

SCHEDULE

	Date	Topic
1.	Wed 28.02.	Lec-1: Introduction
2.	Mon 04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon 04.03.	EXERCISE 1
4.	Wed 06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri 08.03.	Lec-4: Symmetry & Point Groups
6.	Mon 11.03.	EXERCISE 2
7.	Wed 20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri 22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon 25.03.	EXERCISE 3 (Linda)
10.	Thu 04.04.	Lec-7: Rietveld (Linda)
11.	Fri 05.04.	EXERCISE 4: Rietveld (Linda)
	Mon 08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu 11.04.	Lec-8: ND & GI-XRD
13.	Fri 12.04.	Lec-9: XRR (Topias)
14.	Mon 15.04.	EXERCISE 5: XRR (Topias)
	Wed 17.04.	EXERCISE 5: XRR (Topias)
15.	Mon 22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Wed 24.04.	Mössbauer (to 25.10)
17.	Fri 26.04.	EXERCISE 6
18.	Mon 29.04.	Seminars:
19.	Fri 03.05.	Seminars:
20.	Mon 06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY

SEMINARS

- IR
- Raman
- XPS
- SEM Alex Idman
- AFM
- HRTEM
- ED
- EELS

INSTRUCTIONS for SEMINAR PRESENTATIONS

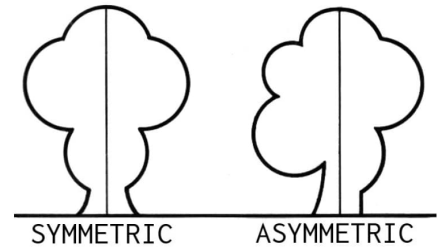
- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Presentation slides will be put up in MyCourses afterwards
- **Seminars are part of the course content and it is likely that there will be questions in the exam related to these seminars**
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation: 25+5 minutes
- Rough content of the presentation:
 - principle of the technique(s)
 - type of information gained
 - interpretation of the measured data
 - pros & cons
 - **two to four research examples**
(you will be given some relevant research papers for an example)

LECTURE 4: SYMMETRY

- Greek "*symmetrein*" (= commensurate, yhteismitallinen)
- Symmetry elements/operations
- Molecular symmetry & **Point groups**
- **Space groups & Crystallography in Lecture 5**

SYMMETRY

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



Kuva: Pearson Scott Foresman



IN CHEMISTRY ...

MOLECULAR SYMMETRY

Important for understanding/explaining/classification

- Molecule structures
- Crystal structures & Local environments
- Quantum chemistry
- Spectroscopy (IR, Raman)
- Material properties, e.g. ferro/piezoelectricity

SYMMETRY OPERATION

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

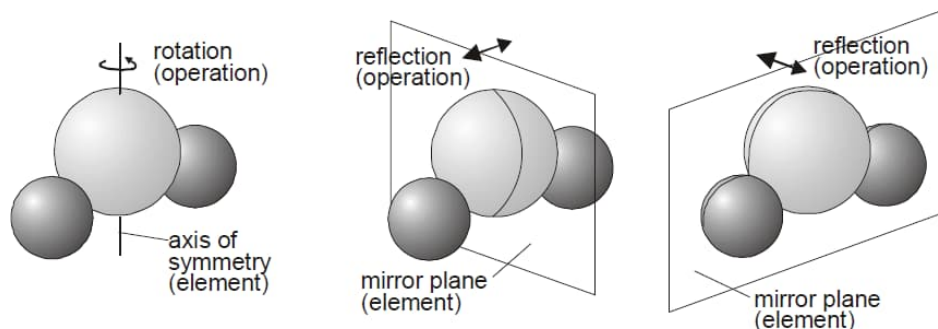
SYMMETRY ELEMENT

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)

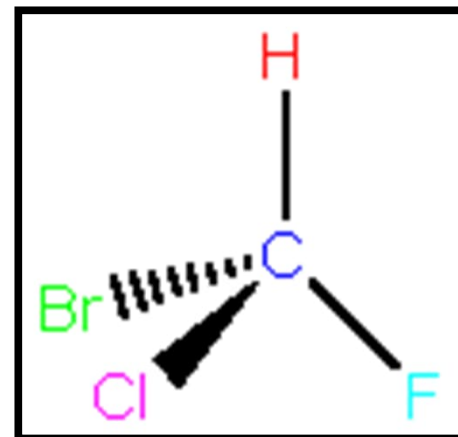
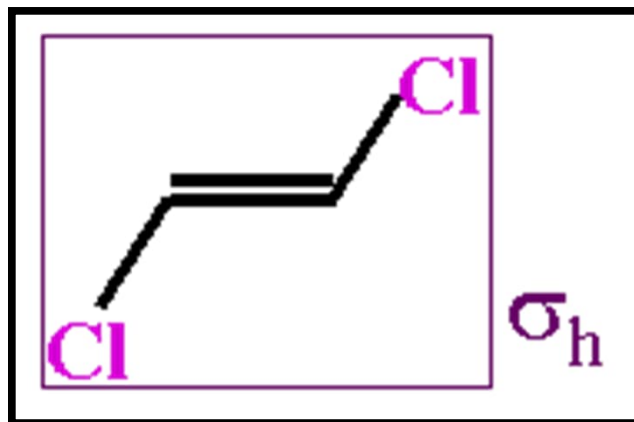
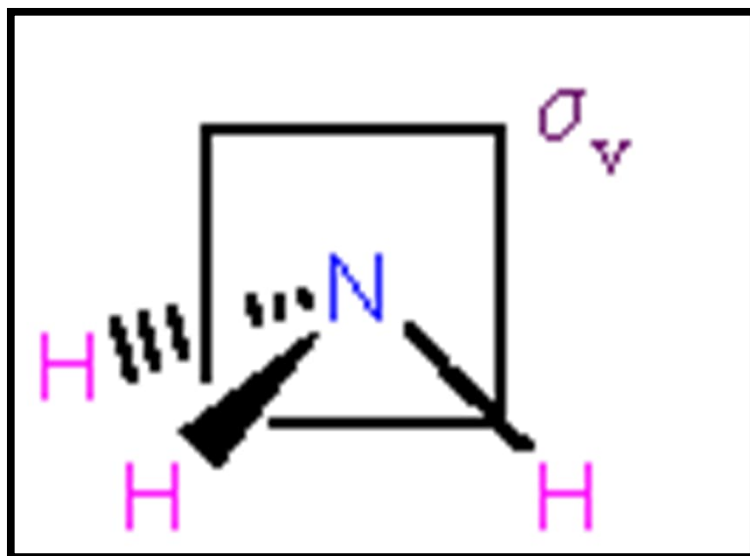
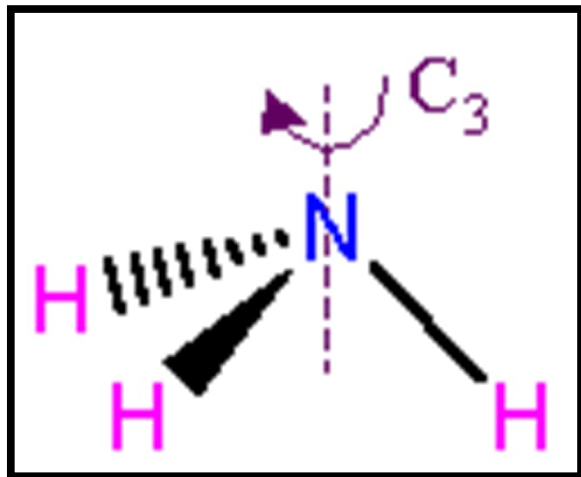


Molecular symmetry: at least one point remains unchanged

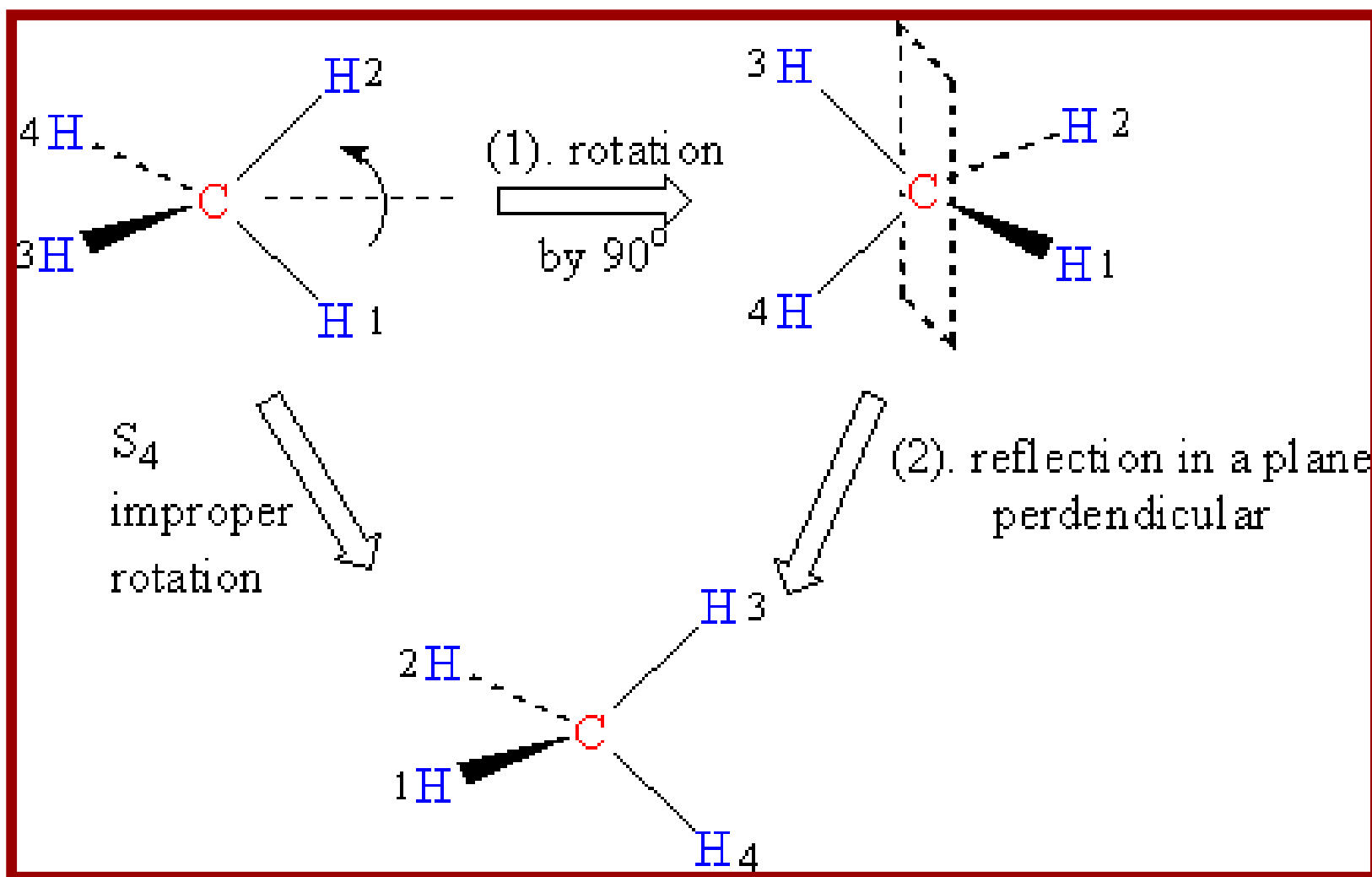
- **Identity (E; German *Einheit*):** No change; every molecule has E
- **Rotation axis (C_n):** Rotation by $360^\circ/n$ ($n = 1, 2, 3, \dots$) about an axis, which leaves the molecule unchanged
- **Symmetry or mirror plane (σ):** Plane through which reflection leaves the molecule unchanged:
 - σ_v : vertical mirror plane (in relation to rotation axis)
 - σ_h : horizontal 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 $360^\circ/n$, followed by reflection in a plane perpendicular to the axis.
Note: $S_1 = \sigma$; $S_2 = i$

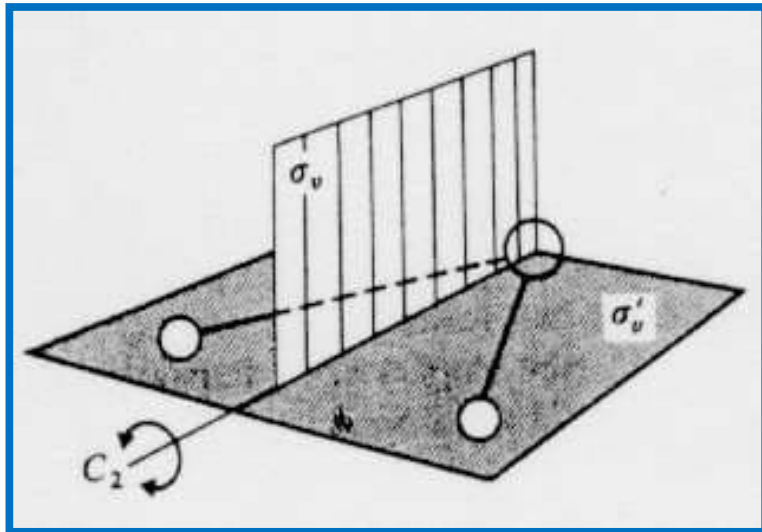
Proper: Can be actually done on a molecule: E, C_n

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

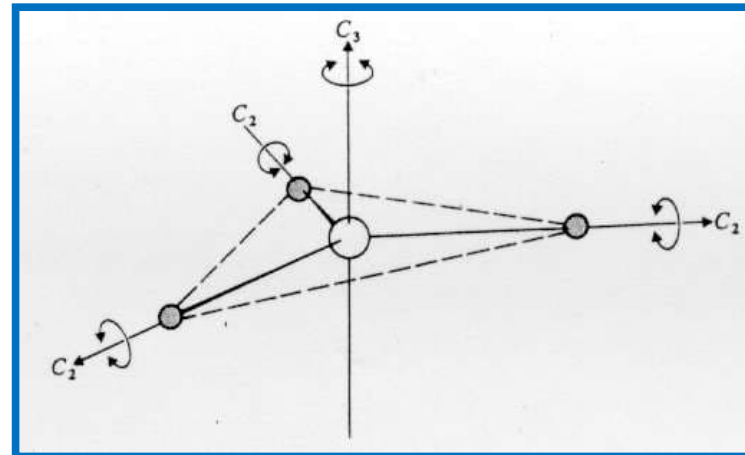


Rotary-reflection: CH₄



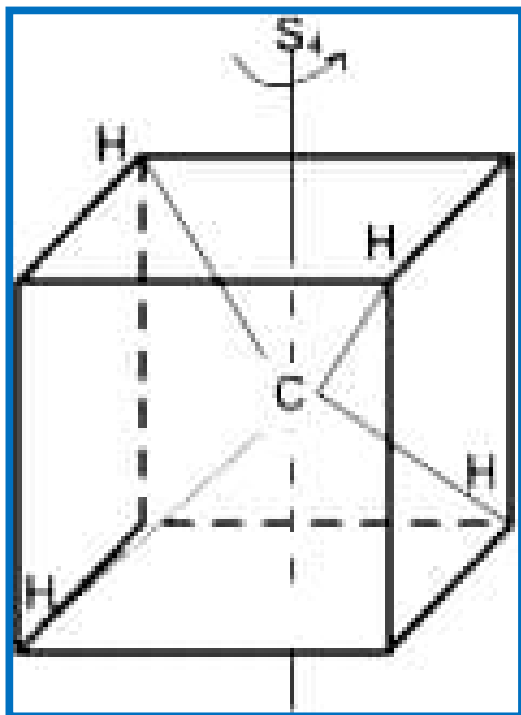


H_2O

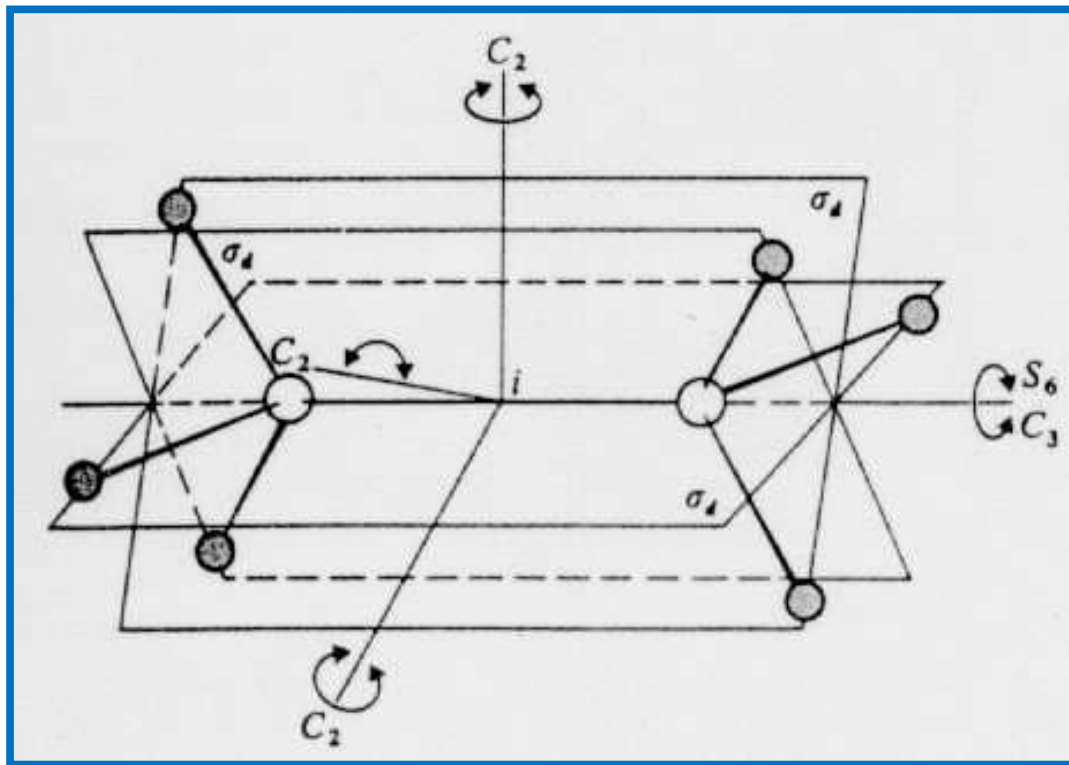


BF_3

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 point 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

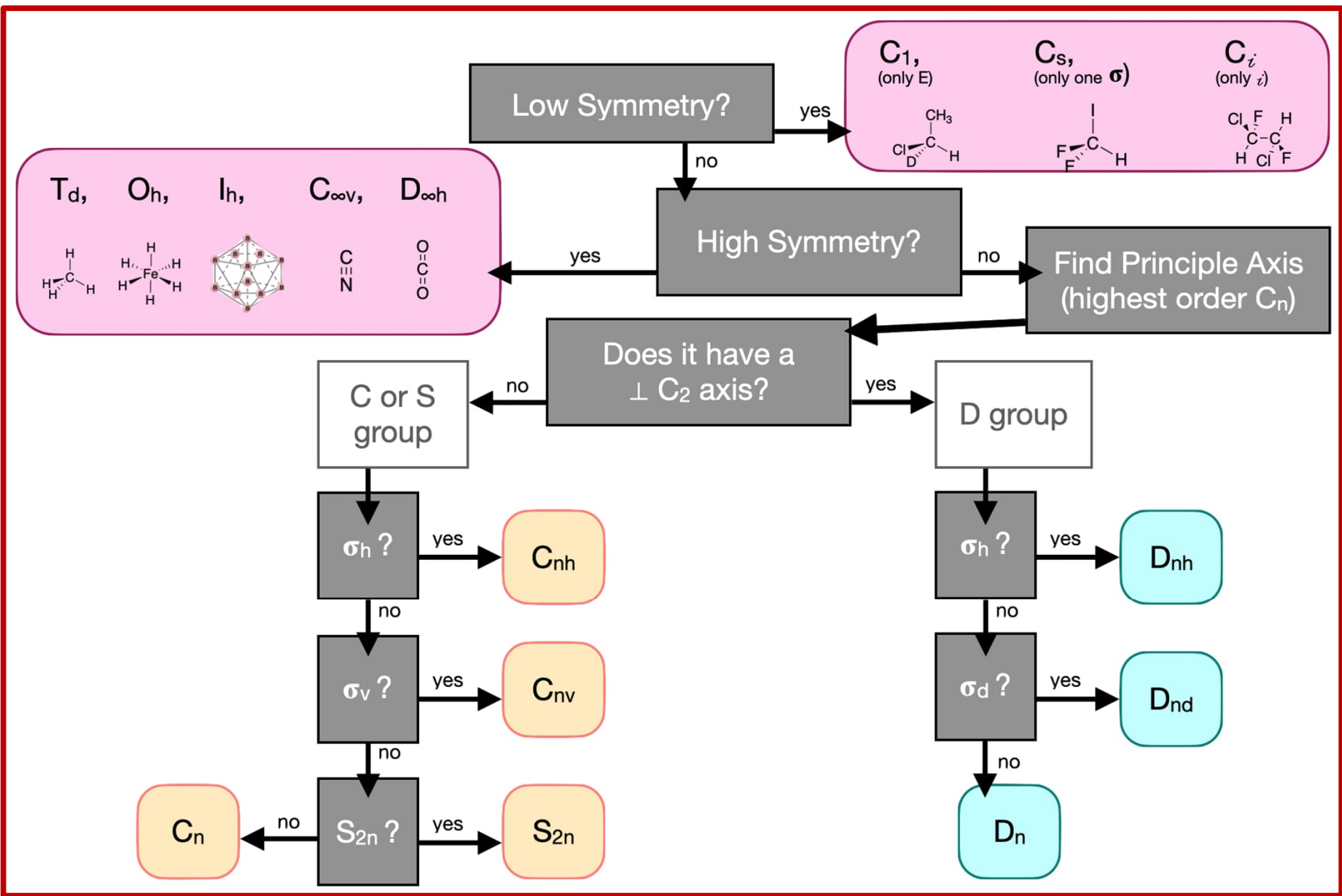
Every molecule has a set of symmetry elements.
This set is called the Point Group of the molecule.

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}			

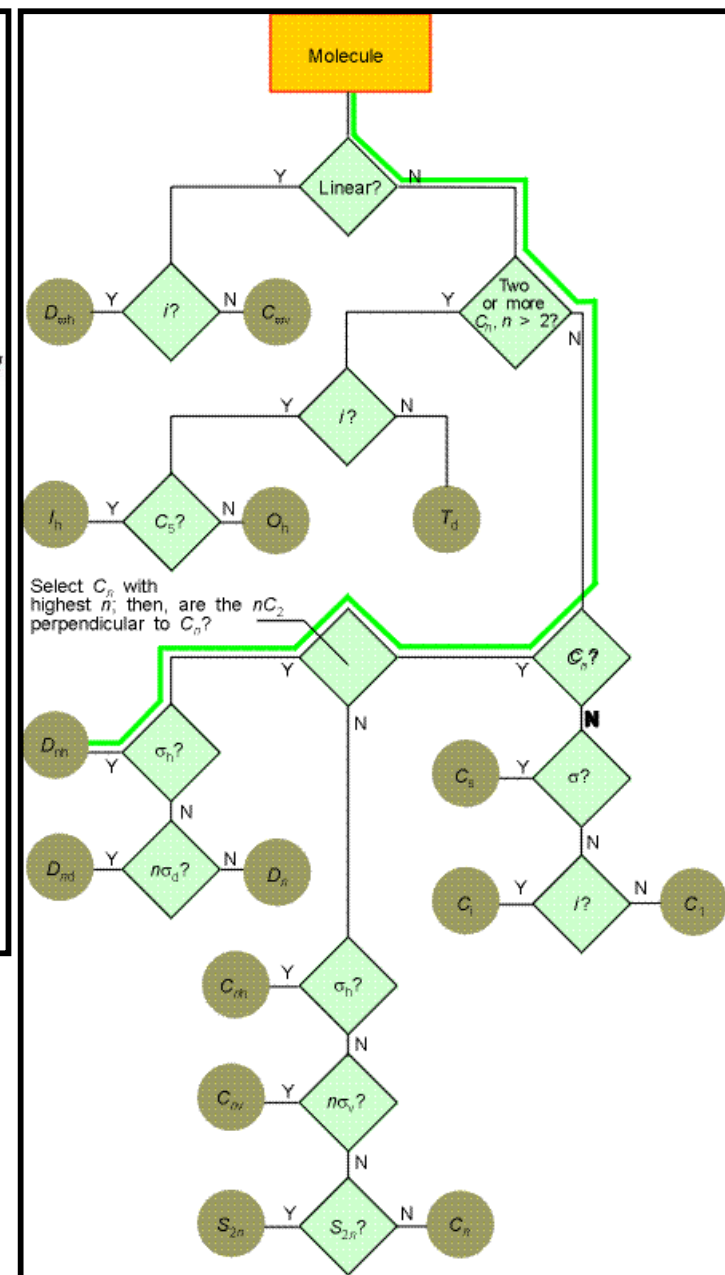
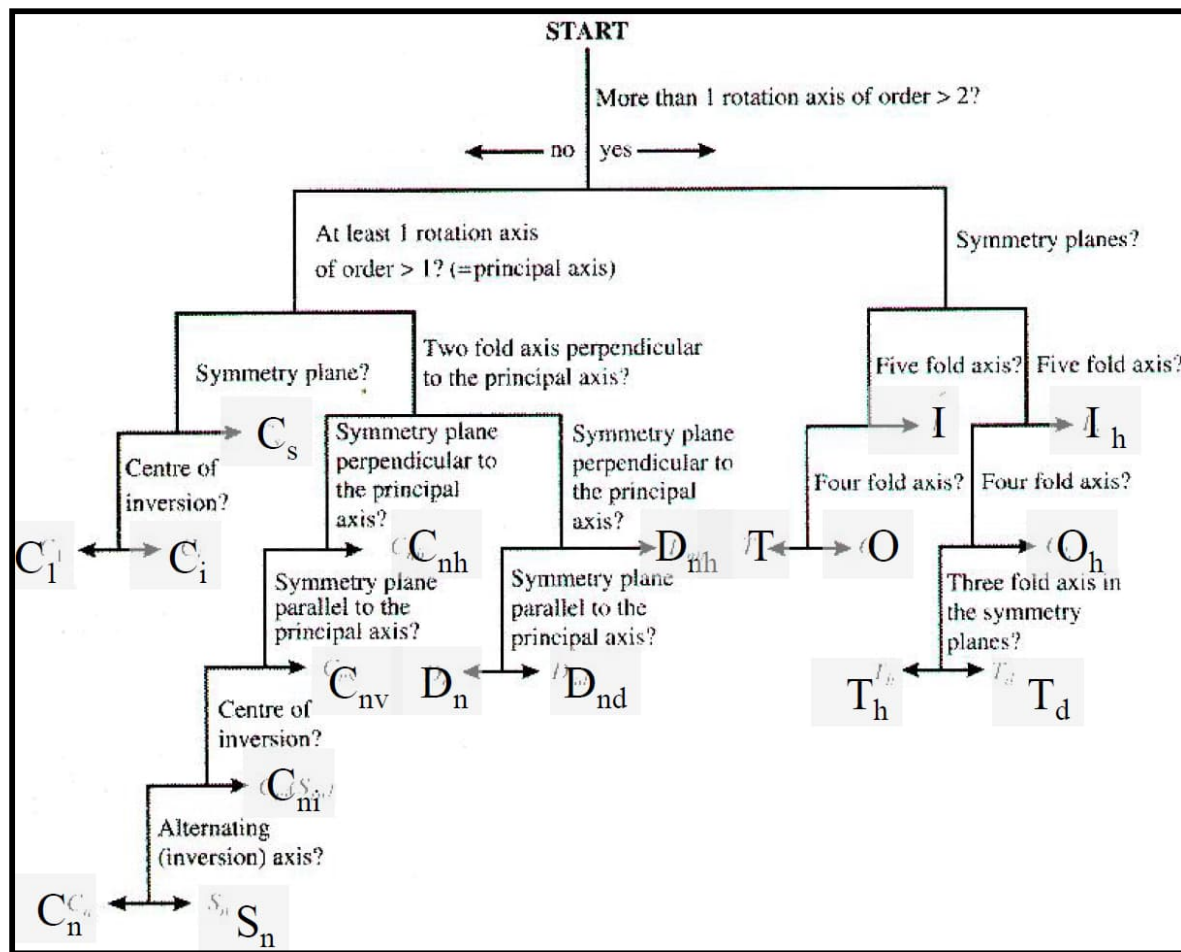
Character table for D_{3h} point group

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

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

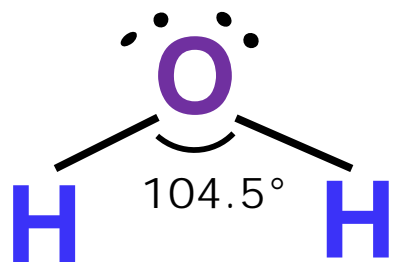


Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

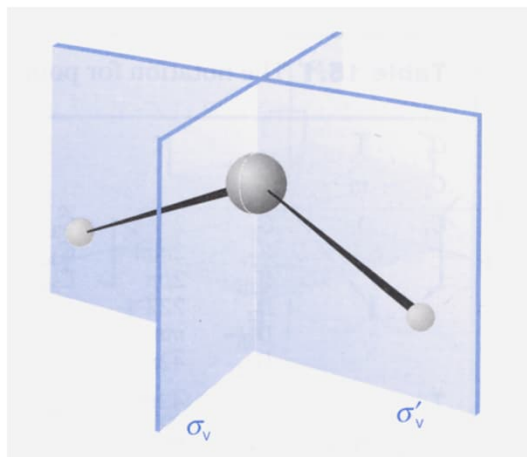
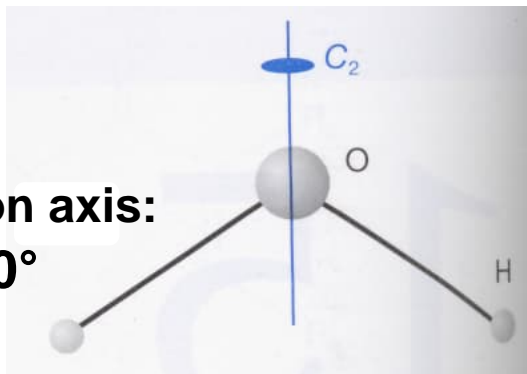


EXAMPLE: H₂O

C_{2v}

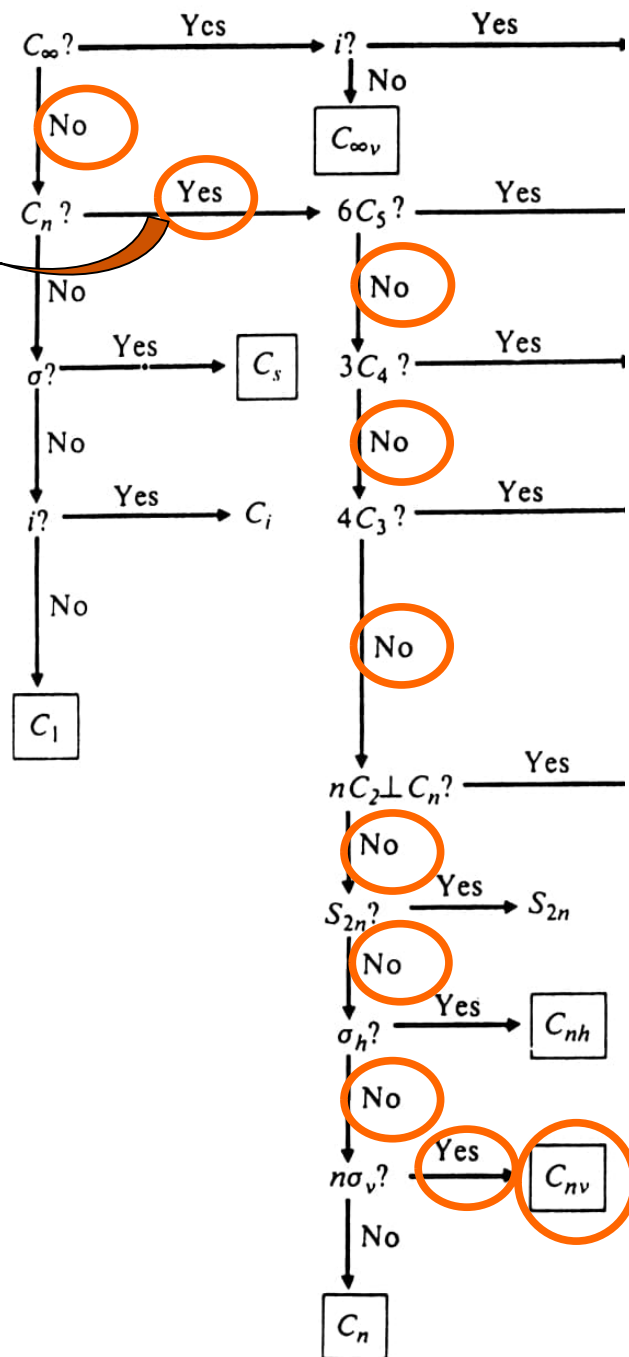


Rotation axis:
180°

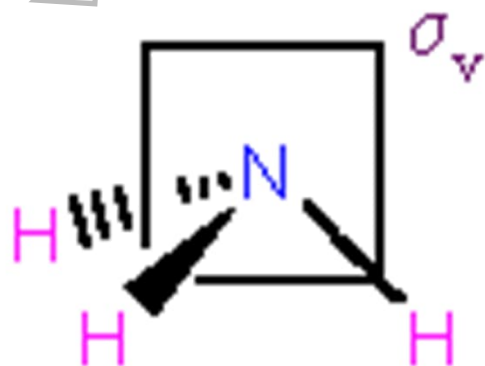
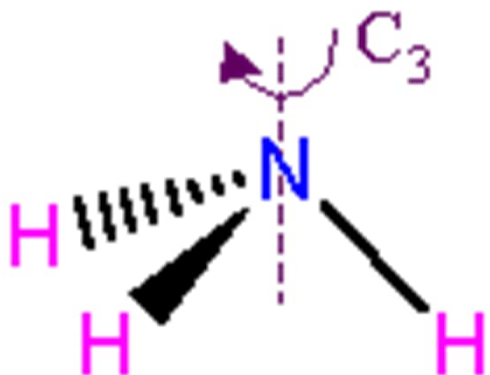
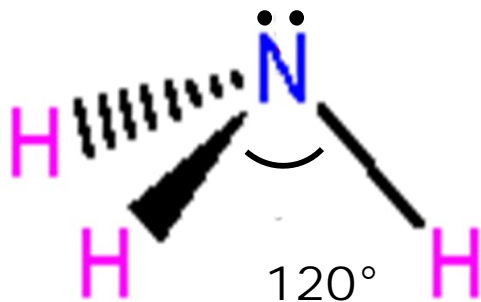


Vertical mirror plane: 2

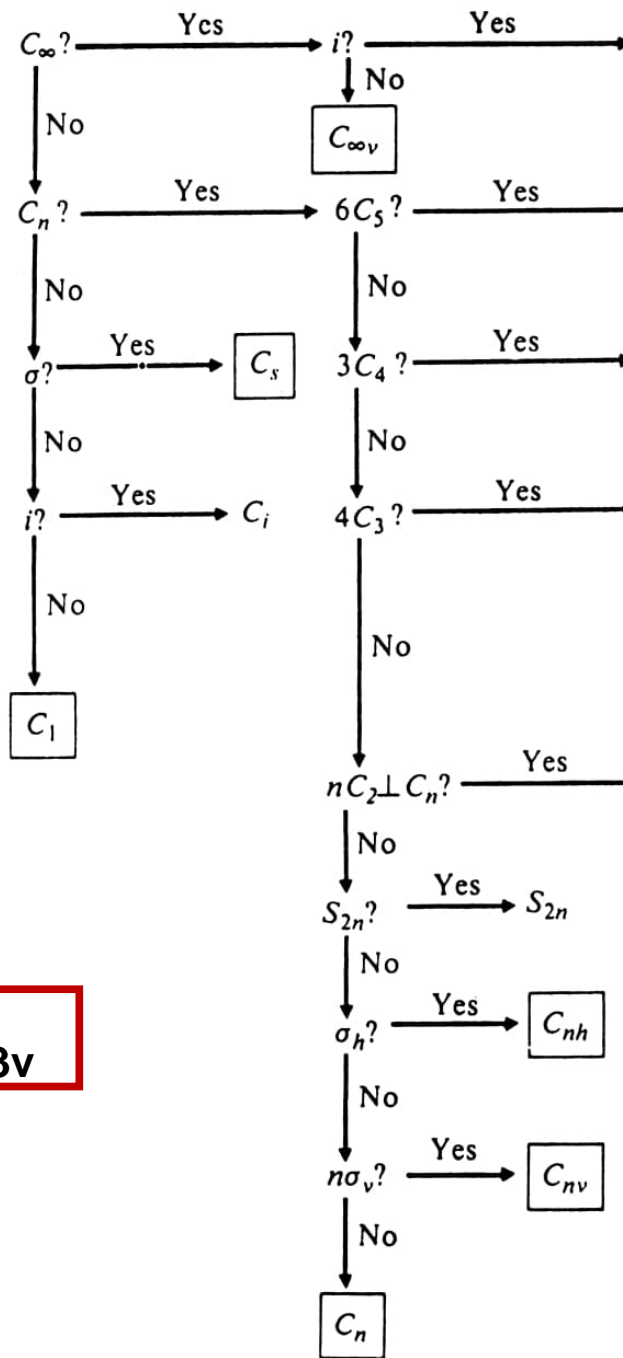
n = 2



EXAMPLE: NH₃



C_{3v}



EXAMPLES

HCl

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

BFCIBr (planar, B in a middle of triangle)

Only symmetry plane (where the atoms are) $\rightarrow C_s$

trans-N₂O₂²⁻ (planar)

One C₂ rotation axis perpendicular to the plane where the atoms are, no S₄ rotary-reflection axis, but horizontal symmetry plane $\rightarrow C_{2h}$

CH₄ (tetrahedral)

Four C₃ rotation axes, no inversion center, six symmetry planes $\rightarrow T_d$

S₈

One C₄ and four C₂ rotation axes perpendicular to C₄, no horizontal symmetry plane, but four vertical symmetry planes $\rightarrow D_{4d}$

