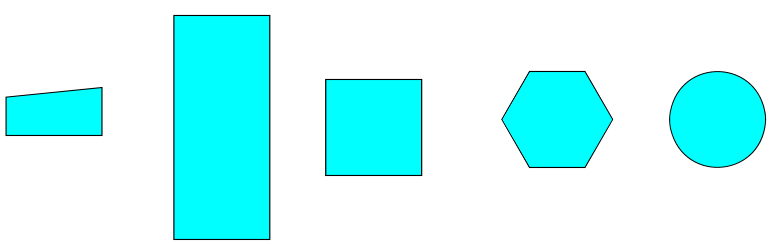
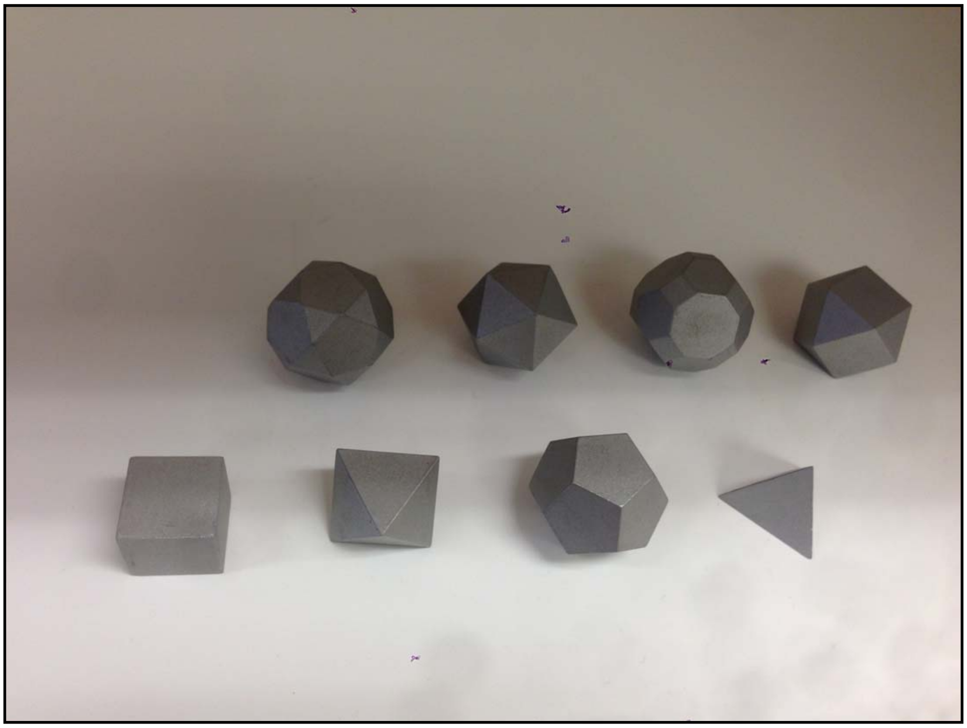
Symmetry & Group Theory

MT Chap. 4
Vincent: Molecular Symmetry and group theory

Symmetry:
The properties of self-similarity





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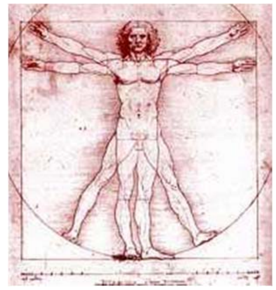


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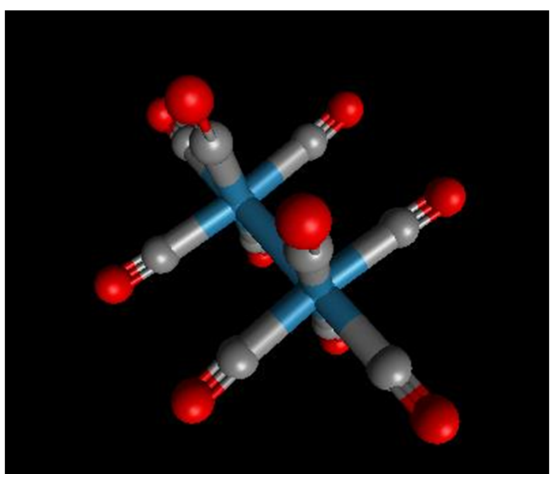
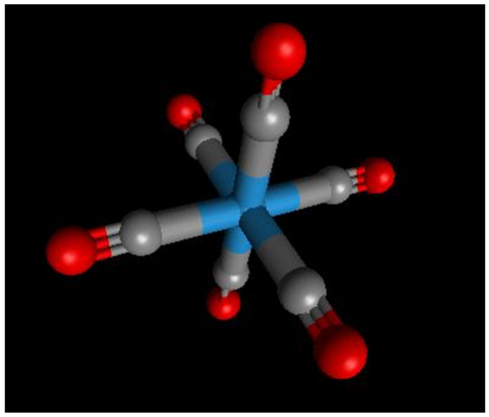


$Re_2(CO)_{10}$



$W(CO)_6$

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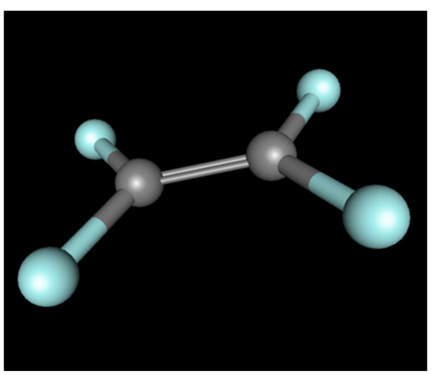
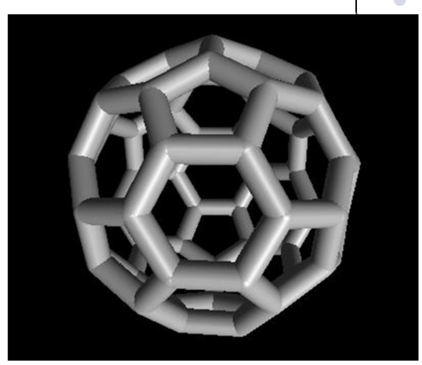




C_2F_4

C_{60}

Symmetry:

•Construct bonding based on atomic orbitals

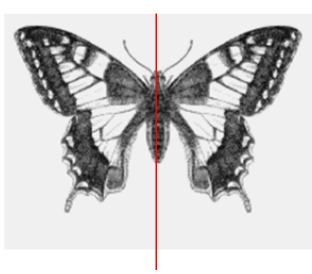
•Predict Raman & IR spectra

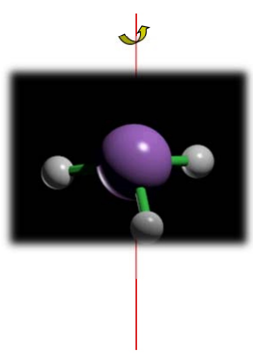
•Access reaction pathway

•Determine optical activity

Symmetry Operation:

Movement of an object into an equivalent or indistinguishable orientation





Symmetry Elements:

A point, line or plane about which a symmetry operation is carried out

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5 types of symmetry operations/elements

Identity: this operation does nothing, symbol: E

Element is entire object

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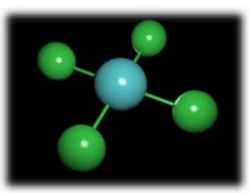
Proper Rotation:

Rotation about an axis by an angle of 2π/n

2

1



3

4

$$C_n^m$$

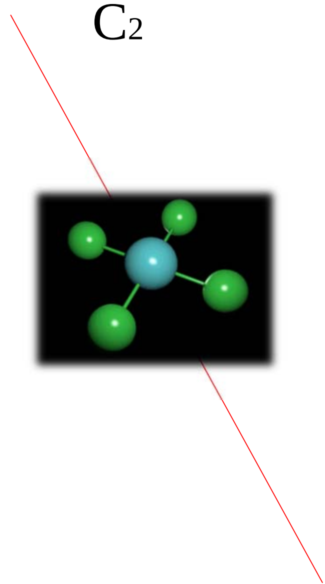
Rotation 2πm/n

$$C_n^n = E$$

$$C_n^{n+1} = C_n$$

C_4 $PtCl_4$

C_2



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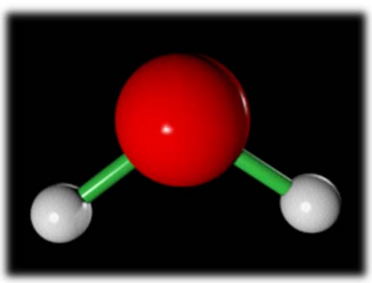
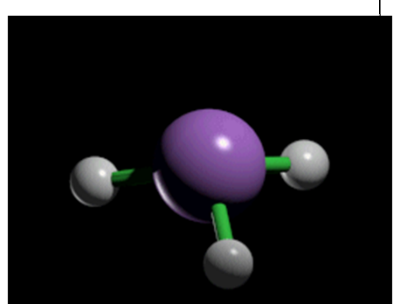
The highest order rotation axis is called the principle axis.

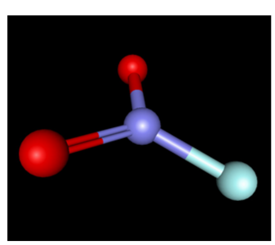


H_2O



NH_3

How about:

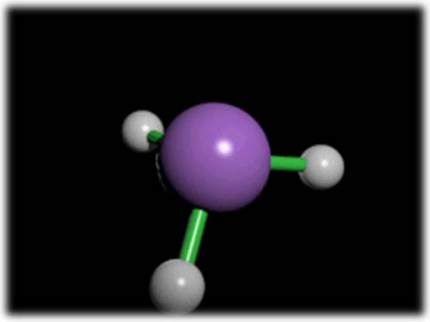


NFO_2?

Identity E
Proper Rotation C_n

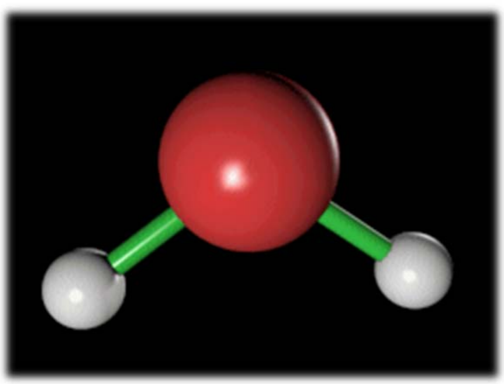
Reflection: σ

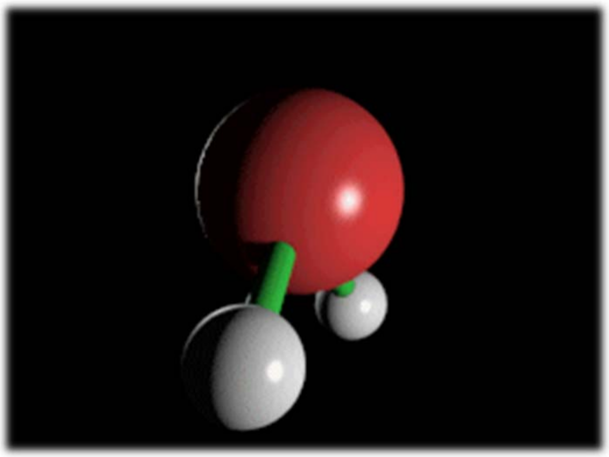
reflection through a mirror plane



NH_3

H_2O





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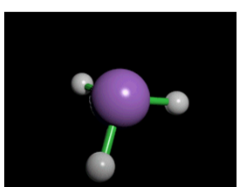
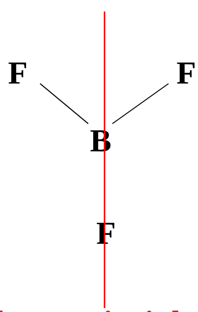
a mirror plane containing a principle rotation axis is labeled

σ_v

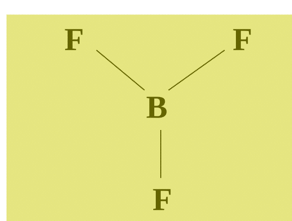




$$\sigma^n = E(n = even)$$
$$\sigma^n = \sigma(n = odd)$$

a mirror plane normal to a principle rotation axis is labeled

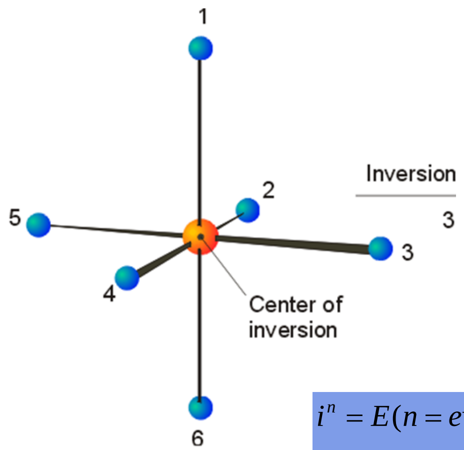
σ_h



Inversion: *i*

inversion center or center of symmetry

(x,y,z) → (-x,-y,-z)



$$i^n = E(n = even)$$

$$i^n = i(n = odd)$$

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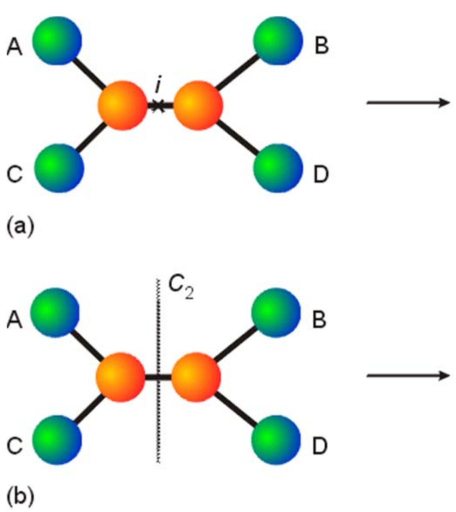
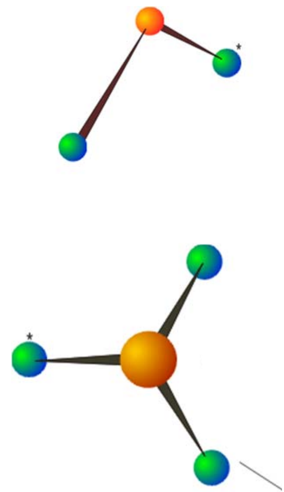


Difference between inversion and 2-fold rotation

Inversion ?



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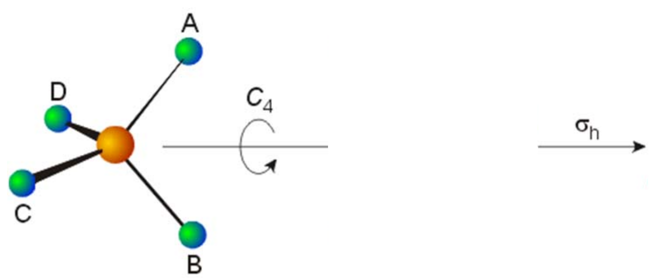
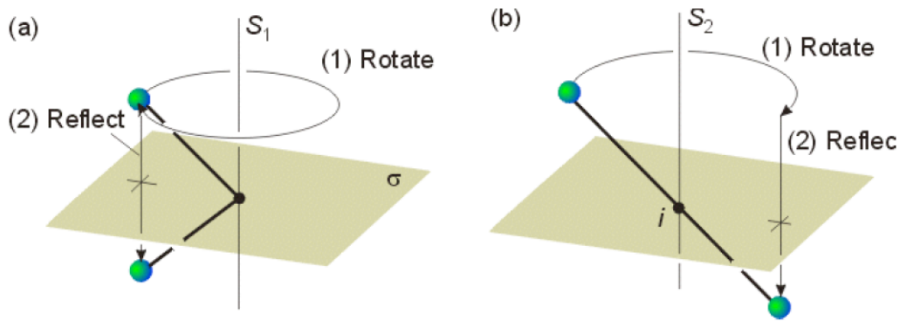
Improper rotation: S_n

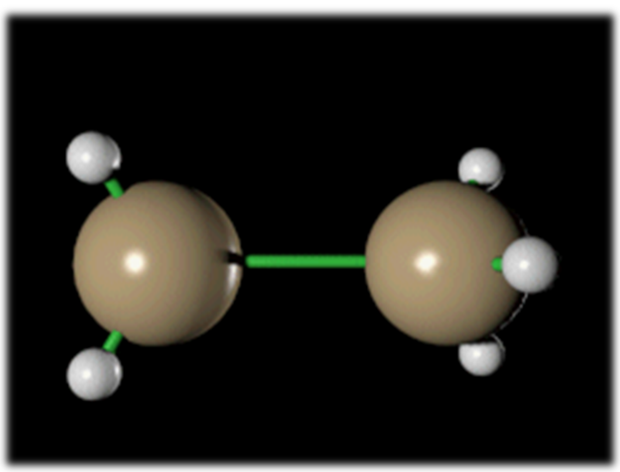
rotation about an axis by an angle of $2\pi/n$ followed by reflection through a perpendicular plane.

(C_n,σ_h symmetry are not necessary for S_n to exist)





S_6



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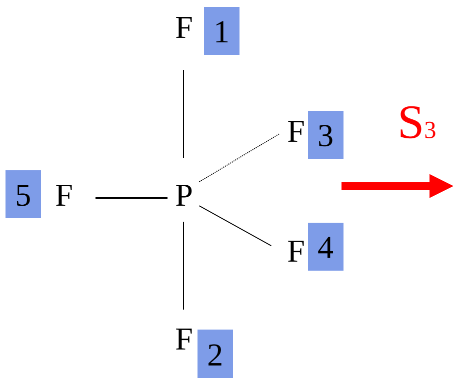

Contain C_3, σ_h

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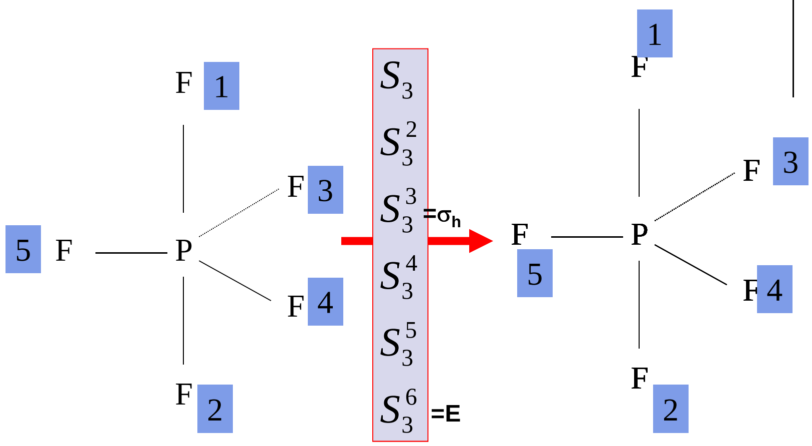
<u>In general:</u>

S_n with n even → molecule contains $C_{n/2}$,

$S_n^n = E$

S_n with n odd → molecule contains C_n + σ_h;

$S_n^n = \sigma_h$, $S_n^{2n} = E$



Contain C_3, σ_h

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S_6

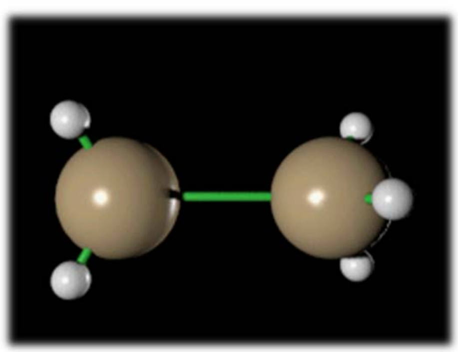
$S_6^2 = C_3$

$S_6^3 = i \equiv S_2$

$S_6^4 = C_3^2$

S_6^5

$S_6^6 = E$



S_6

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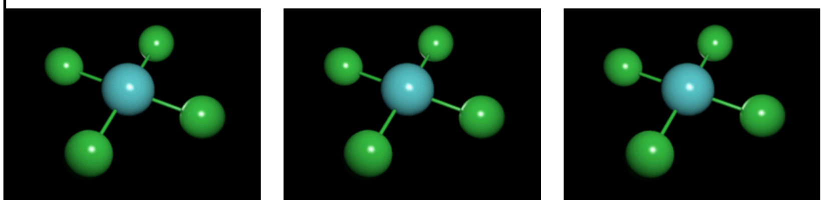
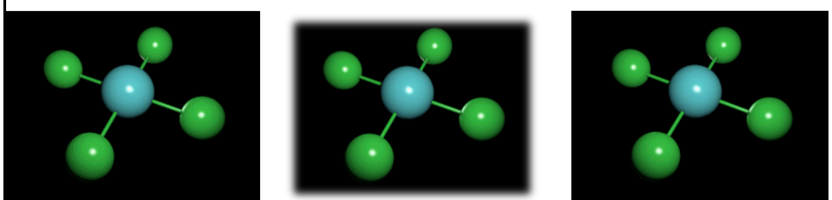
XeF_4

$$E, i, \sigma_h, 2\sigma_v, 2\sigma_v^{'}, C_4, C_2, 2C_2', 2C_2'', S_4$$



C_2' C_2'' σ_v



S_4 C_4 C_2

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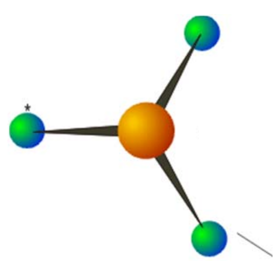
BF_3



$$E, \sigma_h, 3\sigma_v^{'}, C_3, 3C_2, S_3$$

Group Theory

Definition of a Group:

A group is a collection of elements

- **which is closed under a single-valued associative binary operation**
- **which contains a single element satisfying the identity law**
- **which possesses a reciprocal element for each element of the collection.**

Mathematical Group

1. **Closure**: $A, B \in G \Rightarrow AB \in G$
2. **Associativity**: $A, B, C \in G \Rightarrow A(BC) = (AB)C$
3. **Identity**: There exists $E \in G$ such that $AE = EA = A$ for all $A \in G$
4. **Inverse**: $A \in G \Rightarrow$ there exists $A^{-1} \in G$ such that $AA^{-1} = A^{-1}A = E$

Order of a group: the number of elements it contains

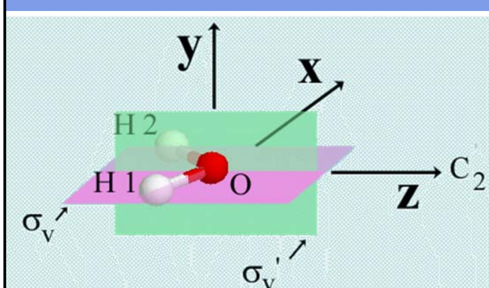
Example:

1. set of all real number, under addition, order =∞
   - Closure: $x + y \in G$
   - Associativity: $x + (y + z) = (x+y) + z$
   - Identity: $x + 0 = 0 + x = x$
   - Inverse: $x + (-x) = (-x) + x = 0$
2. set of all integers, under addition
3. {set of all real number}-{0}, under multiplication
   - Closure: $x * y \in G$
   - Associativity: $x * (y * z) = (x*y) * z$
   - Identity: $x * 1 = 1 * x = x$
   - Inverse: $x * (1/x) = (1/x) * x = 1$
4. {+1, -1}
5. {± 1, ±i}

Symmetry of an object ⇒ point group (symmetry about a point)

$\{E, C_2, \sigma_v, \sigma_{v'}\}$ = point group C_{2v}

Binary operation: one operation followed by another



Closure:
Associativity:
Identity:
Inverse:

Multiplication Table

C_{2v}	E	C_2	σ_v	σ_v'
E				
C_2				
σ_v				
σ_v'				

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

Rearrangement Theorem: each row and each column in a group multiplication table lists each of the elements once and only once.

Proof:

	A	B	C
A	AA		
B	AB		
C	AC		

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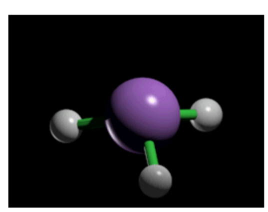
C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

A group is Abelian if AB=BA (the multiplication is completely commutative).

Not all groups are abelian.

$$\sigma_v C_3 \neq C_3 \sigma_v$$



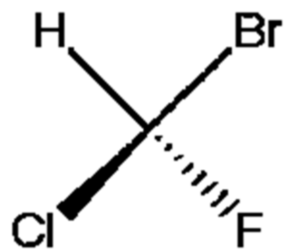
Any object (or molecule) may be classified into a point group uniquely determined by its symmetry.

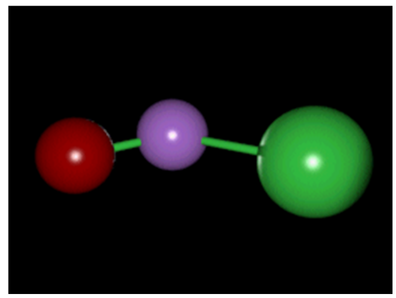
Groups with low symmetry:

{E}=C_1, Schönflies Symbol/notation

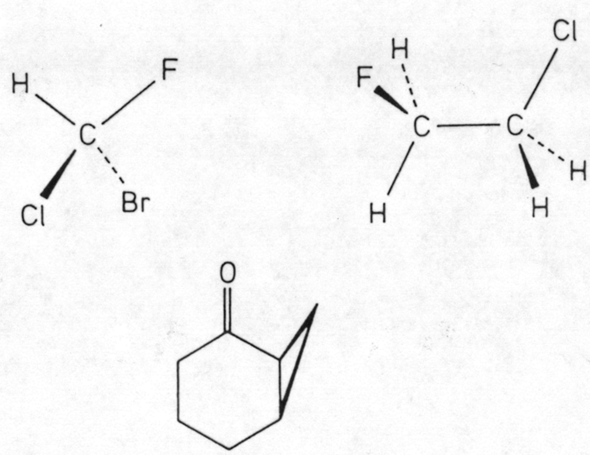
{E,σ} =C_s

{E, i} =C_i

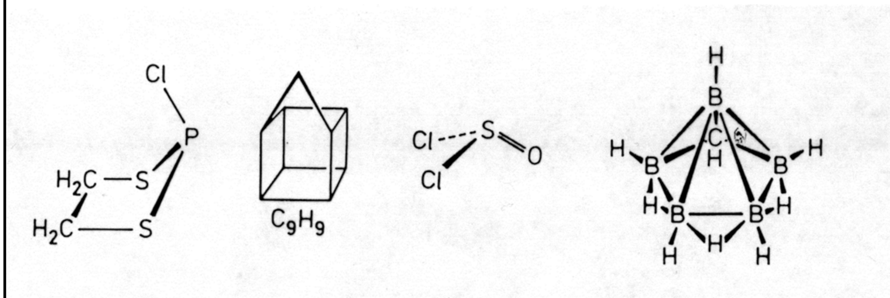




ONCl, C_s



Examples with C_1 symmetry: no symmetry elements except the onefold rotation
nmetry is asymmetry).



C_s

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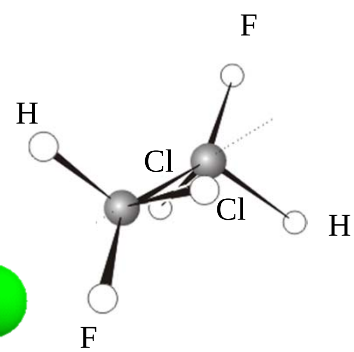

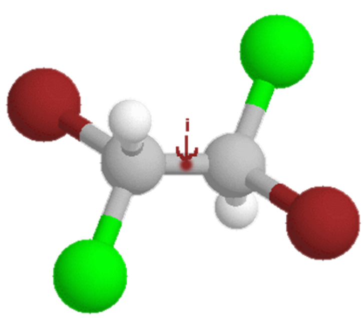

C_i

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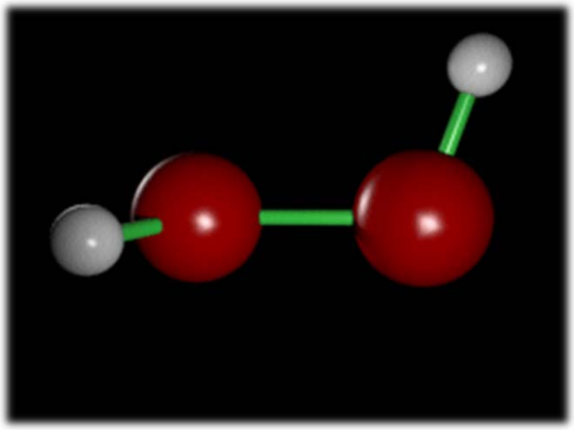
Groups with a single C_n axis

$\{E, C_n, C_n^2, C_n^3 \ldots . C_n^{n-1}\} = C_n$



H_2O_2

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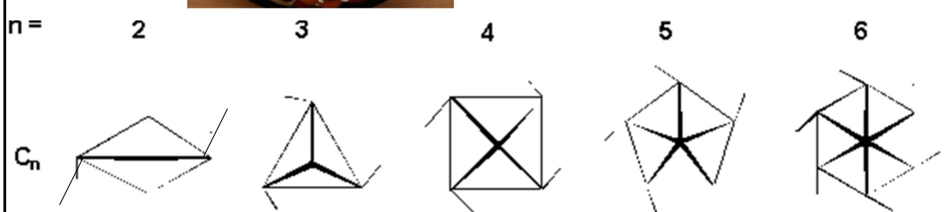
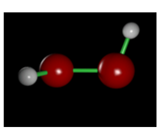
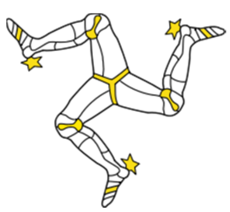
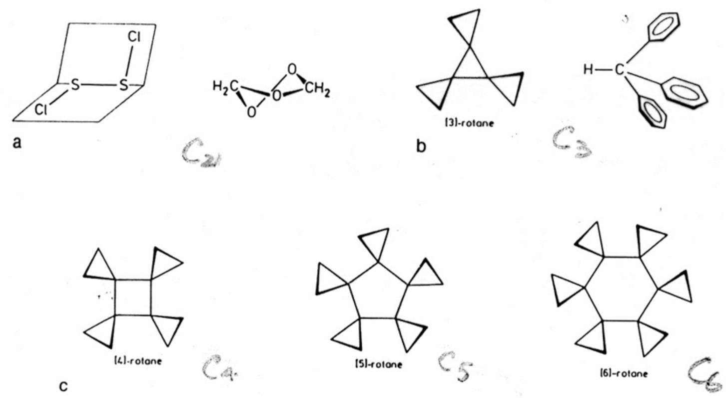
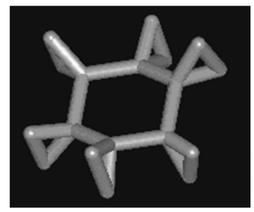




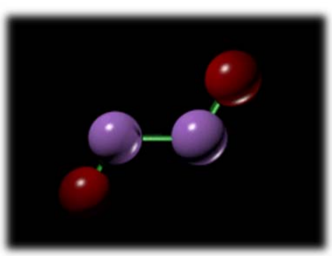


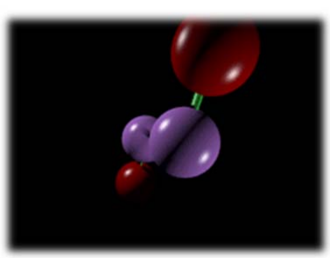




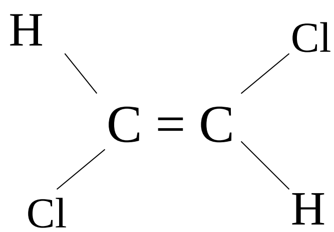
Groups with a single C_n axis plus a perpendicular σ_h plane: C_{nh}

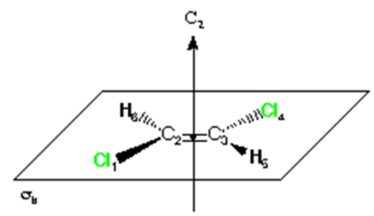
$$N_2O_2^{\,2-} \qquad C_{2h} \qquad \{E, C_2, \sigma_h, i\}$$



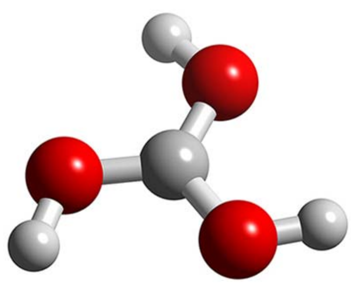


C_{2h} $\{E, C_2, \sigma_h, i\}$





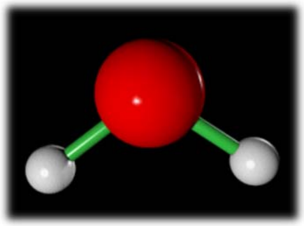
C_{3h} $\{E, C_3, C_3^2, \sigma_h, S_3, S_3^5\}$

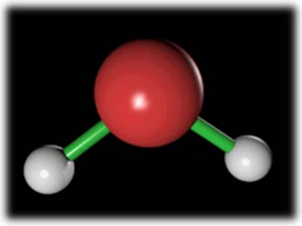


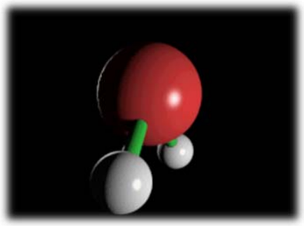
Groups with a single C_n axis plus n vertical σ_v planes: C_{nv}

$$C_{2v} \quad H_2O$$

$$\{E, C_2, \sigma_v, \sigma_{v'}\}$$







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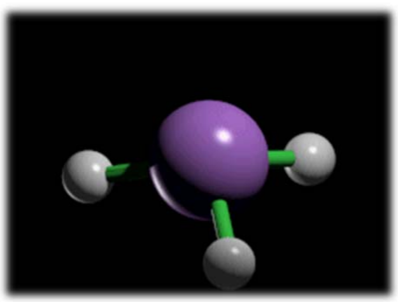
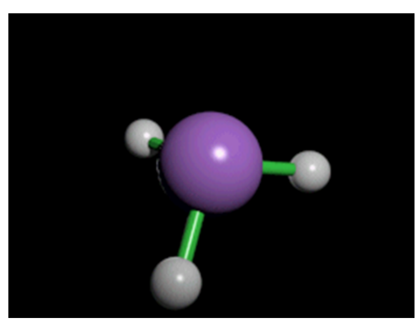
$$C_{3v}$$

$$NH_3 \quad \{E, C_3, C_3^2, \sigma_v, \sigma_{v'}, \sigma_{v''}\}$$

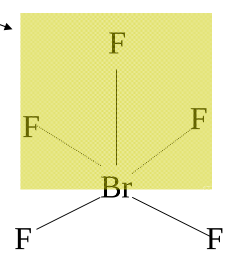




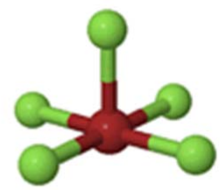
C_{4v}

BrF_5 $\{E, C_4, C_2, C_4^3, \sigma_v, \sigma_{v'}, \sigma_{d,} \sigma_{d'}\}$

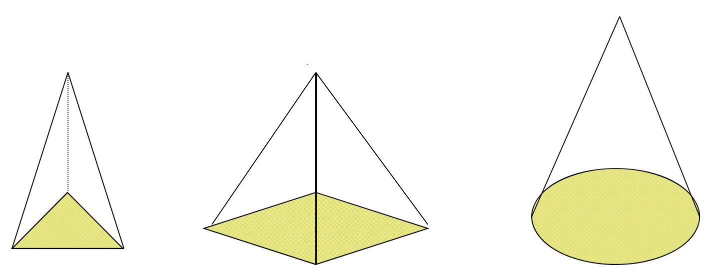
σ_d: dihedral reflection planes (bisects σ_v or C_2)



Square pyramidal



n-gonal pyramidal shape: C_{nv}



$C_{\infty v}$ *HF*

$\{E, C_{\infty}, \ldots \sigma_v \ldots\}$