Lecture 5. Molecular Symmetry

Physical Chemistry 1, Winter 2022

Department of Chemistry

Jiho Son

Seoul National University

Why is symmetry important?

Suppose that a molecule is symmetric under some kind of *symmetry operation*, $\hat{R}$; Hamiltonian of this molecule commutes with $\hat{R}$, $[\hat{H}, \hat{R}] = 0$.

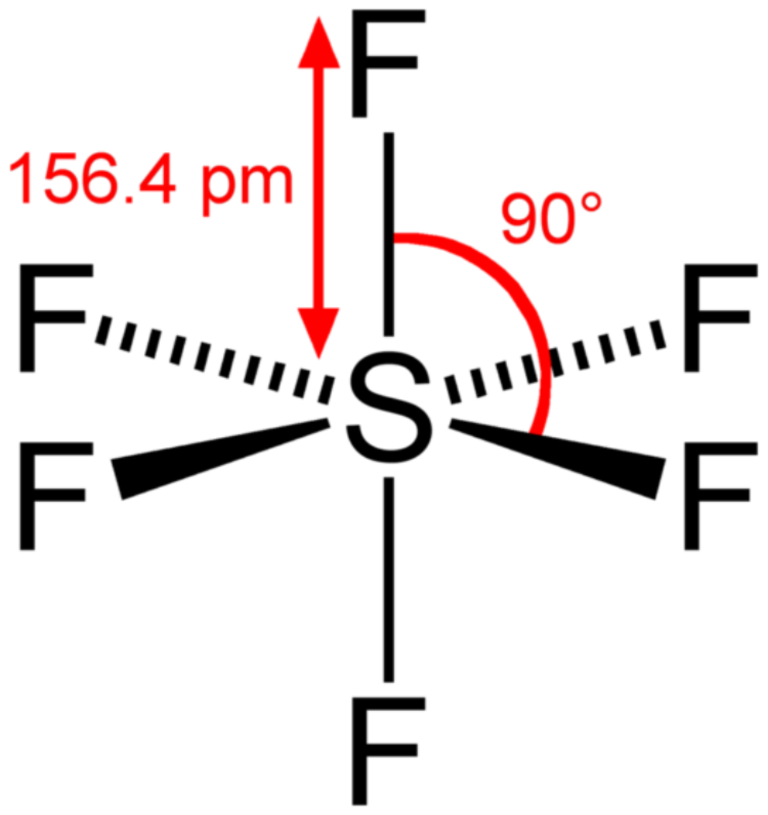
Note that the wavefunction is an eigenfunction of Hamiltonian operator. Since $[\hat{H}, \hat{R}] = 0$, they *share* eigenfunctions.

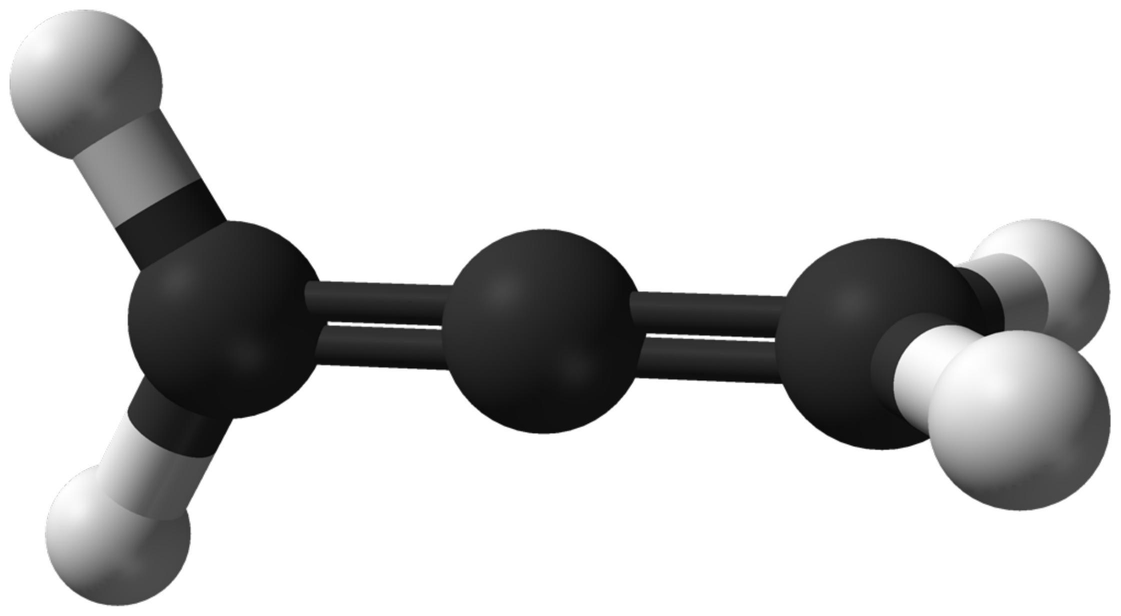
$$\hat{R}\psi = \psi \text{ or } \hat{R}\psi = -\psi$$

In other words, we only consider the wavefunctions (or its linear combinations) that satisfies symmetry condition.

Symmetry operations & symmetry elements

Some molecules possess **symmetry**.





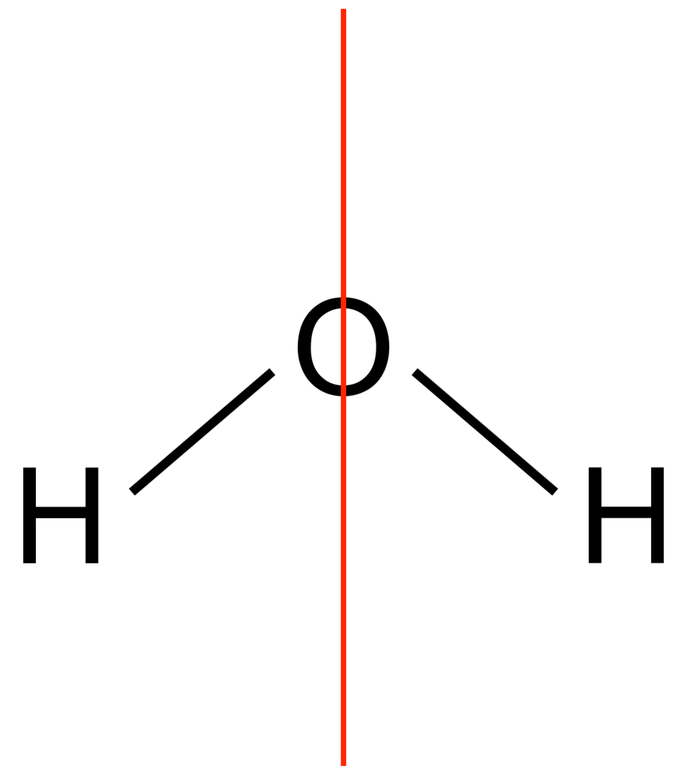
Symmetry operations & symmetry elements

The symmetry of molecules can be described by symmetry *elements*. There are symmetry *operations* related to each symmetry elements.

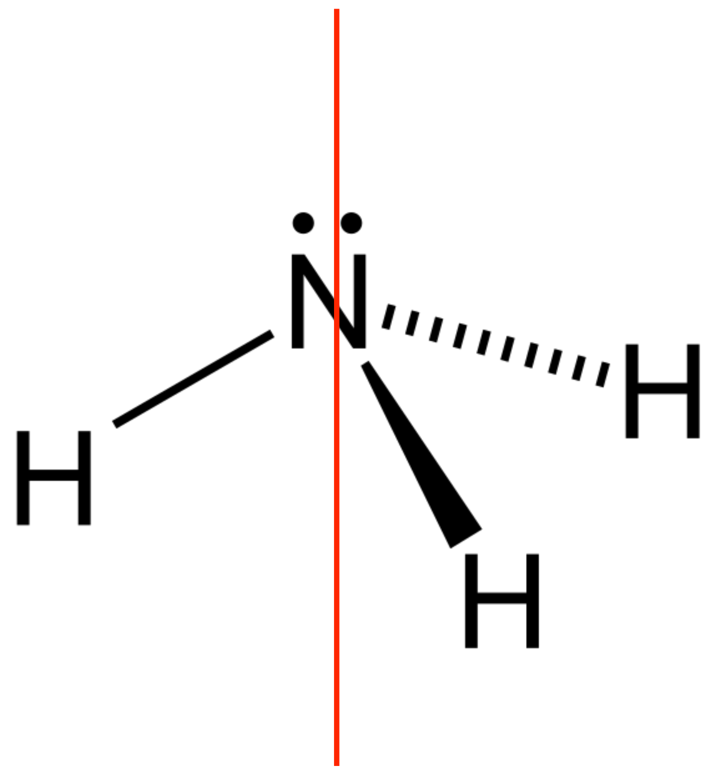
TABLE 12.1
The five symmetry elements and their associated operators.

Symmetry elements		Symmetry operations	
Symbol	Description	Symbol	Description
E	Identity	$\hat{E}$	No change
C_n	n-Fold axis of symmetry	$\hat{C}_n$	Rotation about the axis by $360^\circ/n$
σ	Plane of symmetry	$\hat{\sigma}$	Reflection through the plane
i	Center of symmetry	$\hat{i}$	Reflection through the center
S_n	n-Fold rotation-reflection axis of symmetry, also called an improper rotation	$\hat{S}_n$	Rotation about the axis by $360^\circ/n$ followed by reflection through a plane perpendicular to the axis

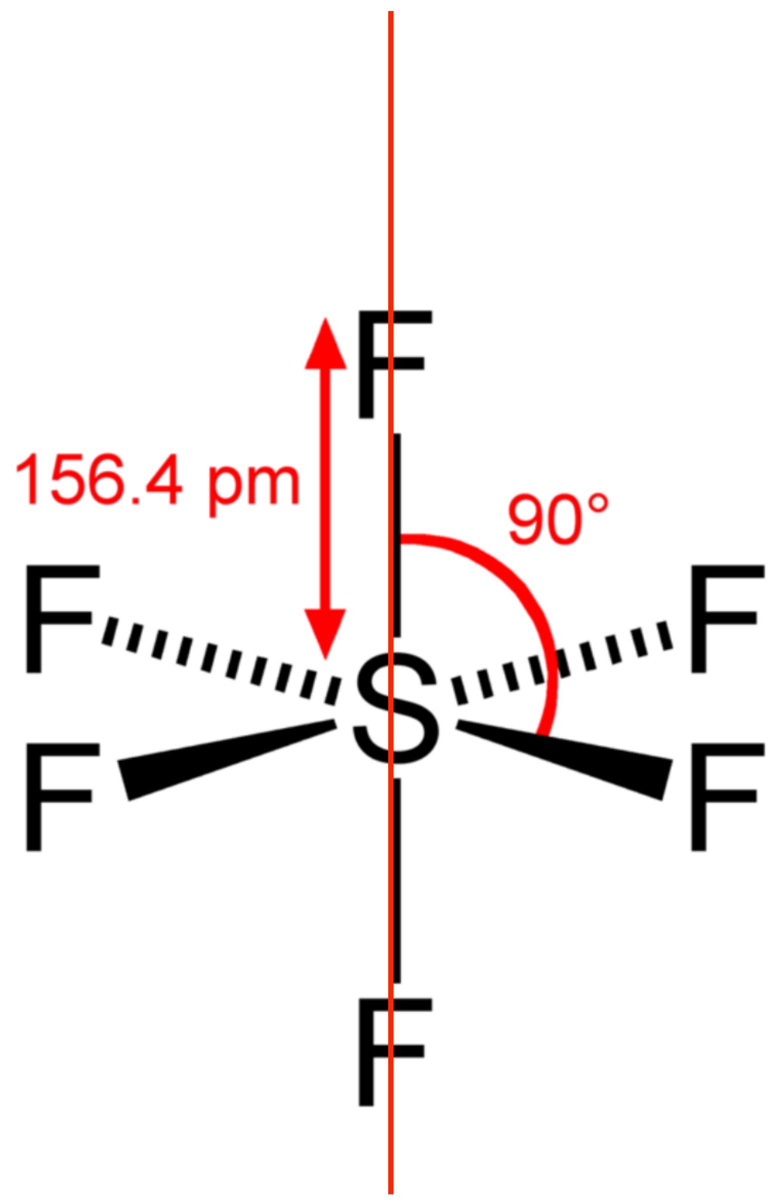
Axis of symmetry (C_n)



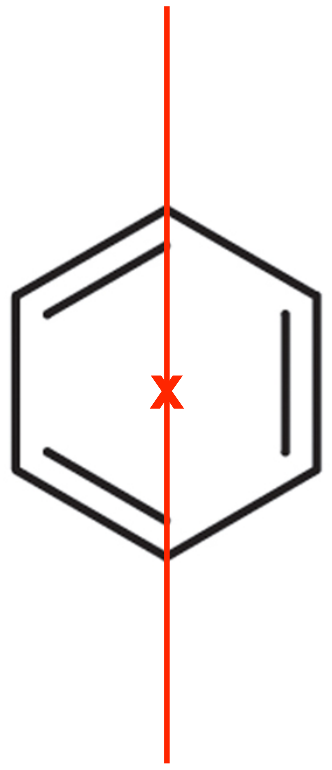
C_2



C_3



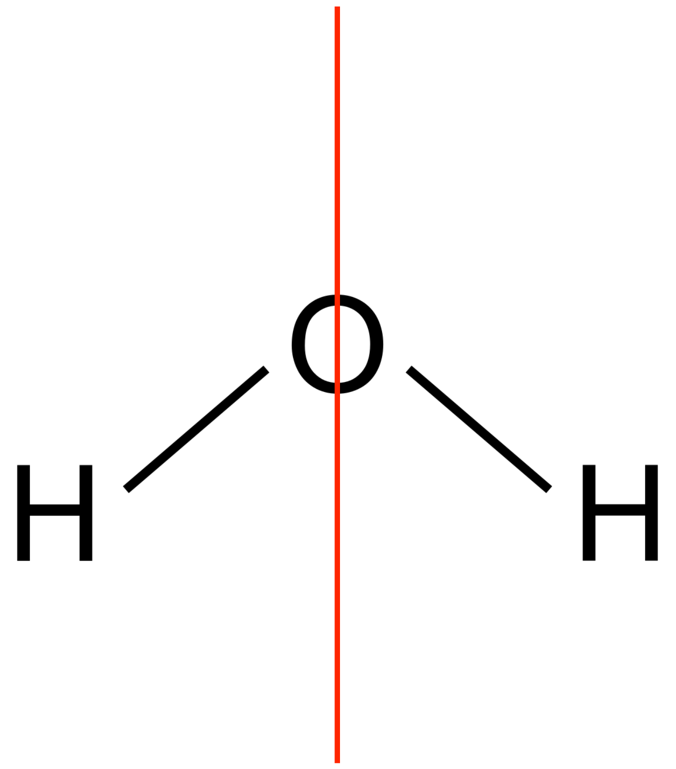
C_4, C_2



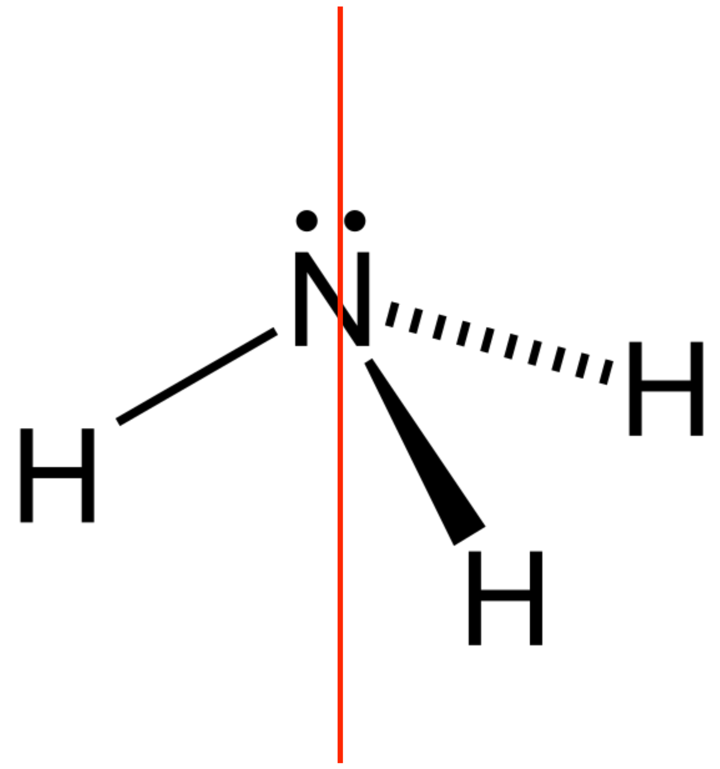
C_6, C_2

Plane of symmetry (σ)

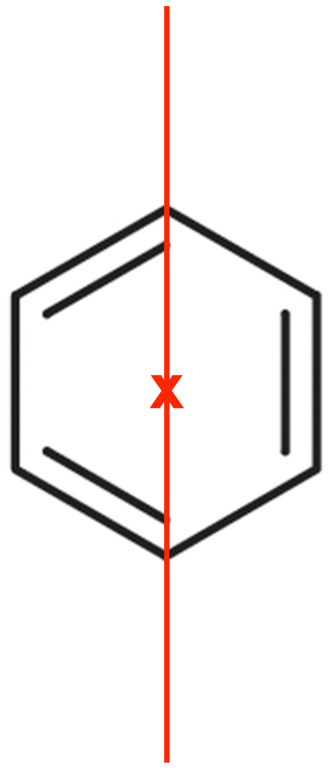
There are three types of symmetry planes: vertical (v), horizontal (h), dihedral (d). If a plane of symmetry bisects the angle between two C_2 axis which are perpendicular to main axis, it is called dihedral.



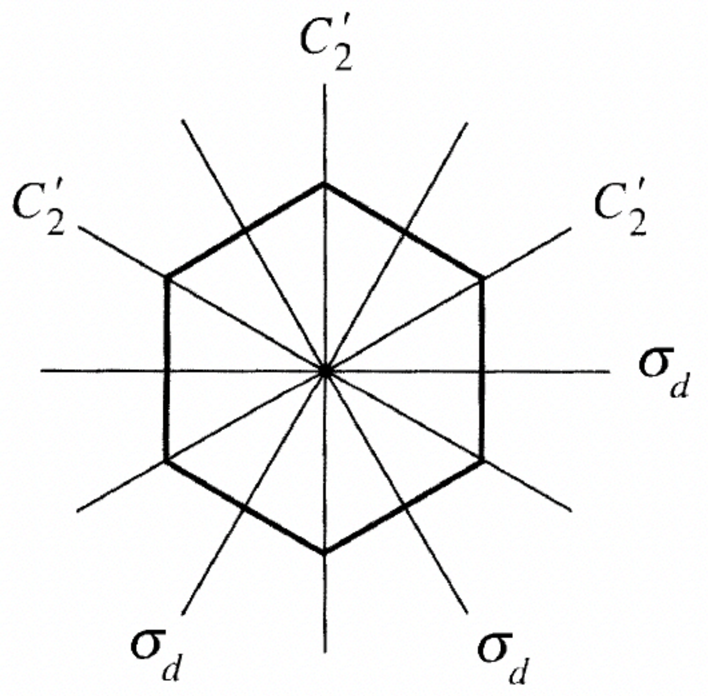
$2\,\sigma_v$



$3\,\sigma_v$

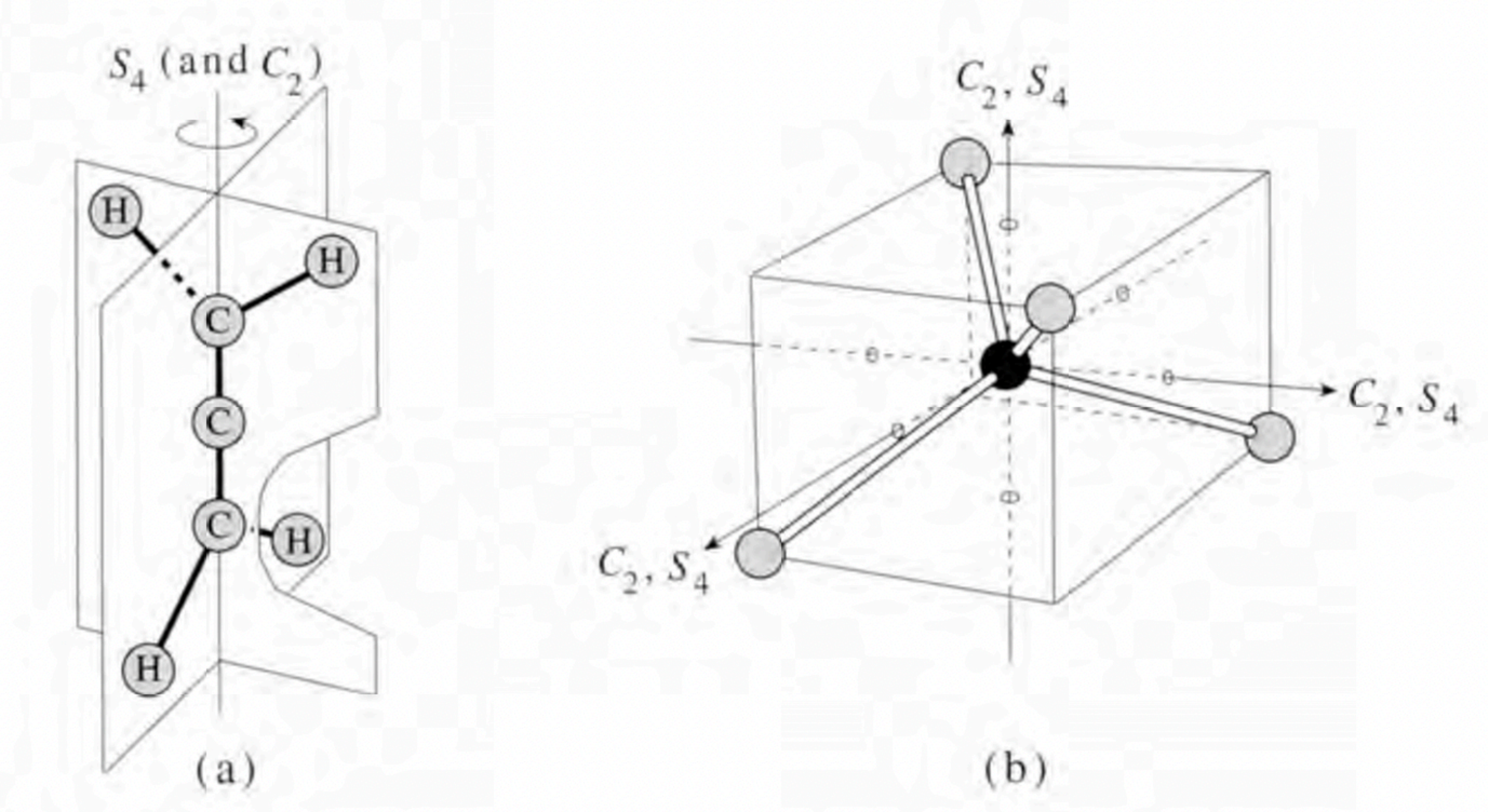


$\sigma_v, \sigma_h, \sigma_d$



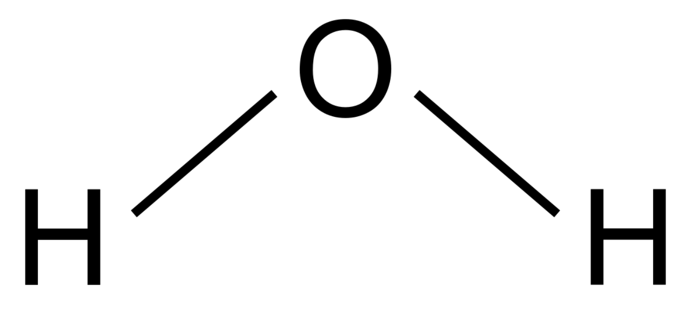
Inversion symmetry (i) and improper rotation (S_n)

Improper rotation is a composition of C_n and σ_h.



Symmetry elements

These symmetry elements that belong to certain molecule, have special mathematical relations that we can exploit. They form a **group**, a special mathematical entity.

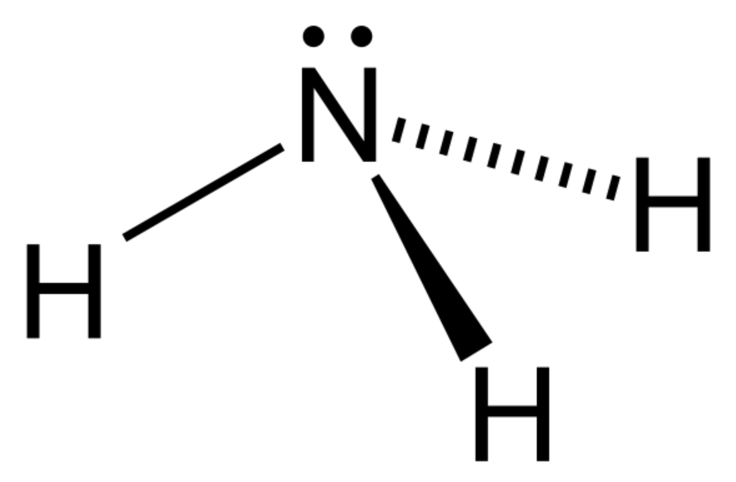


For example, water molecule has following symmetry elements:

E (identity), C_2 axis, two σ_v planes. These symmetry elements has mathematical relations. Actually, they belong to C_{2v} symmetry group.

Similarly, ammonia molecule has following symmetry elements:

E (identity), C_3 axis, three σ_v planes. Ammonia molecule belongs to C_{3v} symmetry group.



Math: Group

To define a group, we need a *set* and *binary operation*, which is called **group multiplication**.

Definition. For a set G and binary operation $*$, $(G, *)$ is a group if it satisfies following conditions.

1. The set is *closed* under group multiplication $*$. (The product of any two elements is in the set)

2. $\forall a, b, c \in G \ a(bc) = (ab)c$ (associative law holds)

3. $\forall a \in G \ \exists e \in G \ \mathrm{s.t.} \ ea = ae = e$ (existence of identity)

4. $\forall a \in G, \exists a^{-1} \in G \ \mathrm{s.t.} \ aa^{-1} = a^{-1}a = e$ (existence of inverse element)

Math: Group

Group multiplication is not always commutative.

Group with commutative multiplication is called **Abelian group**.

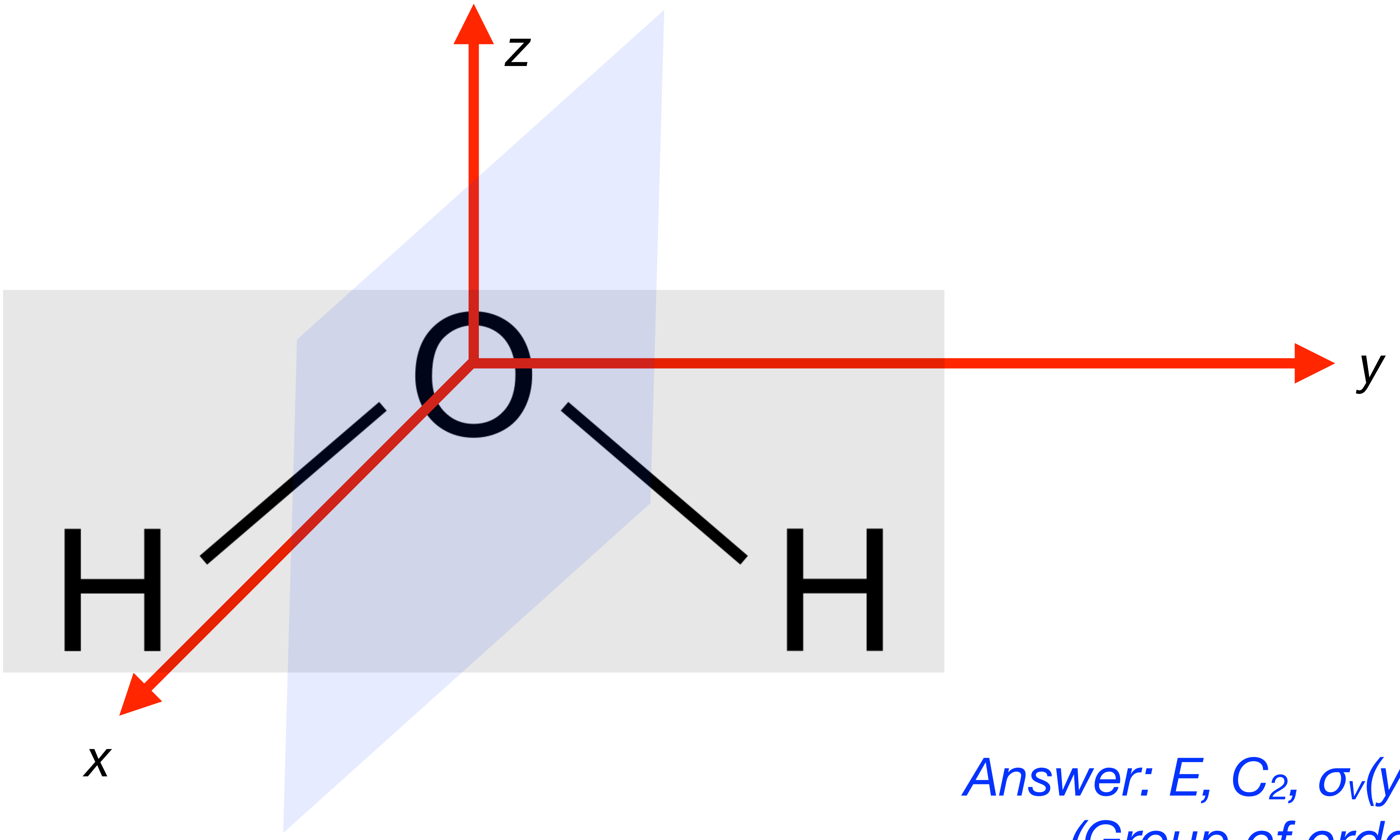
If a subset of a group satisfies conditions 1~4 about the “inherited” group multiplication, it is called a **subgroup** of the original group.

Number of group elements is called a **group order**.

Example: water molecule

Let's find all symmetry elements of water molecule.

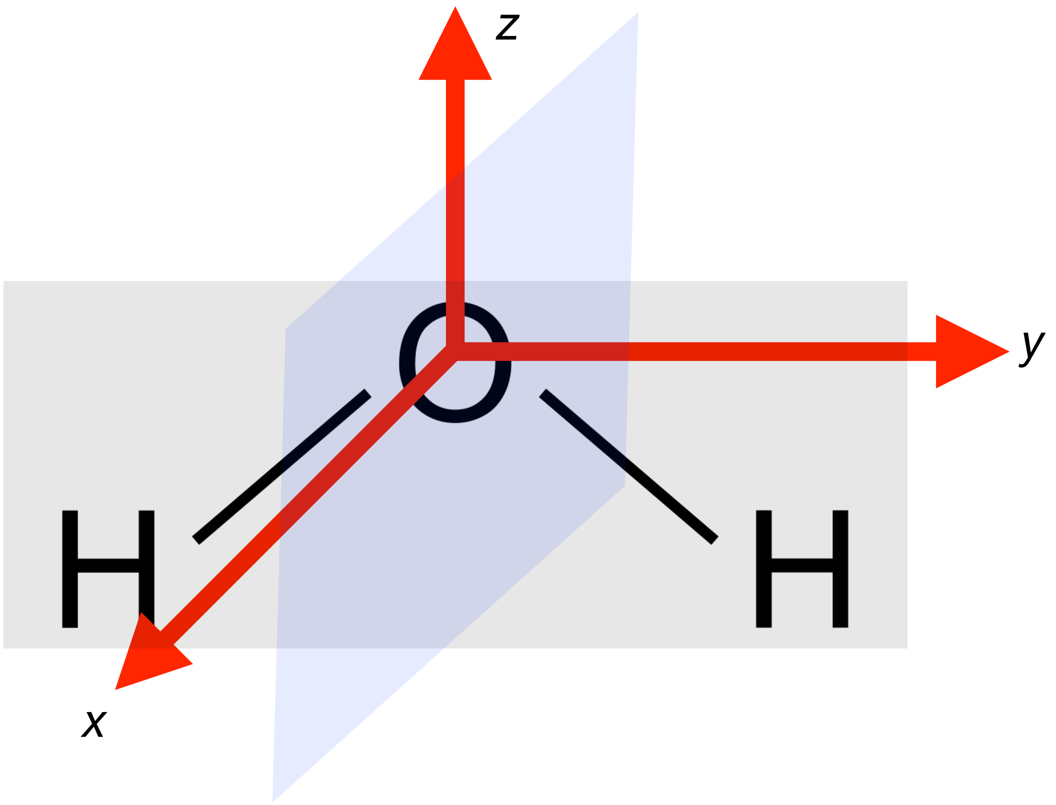
The molecule lies on yz-plane



Answer: E, C_2, $\sigma_v(yz)$, $\sigma_v(xz)$
(Group of order 4)

Example: water molecule

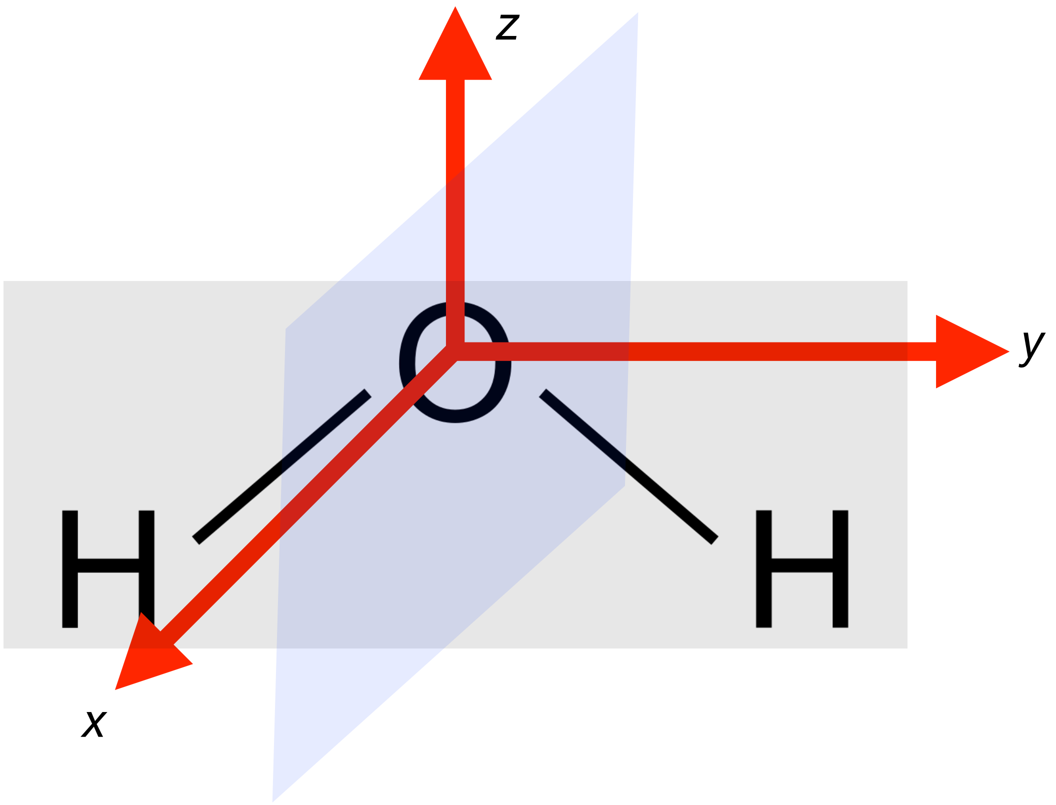
Let's construct **group multiplication table**.



*	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
E	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
C_2	C_2			
$\sigma_v(yz)$	$\sigma_v(yz)$			
$\sigma_v(xz)$	$\sigma_v(xz)$			

Example: water molecule

Let’s construct **group multiplication table**.

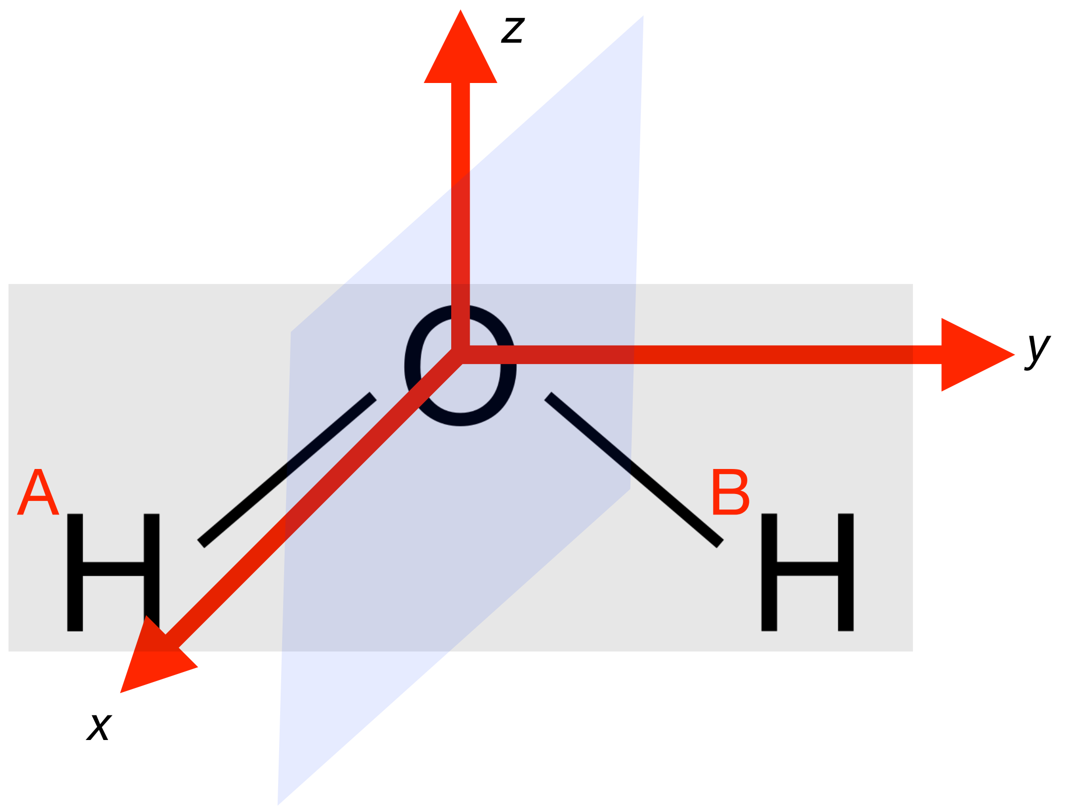


*	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
E	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
C_2	C_2	E	$\sigma_v(xz)$	$\sigma_v(yz)$
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	E	C_2
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	C_2	E

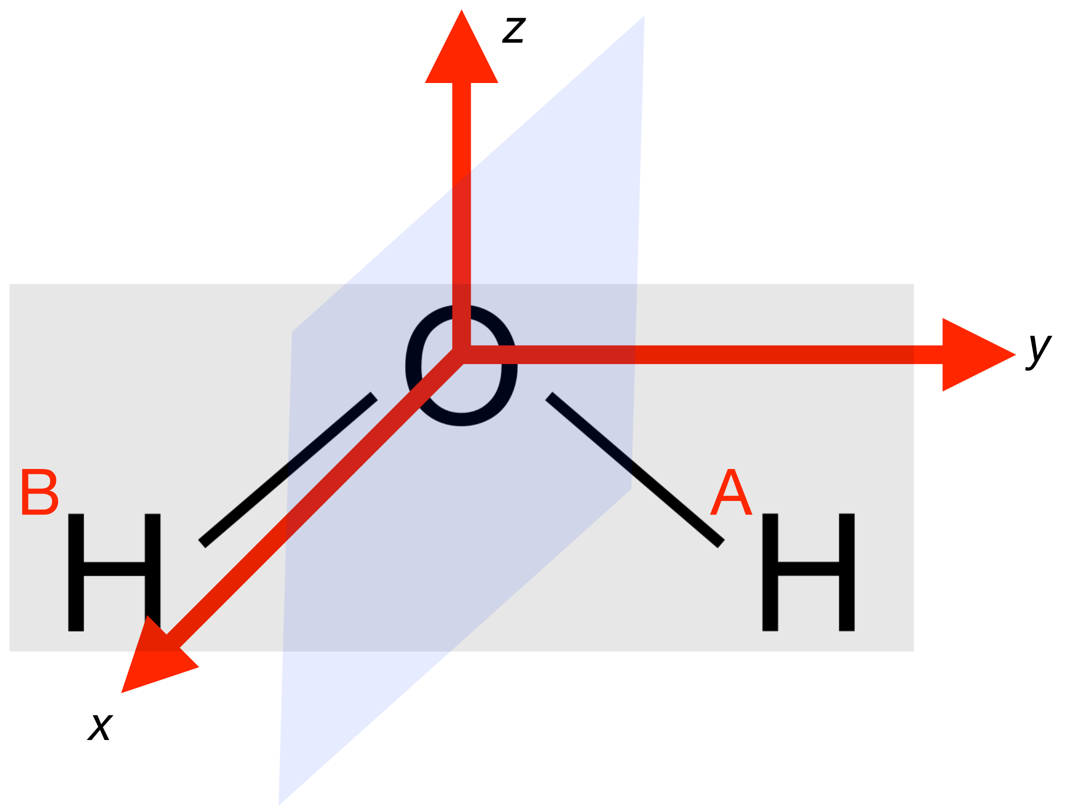
Example: water molecule

Let's construct **group multiplication table**.

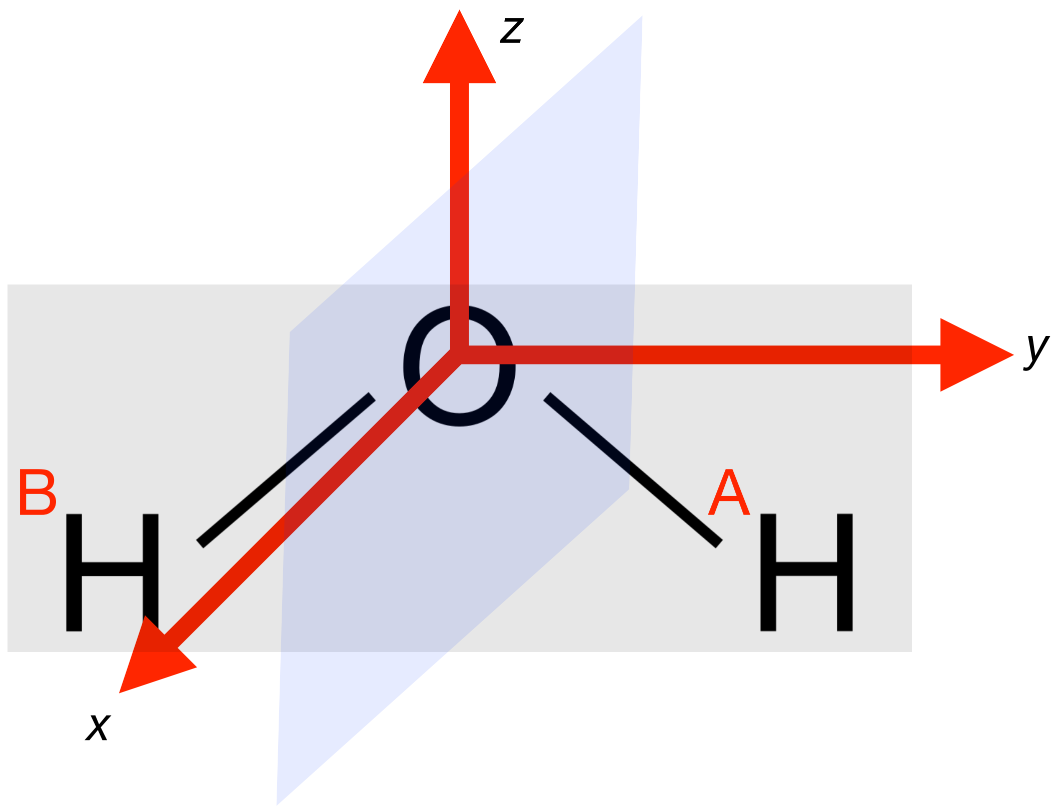
$\sigma_v(yz) * C_2$



$= \sigma_v(yz)$



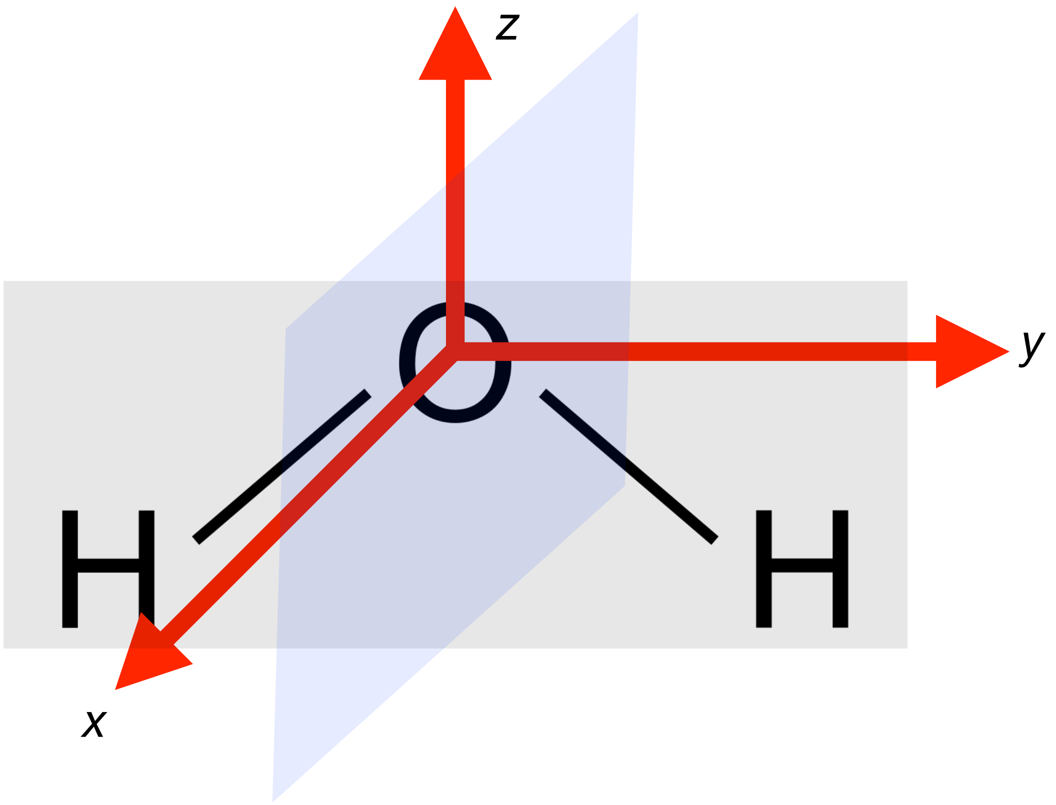
$=$



(equivalent to $\sigma_v(xz)$)

Example: water molecule

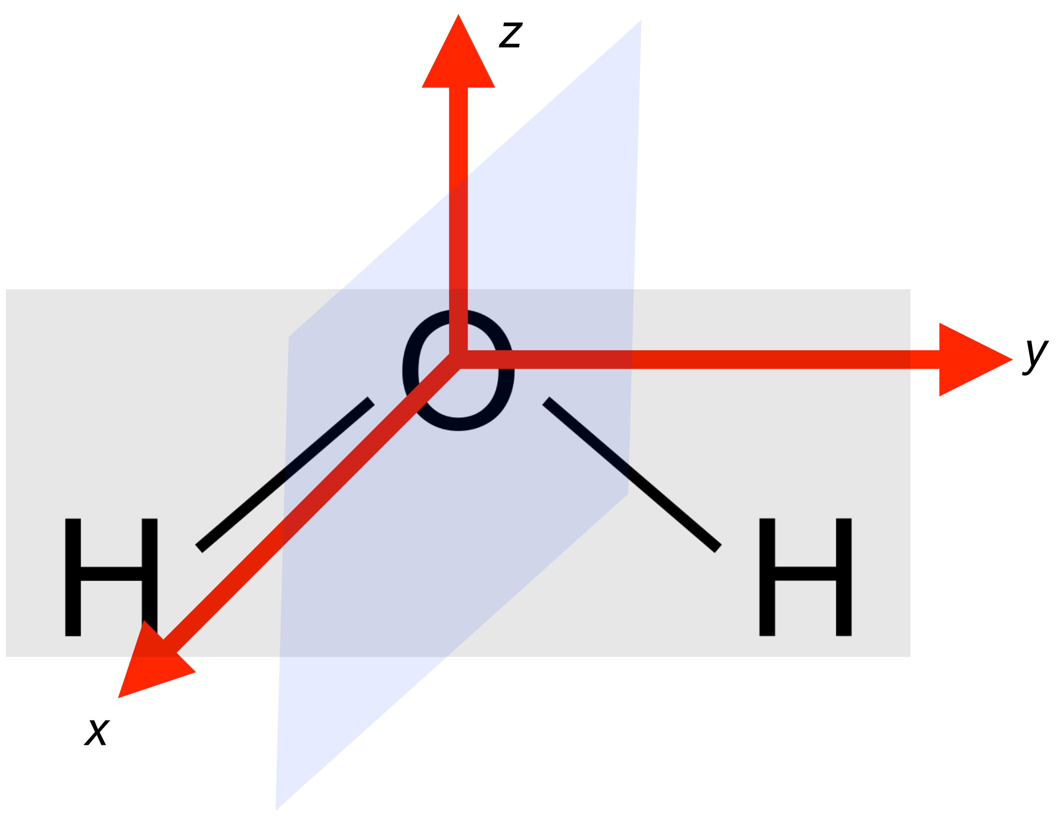
Note that each group element emerges once in the row or column of the table. (Rearrangement theorem)



*	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
E	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
C_2	C_2	E	$\sigma_v(xz)$	$\sigma_v(yz)$
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	E	C_2
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	C_2	E

Group representation

Each symmetry element can be described as **matrices**.



$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

These matrices are one way of representing C_{2v} group. Does simpler representation exist?

Block diagonalization

Matrix is in **block-diagonalized form** if

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_1 & 0 & \cdots & 0 \\ 0 & \mathbf{A}_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \mathbf{A}_n \end{bmatrix}$$

We can block-diagonalize 4 matrices simultaneously. In this case, they are already in block-diagonal form.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character

Character of a matrix is a sum of diagonal elements. For 1 by 1 matrix, character is identical to its only element.

One can represent these matrices with the characters of block-diagonalized matrices.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$	
Γ_1	1	-1	-1	1	x
Γ_2	1	-1	1	-1	y
Γ_3	1	1	1	1	z

Character

We say that these 3 by 3 matrix representation, which can be factored out (can be made simpler) are **reducible**. These are **reducible representation** of C_{2v} group.

Meanwhile, block-diagonalized form (which is diagonalized form in this case) cannot be reduced further. These are **irreducible representation (irrep)** of C_{2v} group.

Irreducible representations are the most simpler ones. Hence, we aim to find irreducible representations.

There are a few mathematical laws that help us to find irreducible representations, but we do not prove them here. Let's just embrace them and find irreducible representations.

Irreducible representations of C_{2v}

Basically, to find the irreducible representations, we need to find reducible representation (which is easy to do), and block-diagonalize it.

We gather all irreducible representations into the **character table**. This table will contain all information about the point group that the molecule belongs to.

Law 1. Number of the irreps = Order of the group. Since order of C_{2v} group is 4, we missed one irrep.

	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
Γ_1	1	-1	-1	1
Γ_2	1	-1	1	-1
Γ_3	1	1	1	1

Irreducible representations of C_{2v}

$\boxed{\textbf{Law 2.}\text{ Sum of the squares of the } \chi(E) \text{ is equal to the order of the group.}}$ Therefore

$$[\chi_{\Gamma_1}(E)]^2 + [\chi_{\Gamma_2}(E)]^2 + [\chi_{\Gamma_3}(E)]^2 + [\chi_{\Gamma_4}(E)]^2 = 4$$

	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
Γ_1	1	-1	-1	1
Γ_2	1	-1	1	-1
Γ_3	1	1	1	1
Γ_4	1			

Irreducible representations of C_{2v}

Law 3. Sum of the squares of the given irrep equals to the order of the group.

$$[\chi_{\Gamma_4}(E)]^2 + [\chi_{\Gamma_4}(C_2)]^2 + [\chi_{\Gamma_4}(\sigma_v(yz))]^2 + [\chi_{\Gamma_4}(\sigma_v(xz))]^2 = 4$$

Law 4. Irreps are orthogonal (taking inner product of two rows of the character table gives 0).

$$\sum_{R \in C_{2v}} \chi_i(R)\chi_j(R) = 0$$

	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
Γ_1	1	-1	-1	1
Γ_2	1	-1	1	-1
Γ_3	1	1	1	1
Γ_4	1	1	-1	-1

Irreducible representations of C_{2v}

Now we have character table of C_{2v} group.

	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
B_2	1	-1	-1	1
B_1	1	-1	1	-1
A_1	1	1	1	1
A_2	1	1	-1	-1

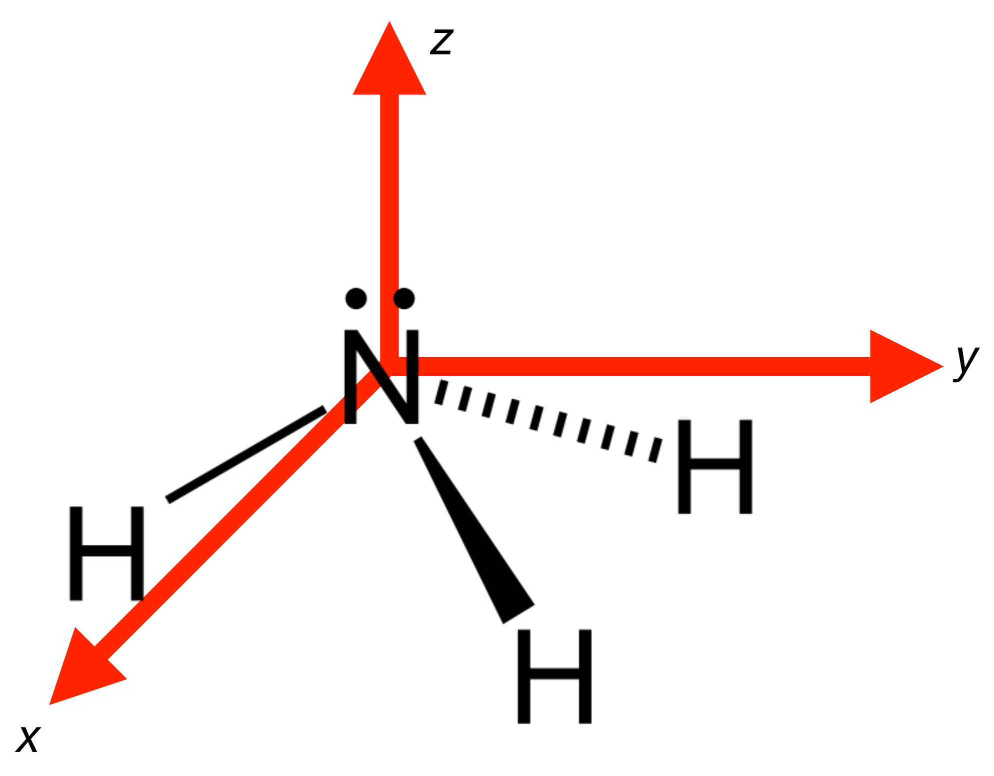
Nomenclatures.

1. A or B? - If symmetric for rotation about the main axis, A.

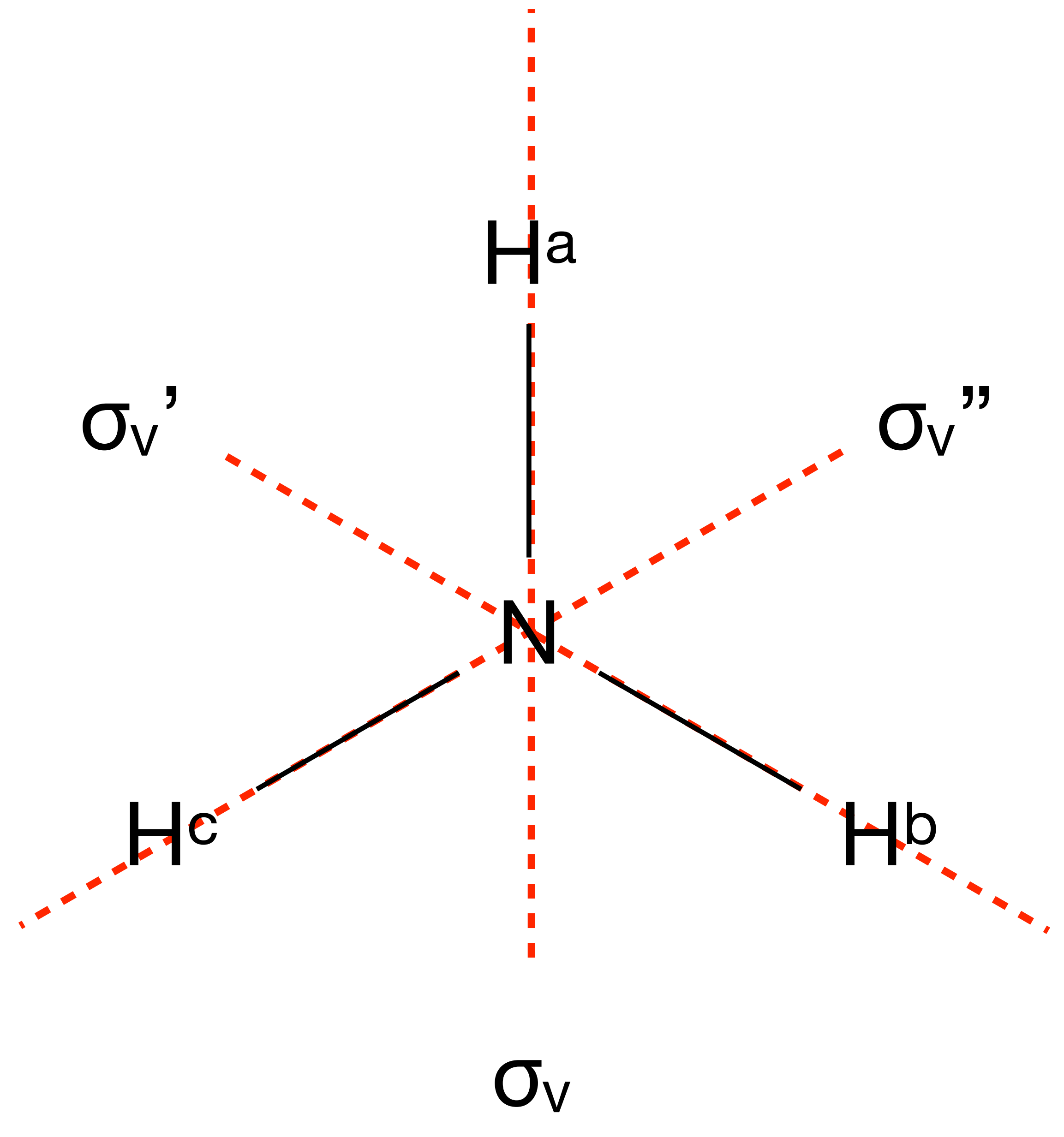
2. 1 or 2? - If symmetric for the vertical reflection, 1.

Irreducible representations of C_{3v}

Let's move on. Ammonia molecule belongs to C_{3v} point group.

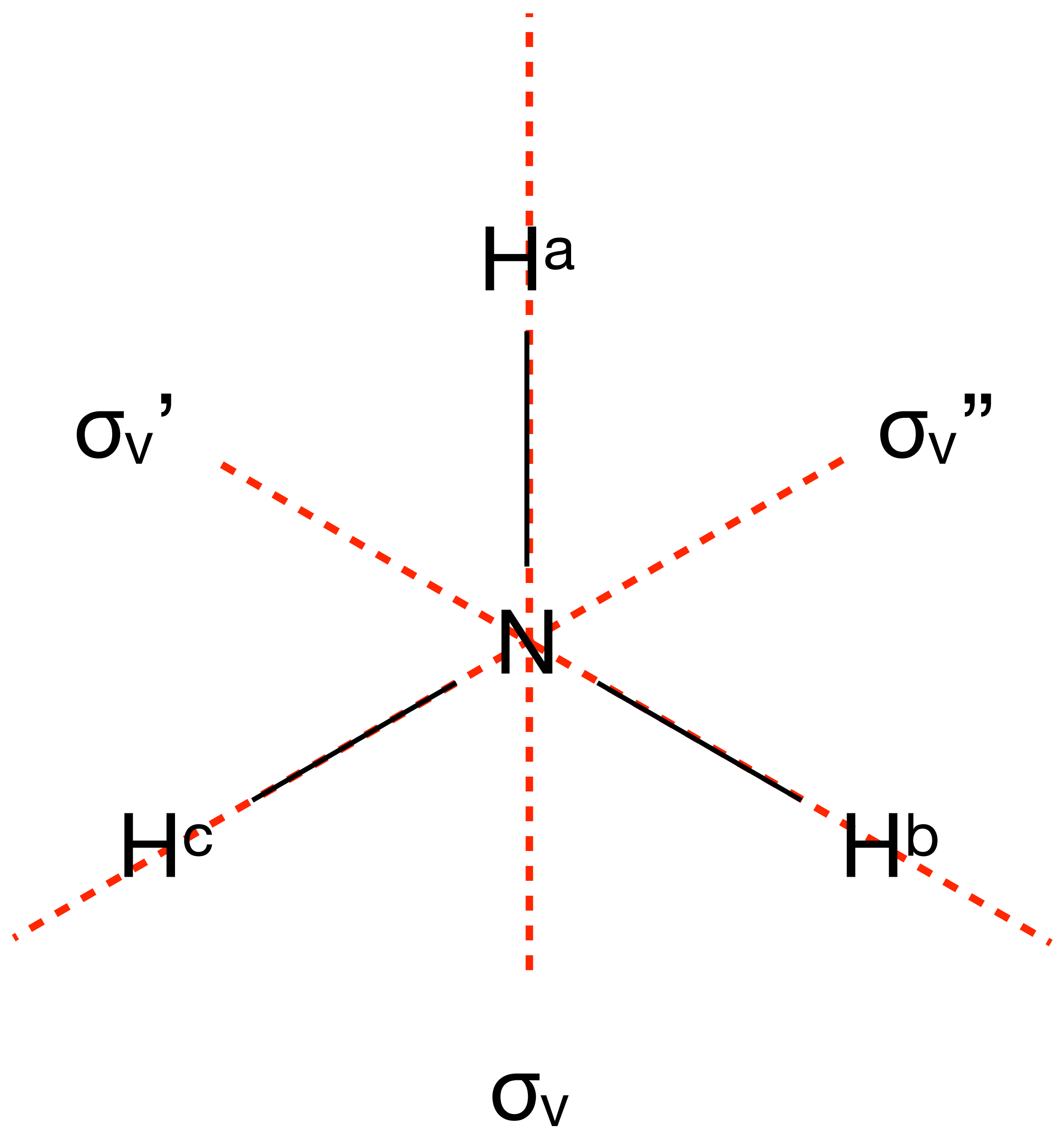


This molecule has C_3 axis and three vertical mirror planes.



Irreducible representations of C_{3v}

Let's find the 3 by 3 matrix representation in this basis.



$$\hat{E}\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

$$\hat{\sigma}_v\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}a\\c\\b\end{bmatrix}=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

$$\hat{C}_3\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}c\\a\\b\end{bmatrix}=\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

$$\hat{\sigma}_v'\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}c\\b\\a\end{bmatrix}=\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

$$\hat{C}_3^2\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}b\\c\\a\end{bmatrix}=\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

$$\hat{\sigma}_v''\begin{bmatrix}a\\b\\c\end{bmatrix}=\begin{bmatrix}b\\a\\c\end{bmatrix}=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}\begin{bmatrix}a\\b\\c\end{bmatrix}$$

Irreducible representations of C_{3v}

Note.

1. Order of C_{3v} group is 6.

2. C_3 and C_3^2 belong to the same **class**.

3. σ_v, σ_v' and σ_v'' belong to the same class, too. In character table, symmetry elements within same class have same character.

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1

Irreducible representations of C_{3v}

These matrices are clearly not block-diagonalized.

Block diagonalization can be done via **similarity transformation**.

$$A = X^{-1}BX$$

$$X = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{bmatrix}$$

We will not go deeper in linear algebra stuff, so let's just assume it.

Irreducible representations of C_{3v}

Block-diagonalized matrices are

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{bmatrix} \qquad C_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \sigma_v' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 1/2 \end{bmatrix} \qquad \sigma_v'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & 1/2 \end{bmatrix}$$

Note that the elements in same class have same character.

Three classes, so we need three irreducible representations.

Irreducible representations of C_{3v}

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{bmatrix} \qquad C_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \sigma_v' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 1/2 \end{bmatrix} \qquad \sigma_v'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & 1/2 \end{bmatrix}$$

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
E	2	-1	0

Irreducible representations of C_{3v}

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{bmatrix} \qquad C_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \sigma_v' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 1/2 \end{bmatrix} \qquad \sigma_v'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & 1/2 \end{bmatrix}$$

(Law 2)

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
	1		
E	2	-1	0

Irreducible representations of C_{3v}

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{bmatrix} \qquad C_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \sigma_v' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 1/2 \end{bmatrix} \qquad \sigma_v'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & 1/2 \end{bmatrix}$$

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

(Law 3 & 4)

Conclusion

We have limited time, so we cannot explore the world of representation theory and its application.

However, these mathematical relations really get involved when it comes to molecular orbital theory.

Maybe you can find more details in *Inorganic Chemistry 1* course.

References of this lecture

If you are interested in serious group theory applied in this field,

Tinkham, M. *Group Theory and Quantum Mechanics.*; Dover Publications, 2003.

Atkins' Physical Chemistry textbook is always your companion, even though I do not mention it.