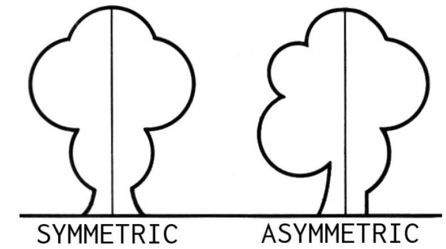
LECTURE 3: SYMMETRY

- **Greek ”*symmetrein*” (= commensurate, yhteismitallinen)**
- **Symmetry elements & operations**
- **Molecular symmetry**
- **Point groups**

SYMMETRY

- Some people see beauty in symmetry, some in asymmetry
- Symmetry is also common in nature



Kuva: Pearson Scott Foresman

IN CHEMISTRY ...

MOLECULAR SYMMETRY

Important for understanding/explaining/classification

- **Molecule structures**
- **Crystal structures**
- **Quantum chemistry**
- **Spectroscopy (IR, Raman)**
- **Material properties, e.g. piezoelectricity**

SYMMETRY OPERATION

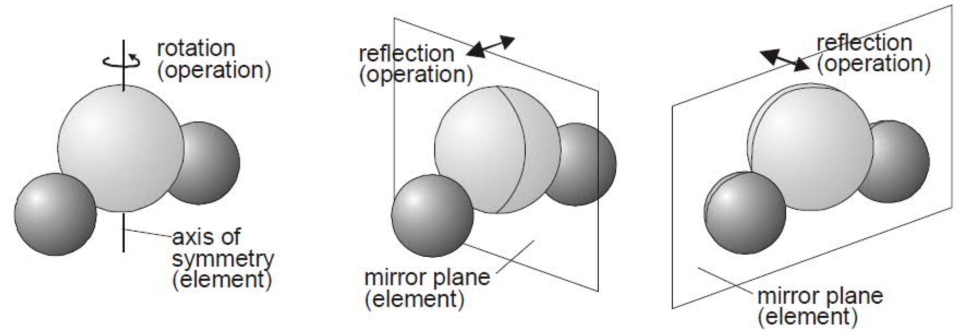
Operation that generates the same representation of an object (molecule)

SYMMETRY ELEMENT

Each symmetry operation has a corresponding symmetry element (point, axis, plane) about which the operation takes place

MOLECULAR SYMMETRY
Operations & Elements

(historical Schönflies notation; used also in spectroscopy)



Molecular symmetry: at least one point remains unchanged

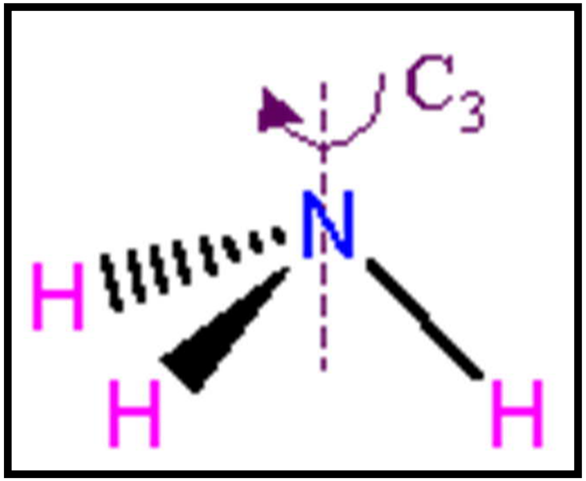
- **Identity (E; *German Einheit*):** No change; every molecule has E
- **Rotation axis (C_n):** Rotation by 360º/n (n = 1, 2, 3, …) about an axis, which leaves the molecule unchanged
- **Symmetry or mirror plane (σ):** Plane through which reflection leaves the molecule unchanged:

  σ_v: vertical mirror plane (in relation to rotation axis)

  σ_h: horisontal mirror plane (in relation to rotation axis)
- **Center of symmetry (i):** center through which inversion leaves the molecule unchanged
- **Improper rotation (or rotary-reflection) axis (S_n):** Rotation about an axis by 360°/n, followed by reflection in a plane perpendicular to the axis. Note: $S_1 = \sigma$; $S_2 = i$

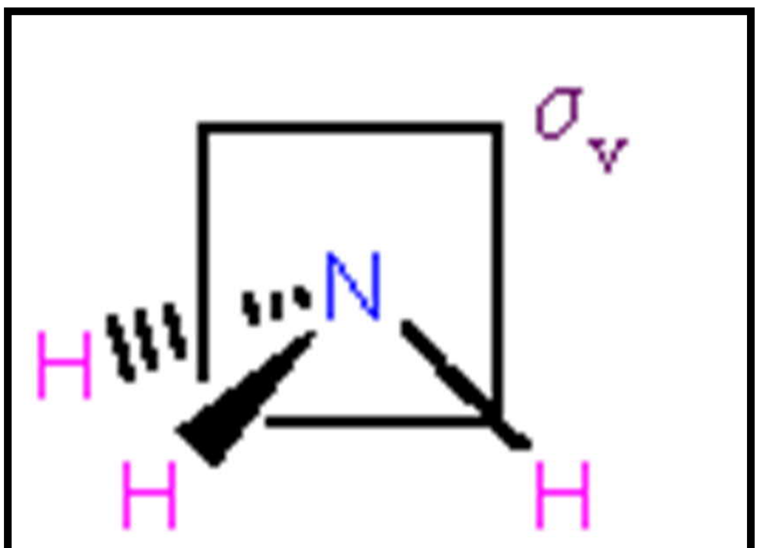
Proper: Can be actually done on a molecule: E, C_n

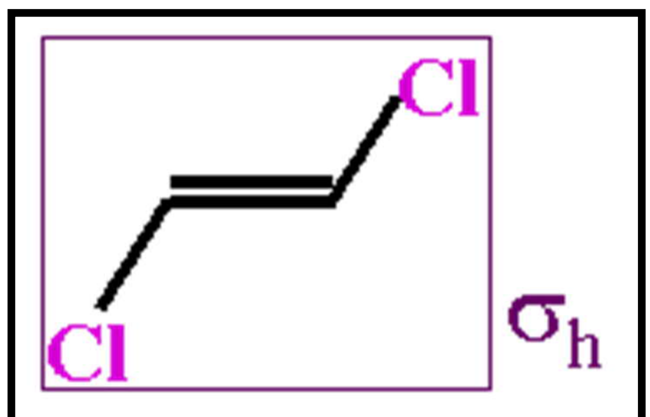
Improper: Can be only imagined, not done: σ, I, S_n
(drastic chemical bond rearrangements)

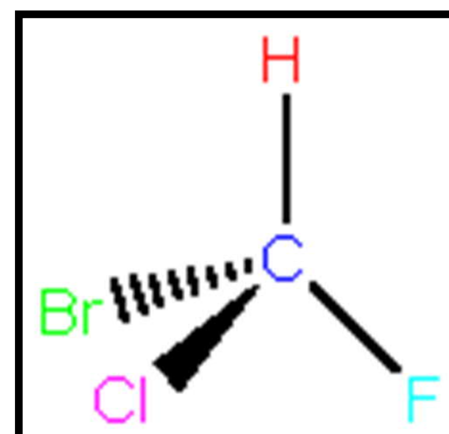

C3
N
H
H
H


C5

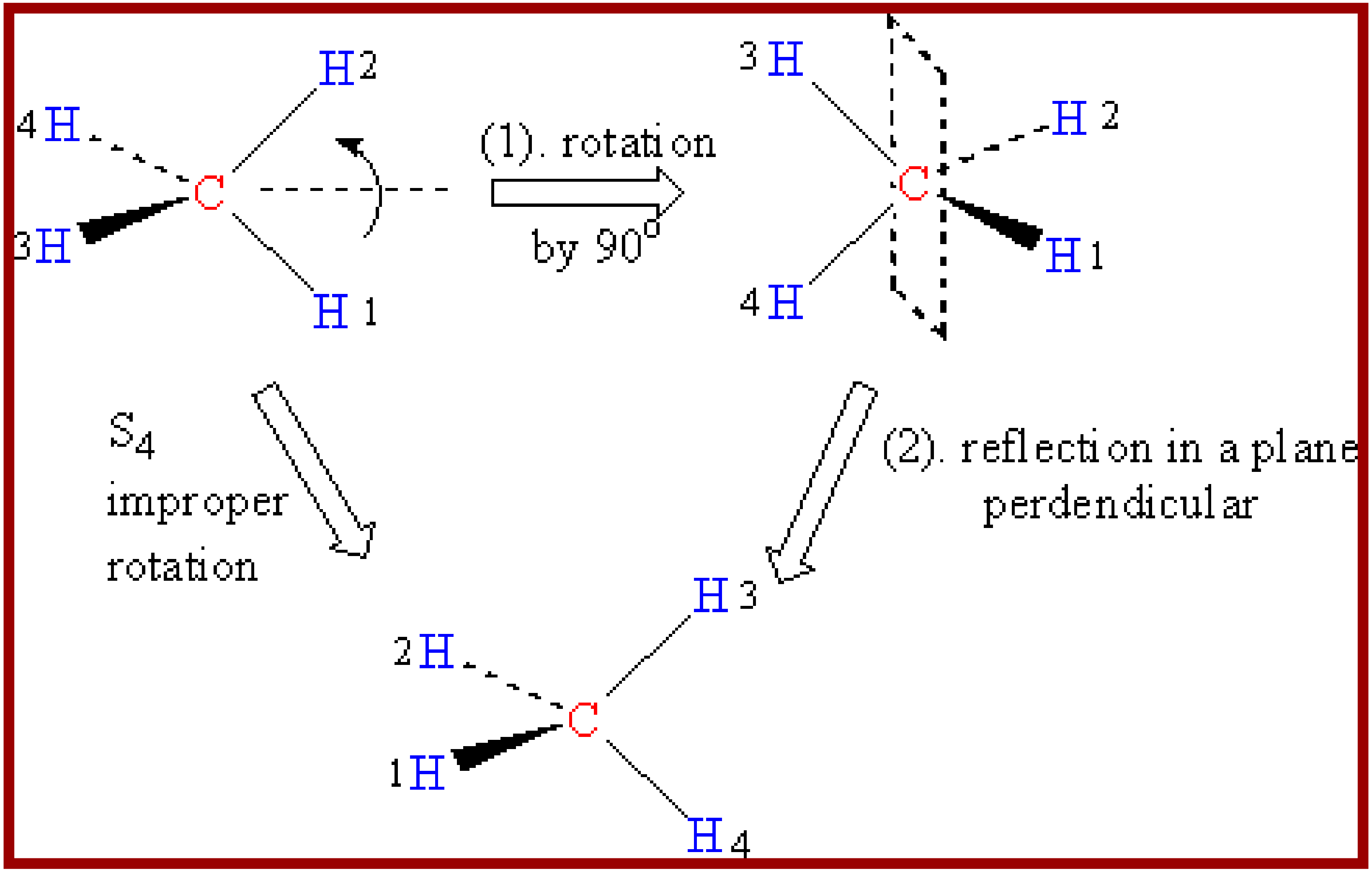

O
C
O
Invert through
centre
O
C
O

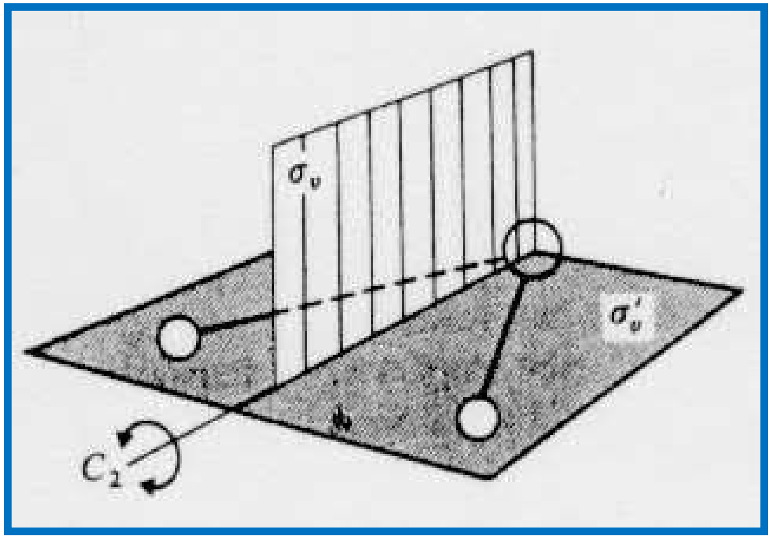

σv
N
H
H
H


Cl
Cl
σh

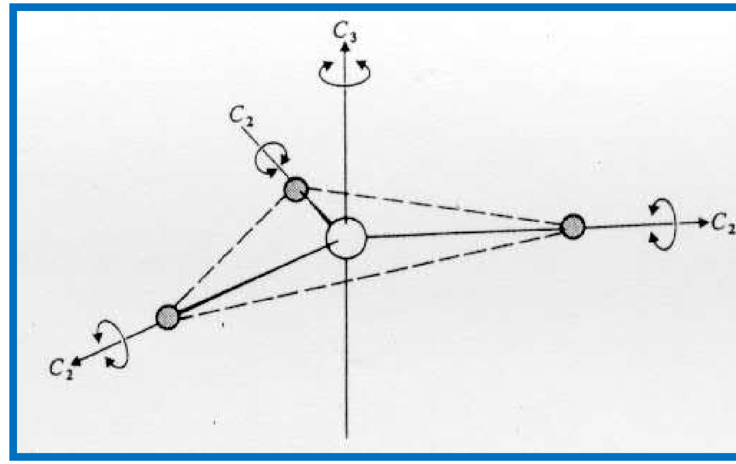

H
C
Br
Cl
F

Rotary-reflection: CH_4



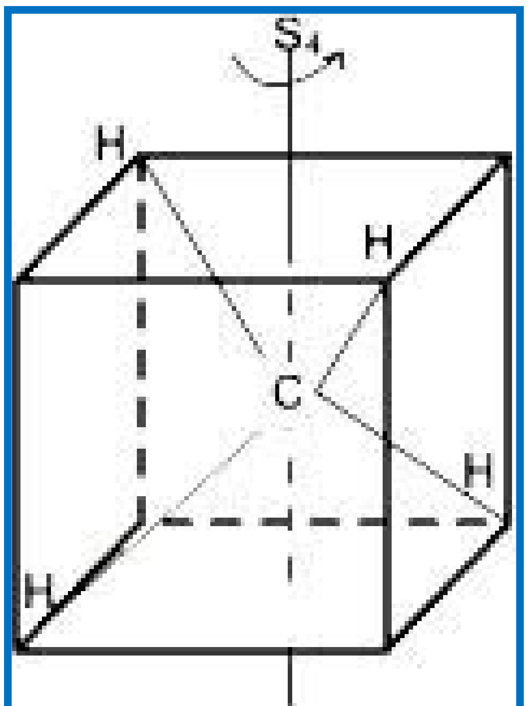


H_2O

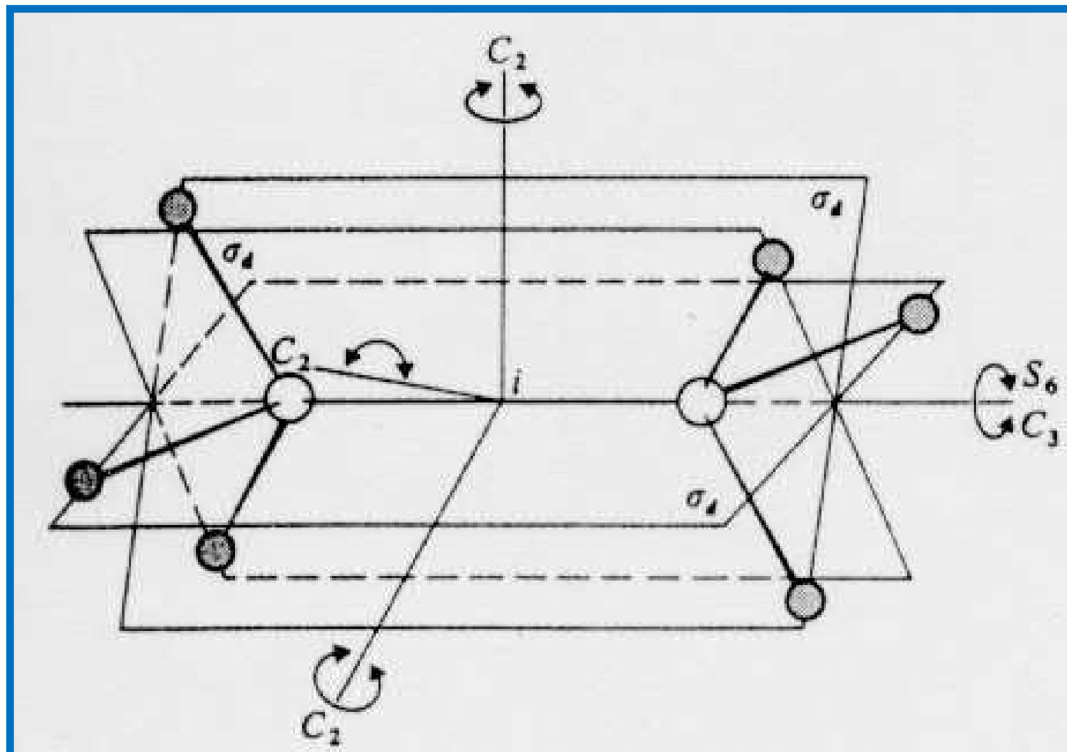


BF_3

CH_4



Ethane (staggered): CH_3-CH_3



POINT GROUP

- Summarizes all the symmetry operations that can be performed on a certain molecule
- Describes unambiguously the symmetry of the molecule
- In principle there are infinite number of space groups (combinations of symmetry elements); in practice ca. 40 different point groups are enough to classify all the known molecules
- Point groups are named: C_2, C_{2v}, D_{3h}, O_h, T_d … (Schönflies)

Point Groups

Every molecule has a set of symmetry elements.
This set is called the Point Group of the molecule.

Nonaxial	C_n	C_{nv}	C_{nh}	D_n	D_{nh}	D_{nd}	S_n	Higher	Linear
C_1	C_2	C_{2v}	C_{2h}	D_2	D_{2h}	D_{2d}	S_4	T_d	$C_{\infty v}$
C_s	C_3	C_{3v}	C_{3h}	D_3	D_{3h}	D_{3d}	S_6	O_h	$D_{\infty h}$
C_i	C_4	C_{4v}	C_{4h}	D_4	D_{4h}	D_{4d}	S_8	I_h	
	C_5	C_{5v}	C_{5h}	D_5	D_{5h}	D_{5d}	S_{10}		
	C_6	C_{6v}	C_{6h}	D_6	D_{6h}	D_{6d}			

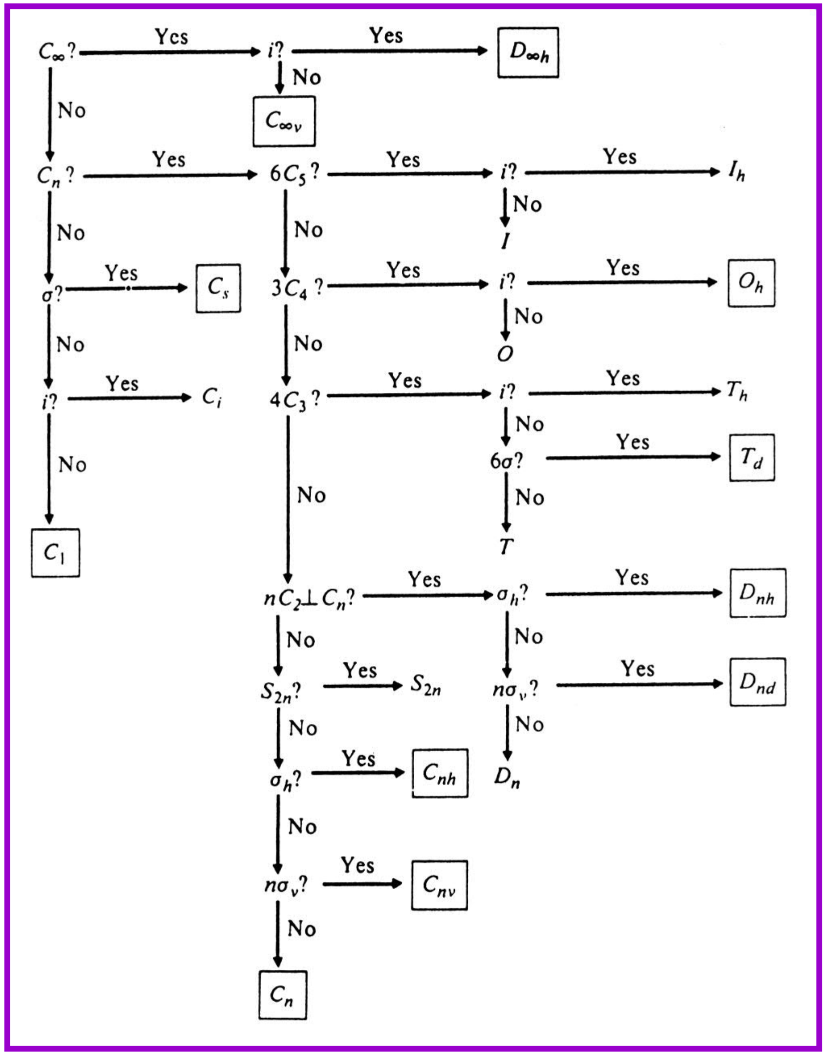
Character table for D_{3h} point group

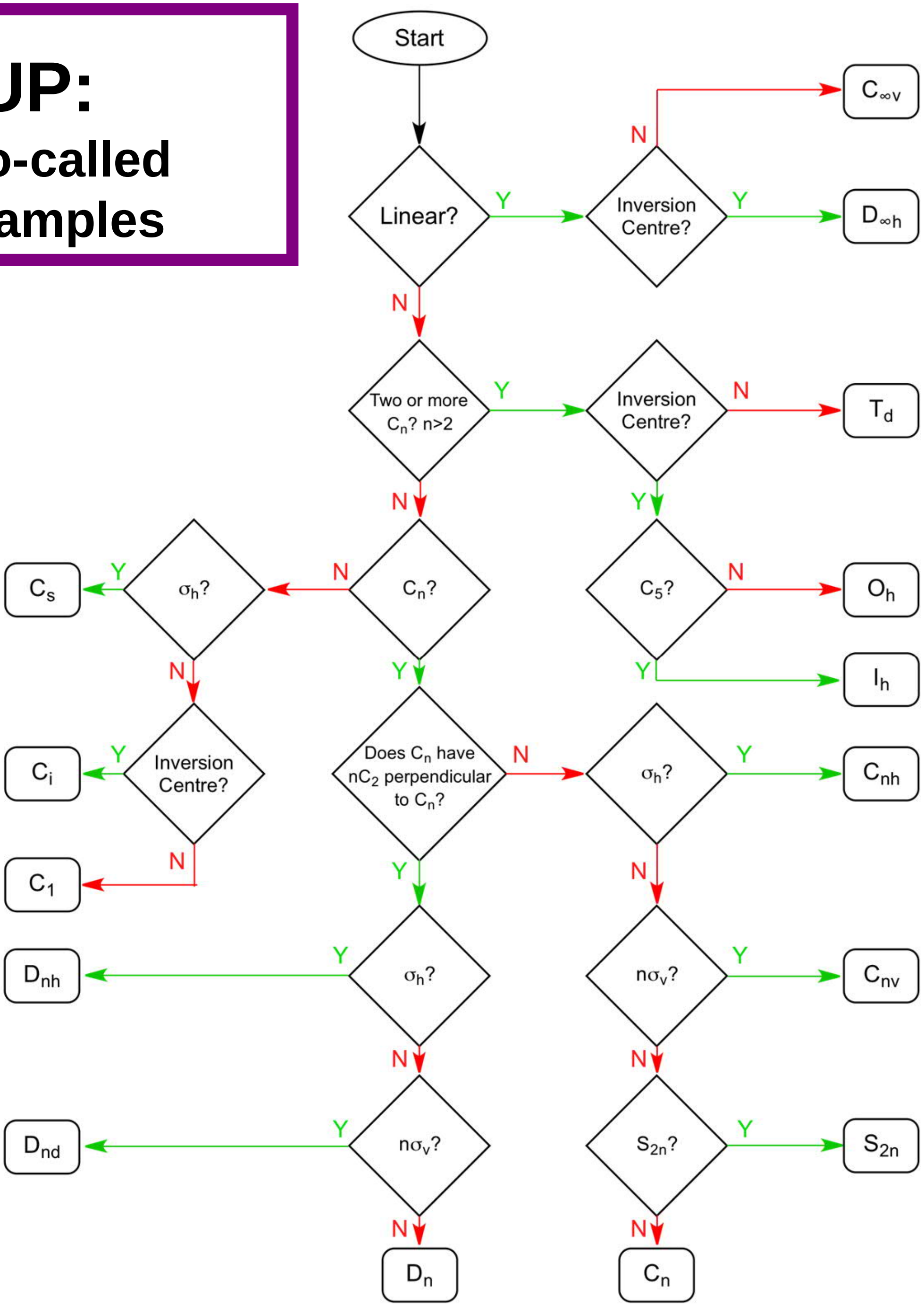
	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic

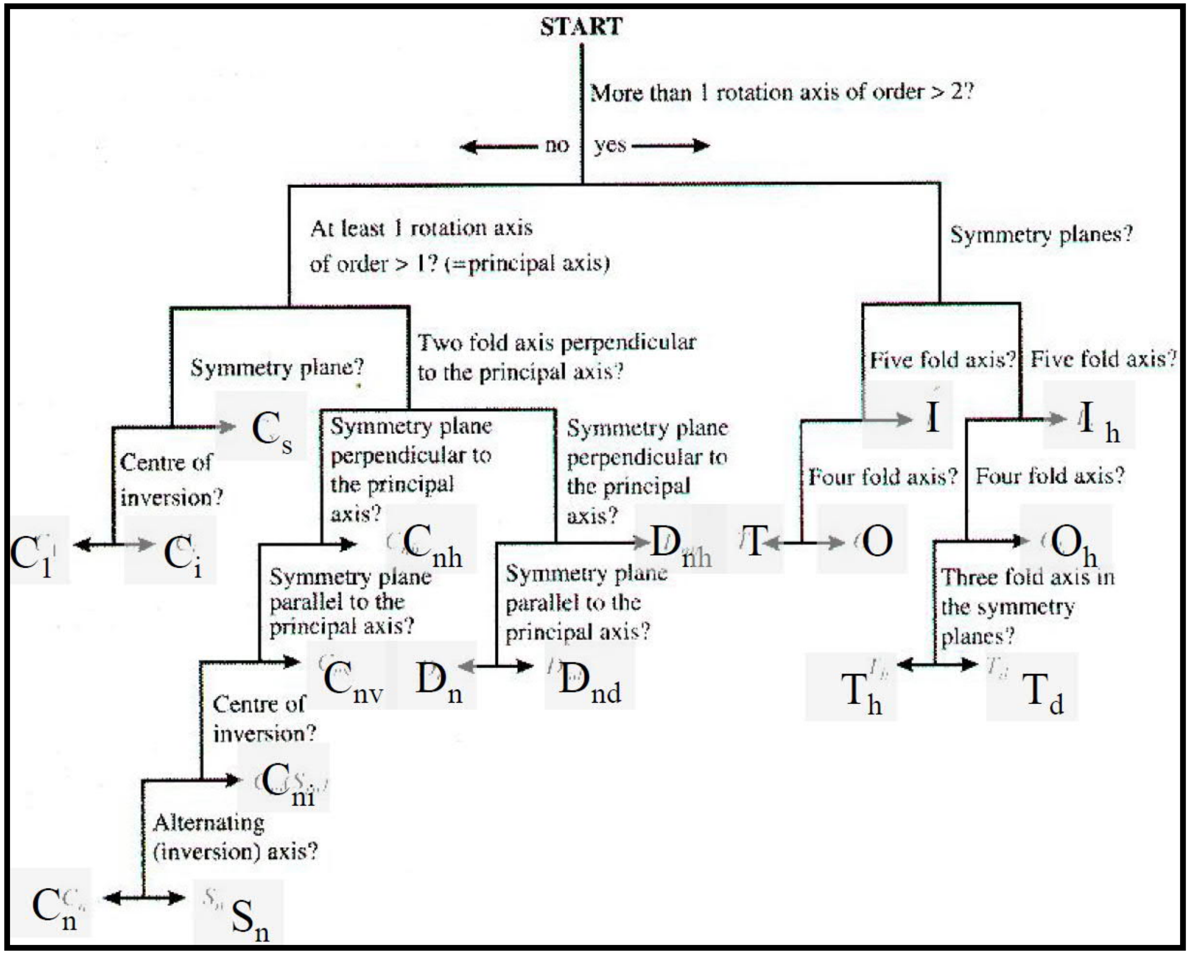
http://www.webqc.org/symmetry.php

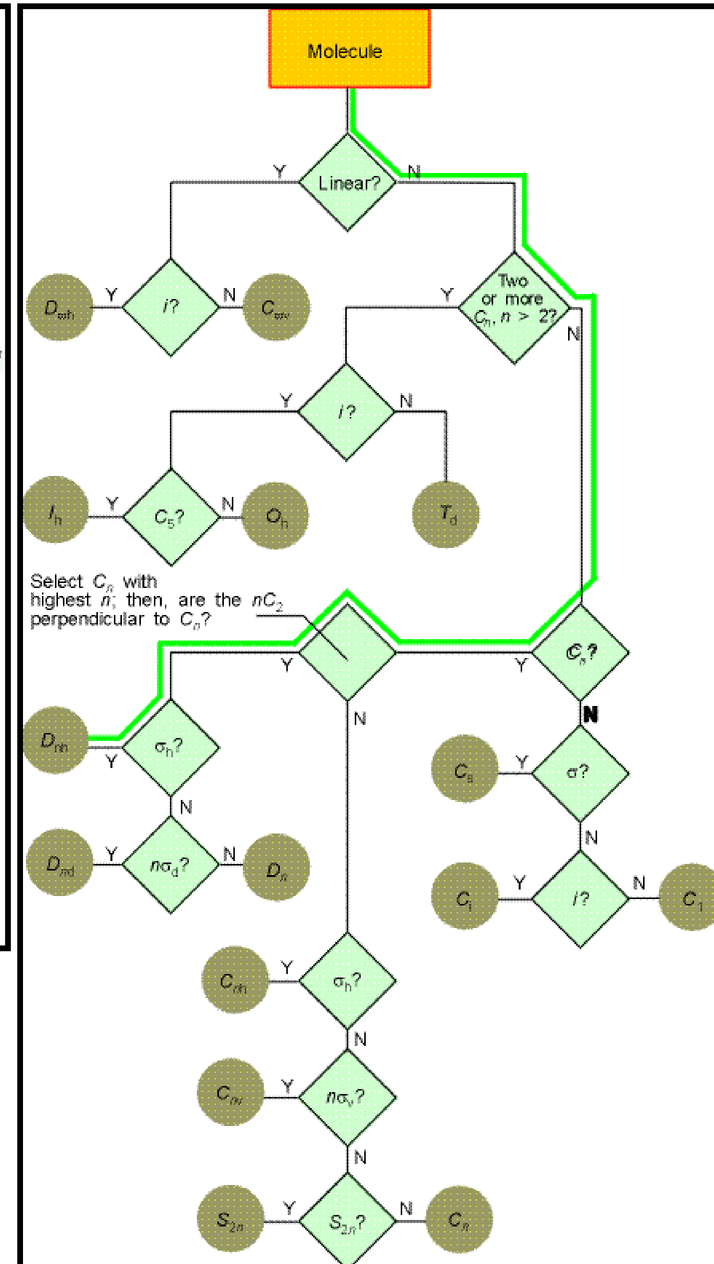
Finding the POINT GROUP:

There are a number of routes or so-called symmetry trees; here are some examples



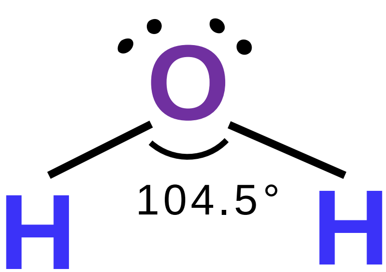



START
More than 1 rotation axis of order > 2?
no
yes
At least 1 rotation axis of order > 1? (=principal axis)
Symmetry planes?
Symmetry plane?
Two fold axis perpendicular to the principal axis?
Five fold axis?
Five fold axis?
Cs
Centre of inversion?
Symmetry plane perpendicular to the principal axis?
Symmetry plane perpendicular to the principal axis?
I
Ih
Four fold axis?
Four fold axis?
C1
Ci
Cnh
Dnh
T
O
Oh
Symmetry plane parallel to the principal axis?
Symmetry plane parallel to the principal axis?
Three fold axis in the symmetry planes?
Cnv
Dn
Dnd
Th
Td
Centre of inversion?
Cni
Alternating (inversion) axis?
Cn
Sn

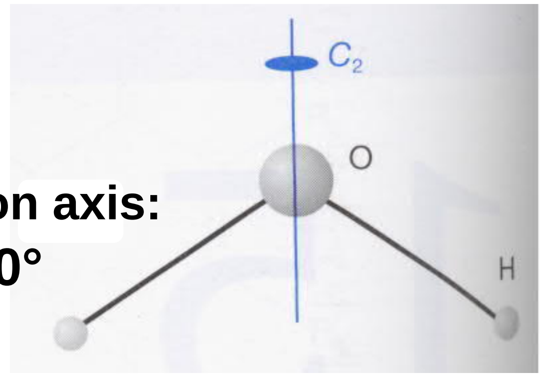

Molecule
Linear?
Y
N
i?
D∞h
C∞v
Two or more Cn, n > 2?
i?
C5?
Ih
Oh
Td
Select Cn with highest n; then, are the nC2 perpendicular to Cn?
Cn?
σh?
Dnh
nσd?
Dnd
Dn
σ?
Cs
i?
Ci
C1
σh?
Cnh
nσv?
Cnv
S2n?
S2n
Cn

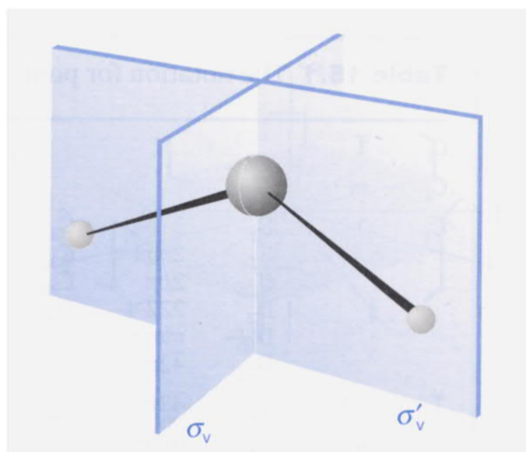
EXAMPLE: H_2O

C_{2v}

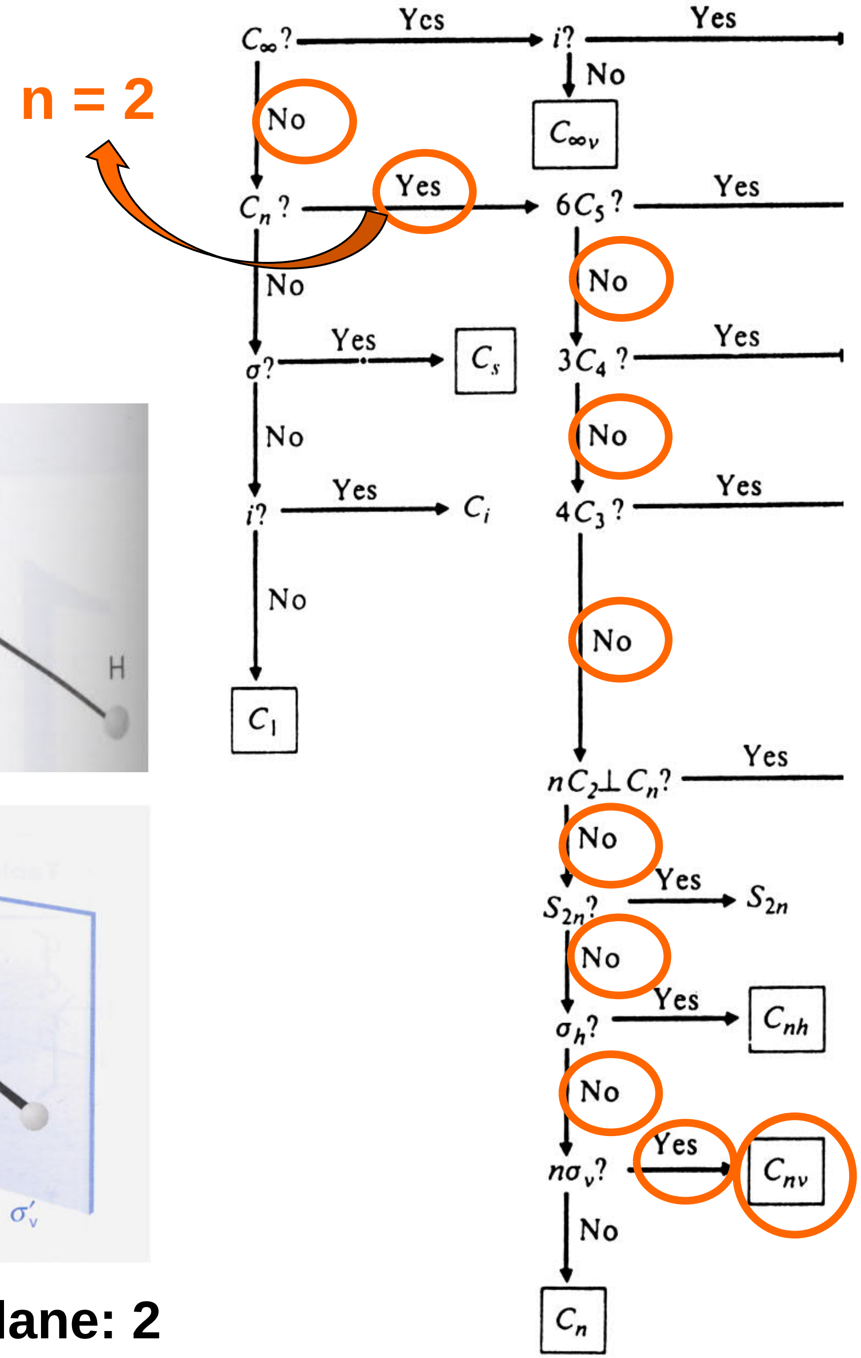


Rotation axis: 180°

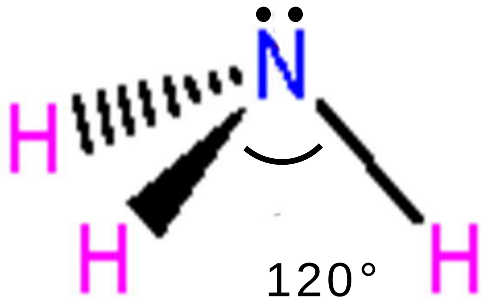


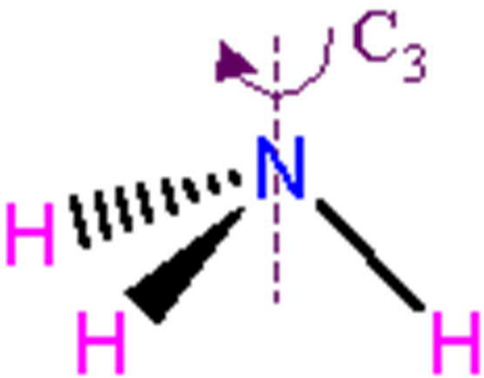


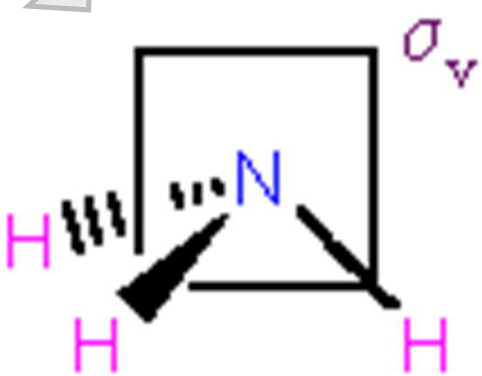
Vertical mirror plane: 2



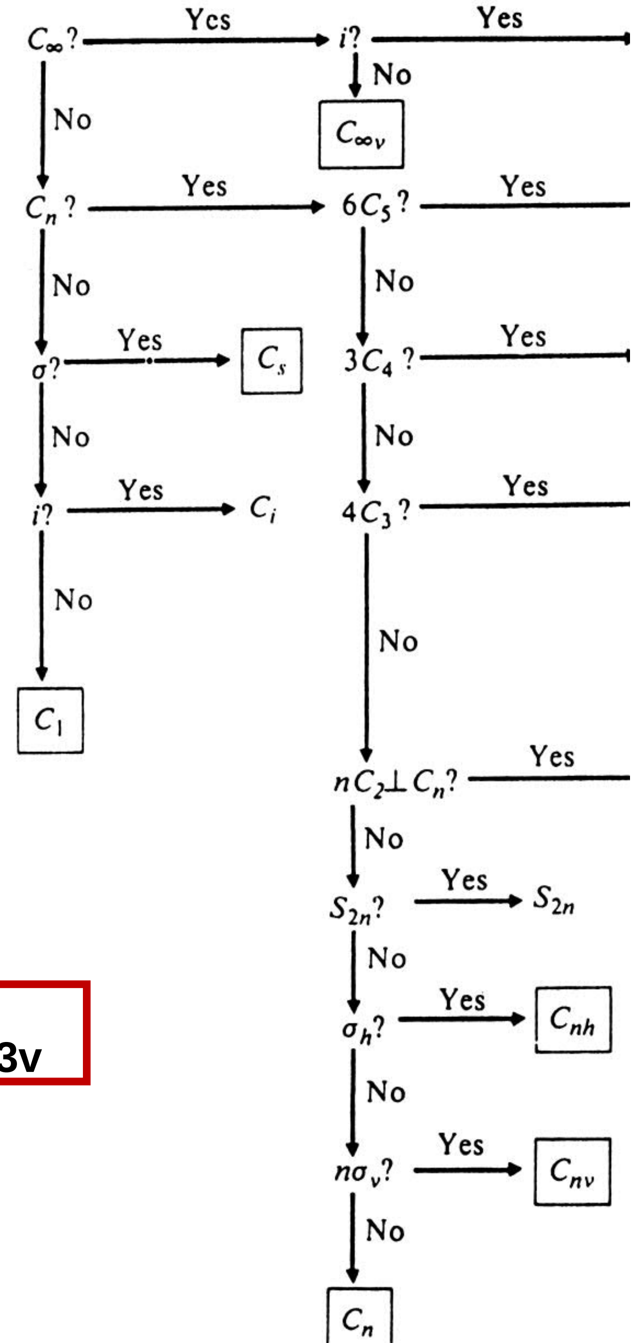
EXAMPLE: NH_3







C_{3v}



EXAMPLES

HCl

∞-fold rotation axis along the H-Cl bond, but no inversion center → $C_{\infty v}$

BFClBr (planar, B in a middle of triangle)

Only symmetry plane (where the atoms are) → C_s

trans-$N_2O_2^{2-}$ (planar)

One C_2 rotation axis perpendicular to the plane where the atoms are, no S_4 rotary-reflecion axis, but horizontal symmetry plane → C_{2h}

CH_4 (tetraedric)

Four C_3 rotation axes, no inversion center, six symmetry planes → T_d

S_8

One C_4 and four C_2 rotation axes perpendicular to C_4, no horizontal symmetry plane, but four vertical symmetry planes → D_{4d}