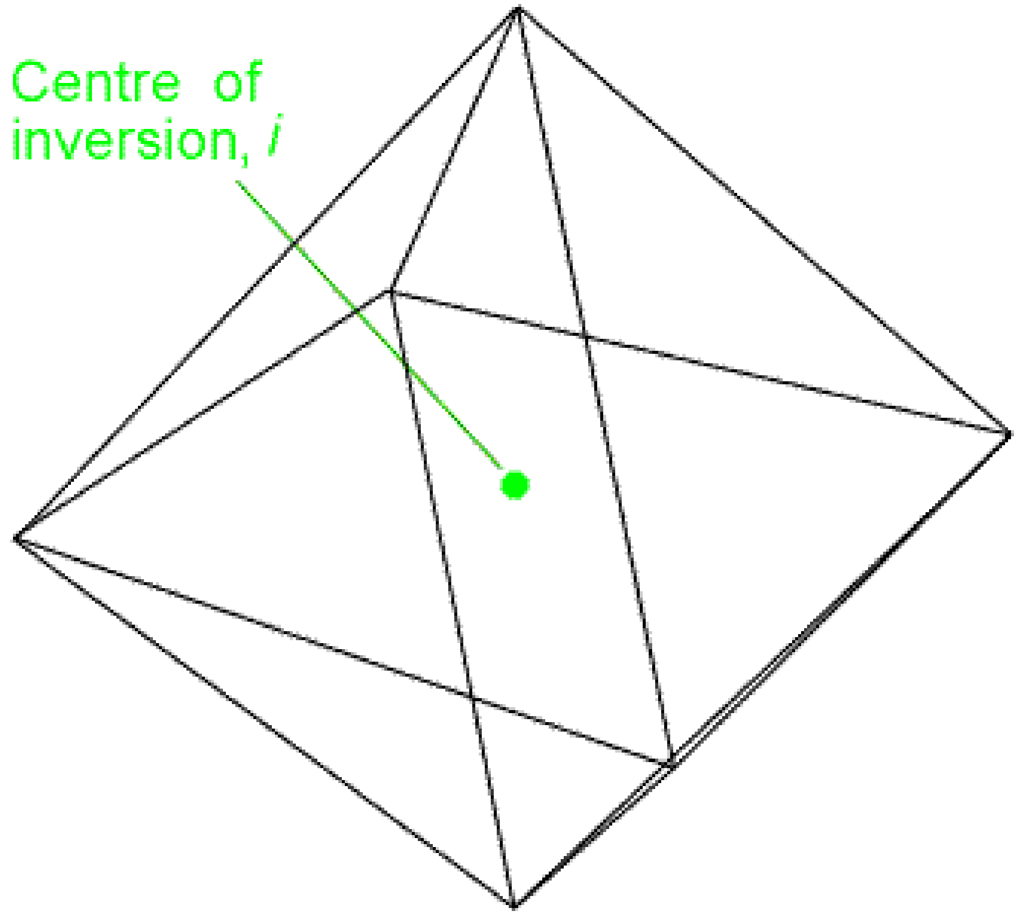
An H_2O molecule has two mirror planes. They are both vertical (i.e. contain the principle axis), so are donated σ_v and σ_v'

Dihedral mirror plane (σ_d) bisect the C_2 axes perpendicular to the principle axis





- In an **inversion** (the operation) through a **centre of symmetry,** *i* (the element), we imagine taking each point in a molecule, moving it to the centre of the molecule, and then moving it out the same distance on the other side; that is, the point (x, y, z) is taken into the point ($-x, -y, -z$).
- Neither an H_2O molecule nor an NH_3 molecule has a centre of inversion, **but** a sphere and a cube do have one.

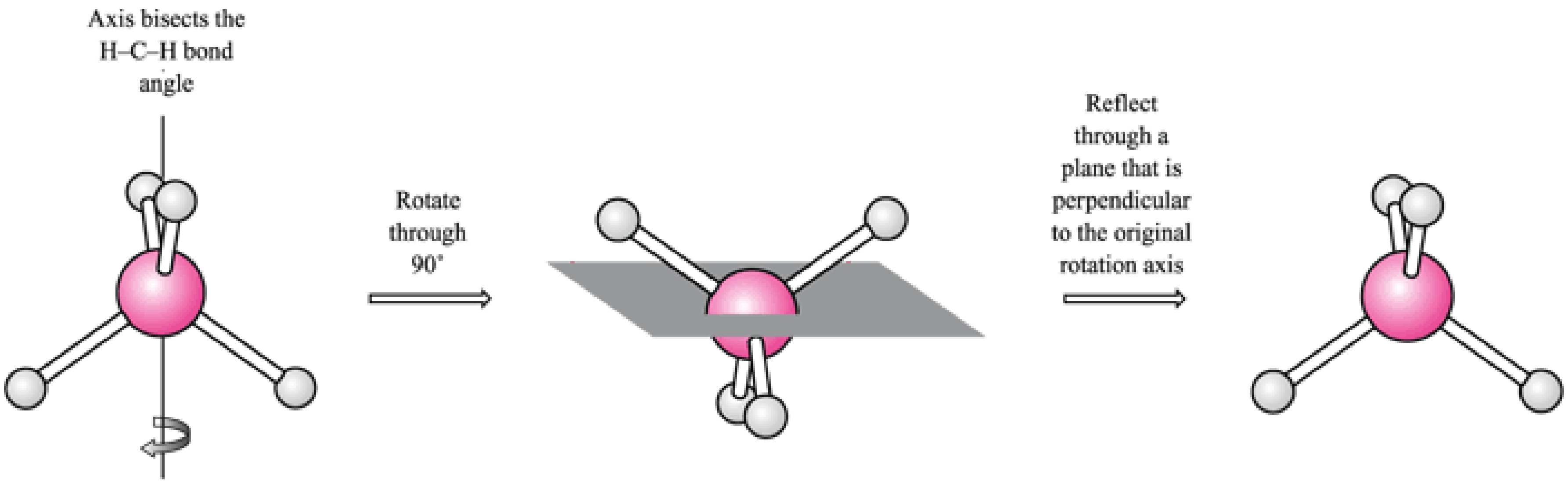


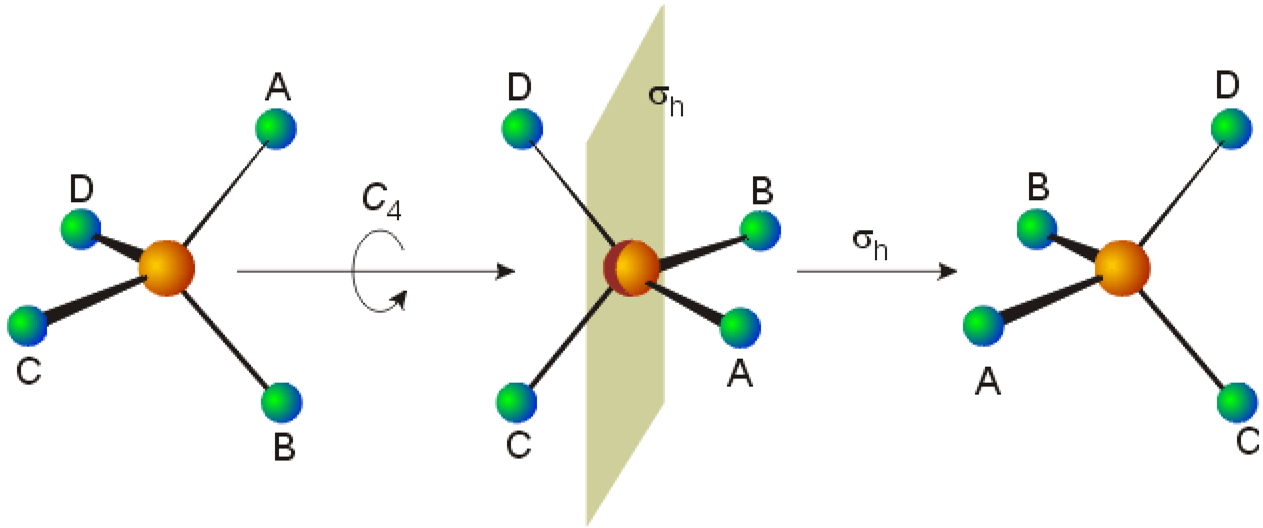
Regular octahedron has a center of inversion (*i*)

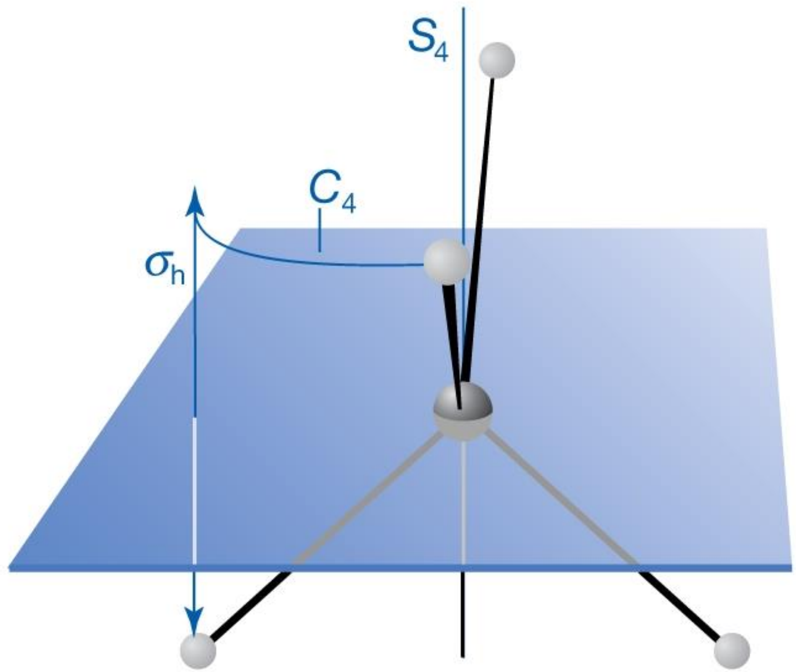
A C_6H_6 molecule does have a centre of inversion, as does a regular octahedron ; a regular tetrahedron and a CH_4 molecule do not

- An **n-fold improper rotation** (the operation) about an **n-fold axis of improper rotation** or **an n-fold improper rotation axis,** S_n, (the symmetry element) is composed of two successive transformations
- The first component is a rotation through 360°/n, and the second is a reflection through a plane perpendicular to the axis of that rotation
- Neither operation alone needs to be a symmetry operation. A CH_4 molecule has three S_4 axes

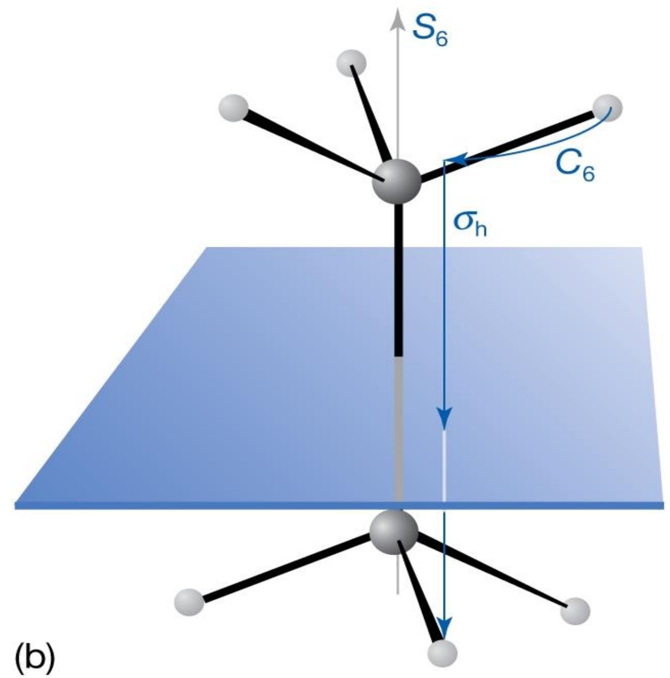
Improper Rotation in a Tetrahedral Molecule







A CH_4 molecule has fourfold improper rotation axis (S_4): the molecule is indistinguishable after 90º rotation followed by a reflection across the horizontal plane, but neither operation alone is a symmetry operation



(b) the staggered form of ethane has an S_6 axis composed of a rotation followed by a reflection.