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Optical Spectroscopy in Materials Science

Symmetry and selection rules in vibrational spectroscopy

Vibrational degrees of freedom

For a molecule with N atoms: 3N – 6 (3N- 3 translations– 3 rotations)
For linear molecules: 3N – 5 (rotation around axis does not cause atomic displacement)

Selection rules:

IR $\frac{\partial \mu}{\partial Q} \neq 0$ Raman $\frac{\partial \alpha}{\partial Q} \neq 0$

Q normal coordinate, also for more complicated vibrations

Example: CS_2

normal vibrations

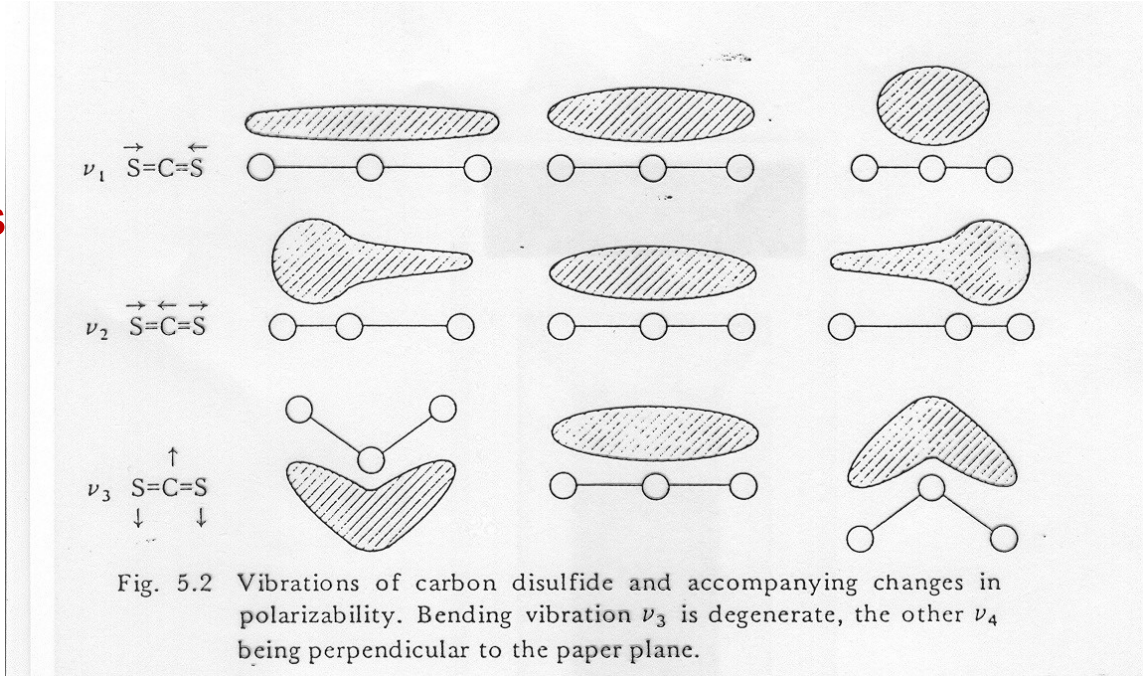


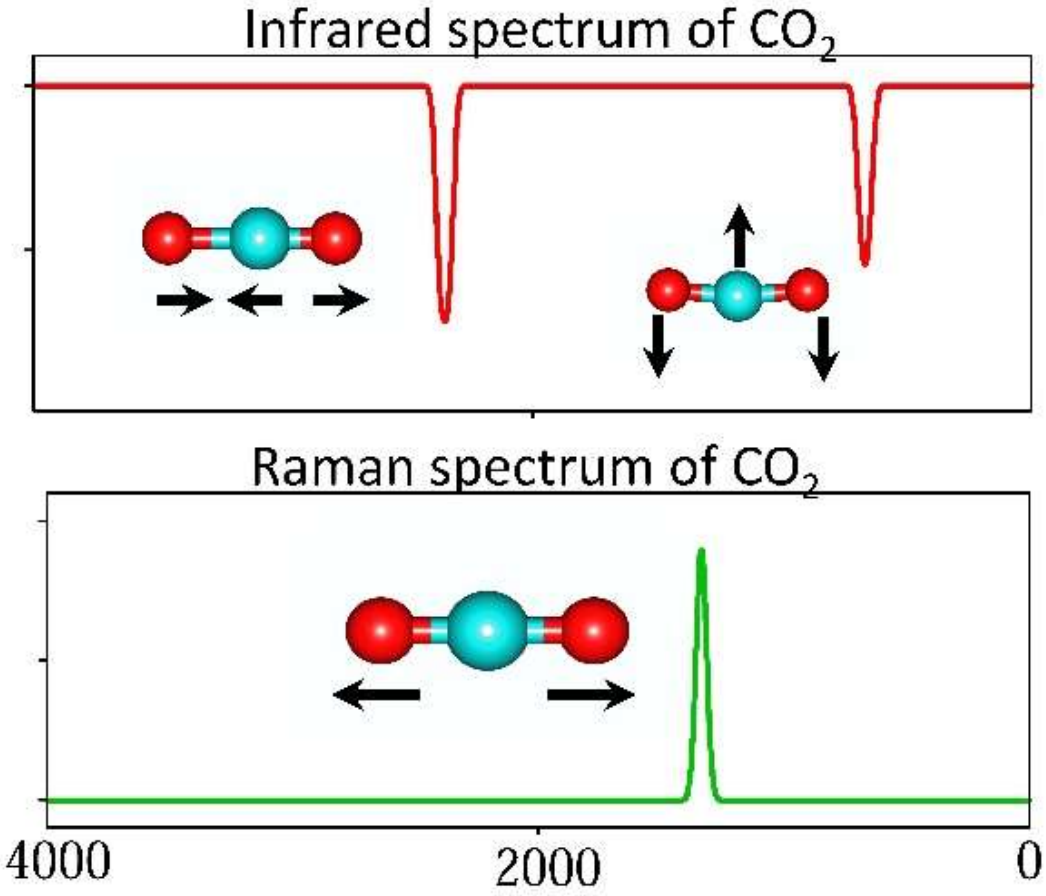
Fig. 5.2 Vibrations of carbon disulfide and accompanying changes in polarizability. Bending vibration ν_3 is degenerate, the other ν_4 being perpendicular to the paper plane.

symmetric stretch

asymmetric stretch

bend

Vibrational spectra of CO_2

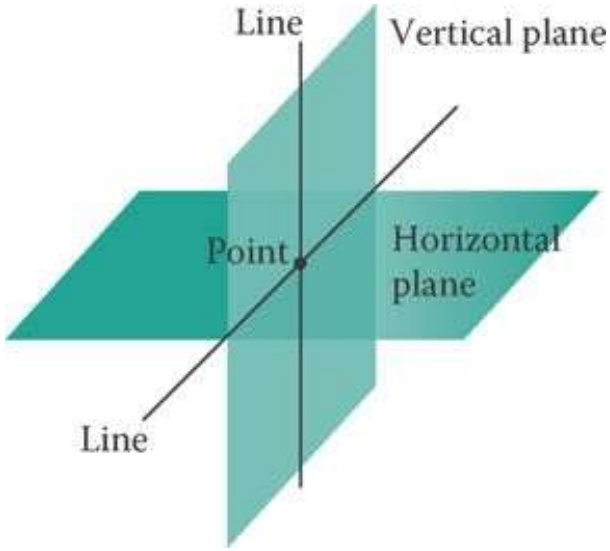


https://scilearn.sydney.edu.au/fychemistry/chem2401/Lecture%209.pdf

Basic concepts - symmetry

Symmetry elements:

- point
- line (rotation axis)
- plane



Iulian Ionita: Condensed Matter Optical Spectroscopy. An Illustrated Introduction.CRC Press, 2015

Symmetry operations:

- identity
- rotations
- reflections

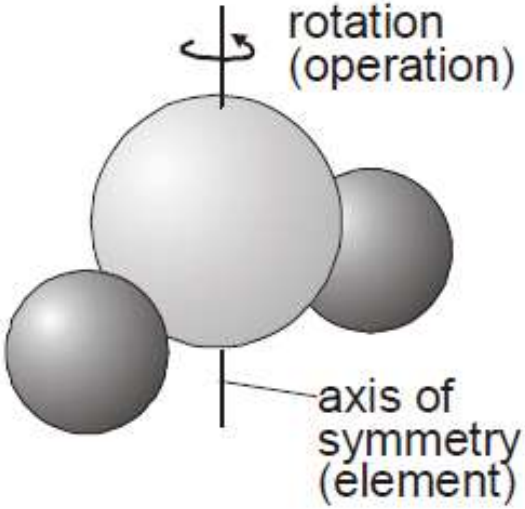
Symmetry point group:

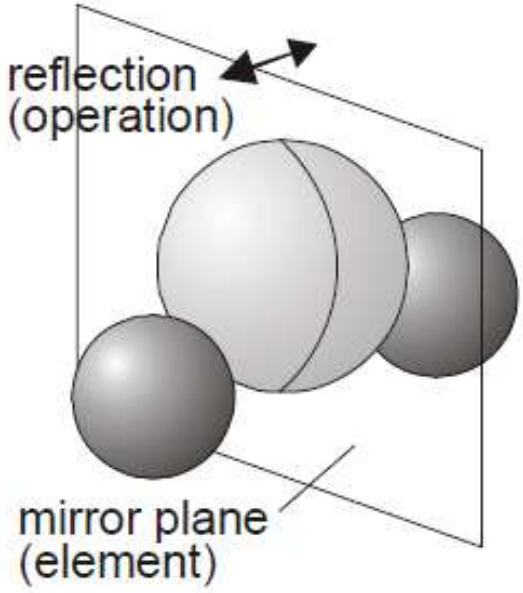
all symmetry operations which leave at least one point in the object fixed

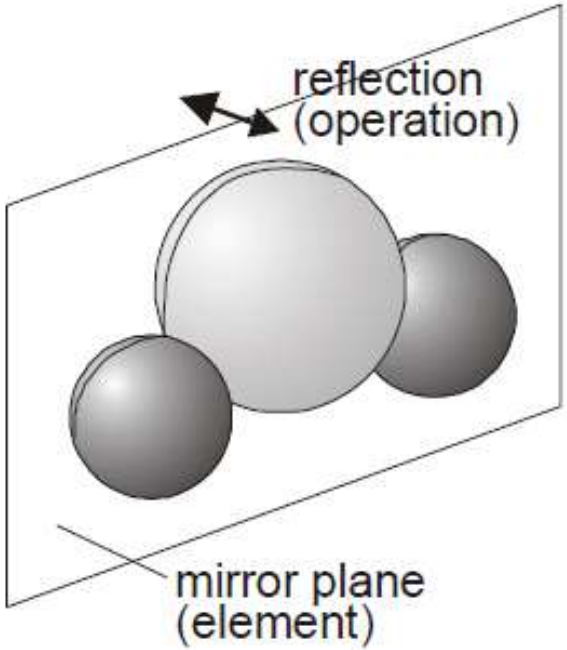
Basic concepts - symmetry

Symmetry elements and operations: (Schoenflies' notation)

- C_n^m axis of rotation: rotation by $2\pi/n$ m times
  principal axis: largest *n*
- σ: mirror plane
  - σ_v: vertical
  - σ_h: horizontal
  - σ_d: diagonal (dihedral) vertical, bisects two C_2 axes perpendicular to principal axis
- S_n^m : improper rotation (C_n^m , then σ_h) rotation-reflection
- *i*: inversion center







https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Symmetry_(Vallance)

Basic concepts - groups

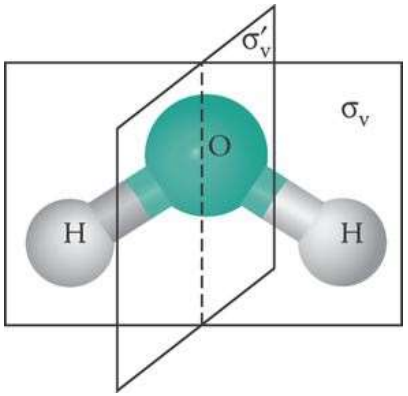
Symmetry operations form a group

Group multiplication: subsequent application of operations

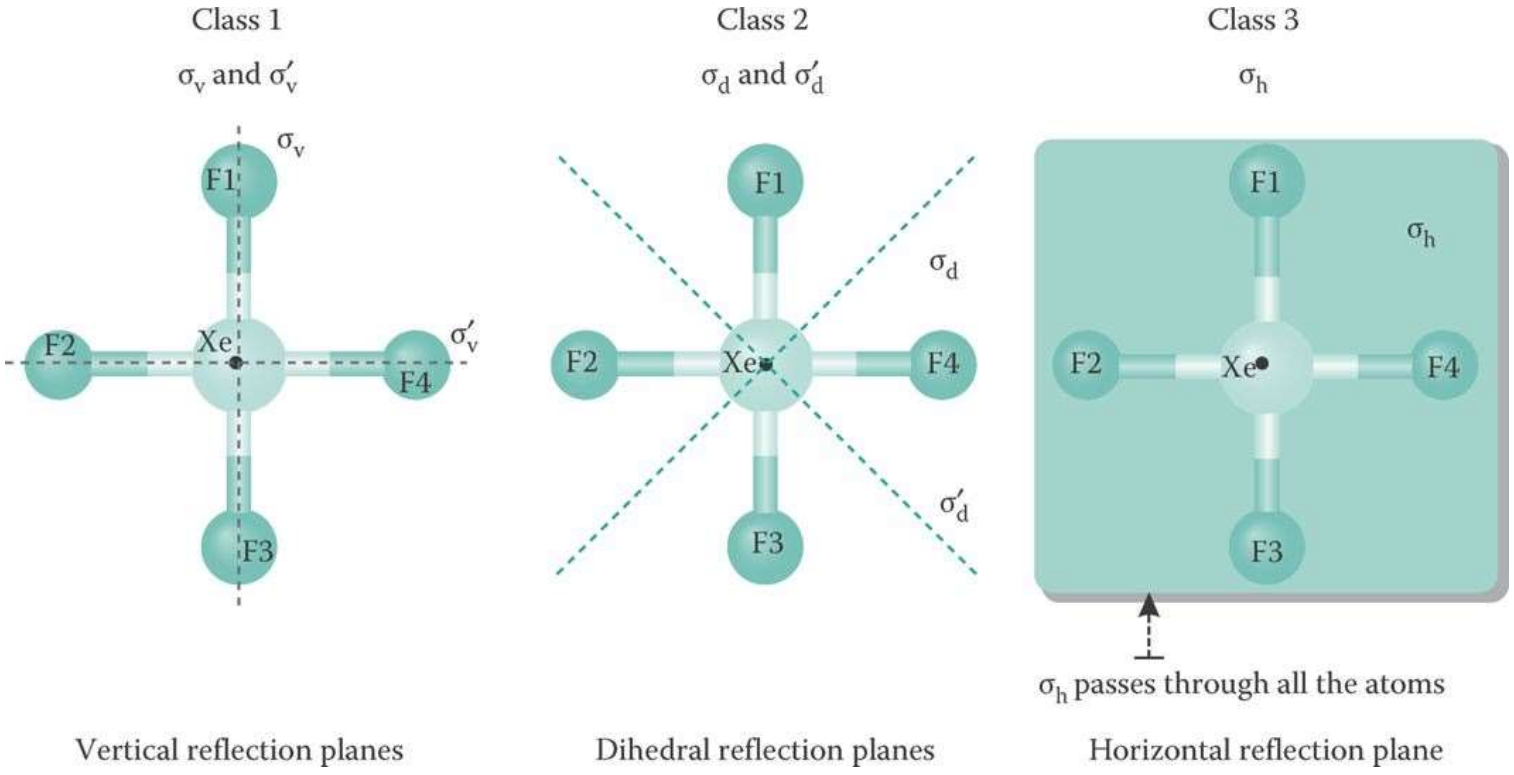
Group:

$AB \in G$	closed
$A(BC) = (AB)C$	associative
$E \in G$	contains identity element
$A^{-1}A = E, A \in G, A^{-1} \in G$	contains inverse element

Reflection planes



Water
2 reflection planes

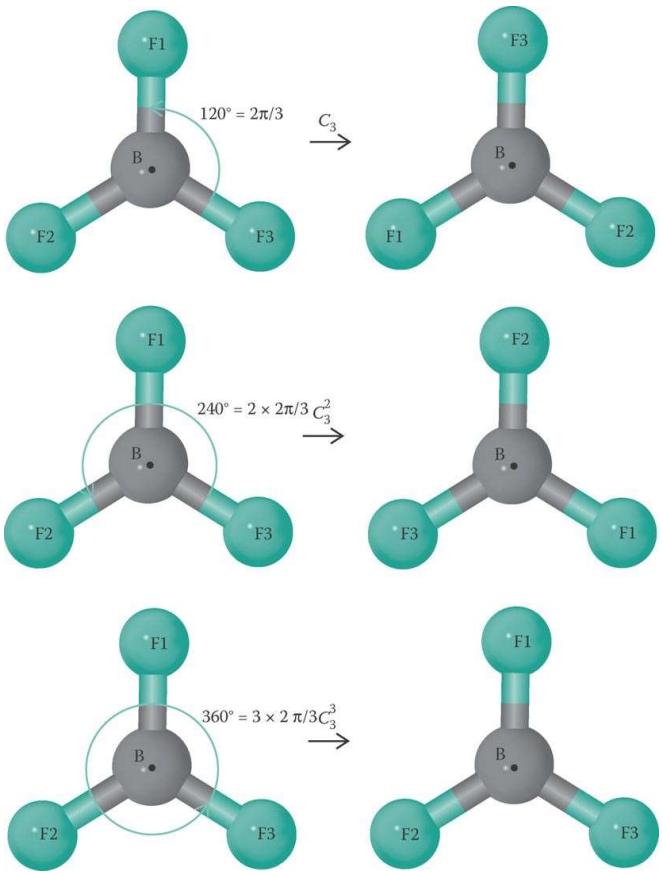


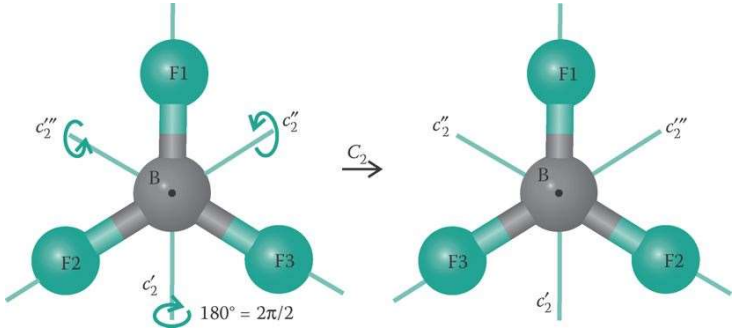
XeF_4

dihedral plane bisects two C_2 axes perpendicular to principal axis
in most cases, the vertical plane contains more atoms

Proper rotations

BF_3: principal axis C_3





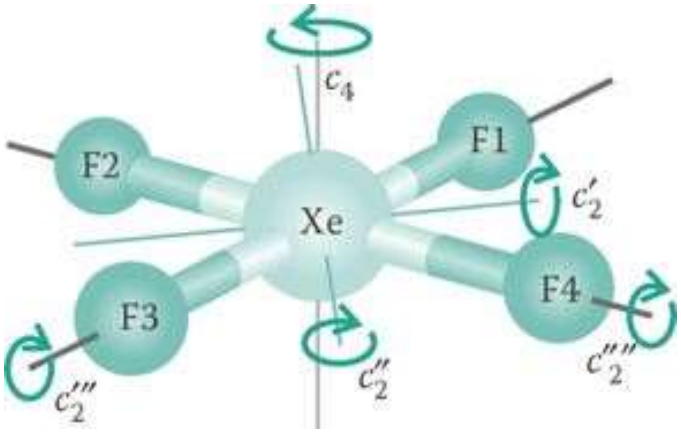
C_2 axes are generated from each other by C_3

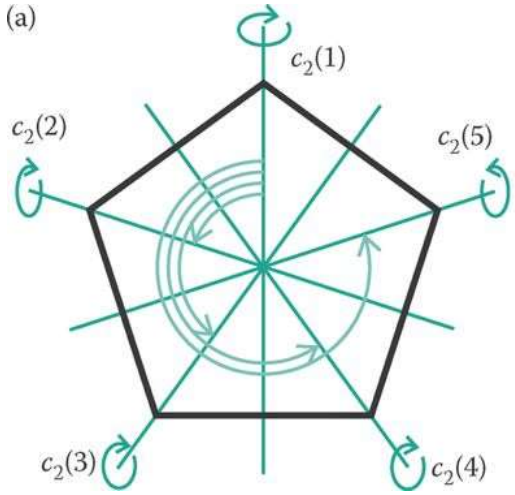
Proper rotations for higher axes

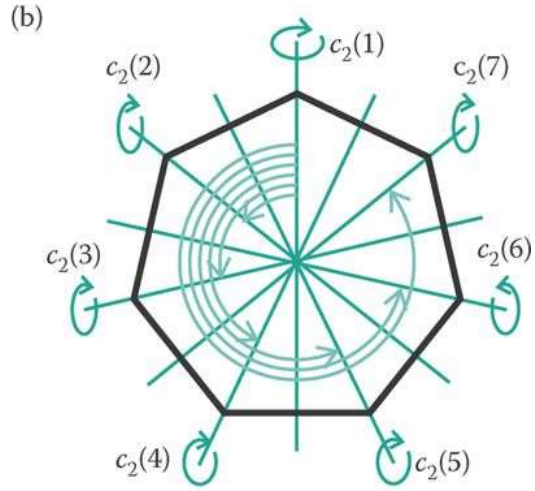
n even

n odd

XeF_4: principal axis C_4





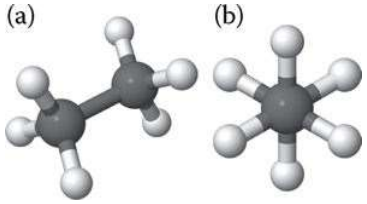


two types of C_2 axes

one type of C_2 axis

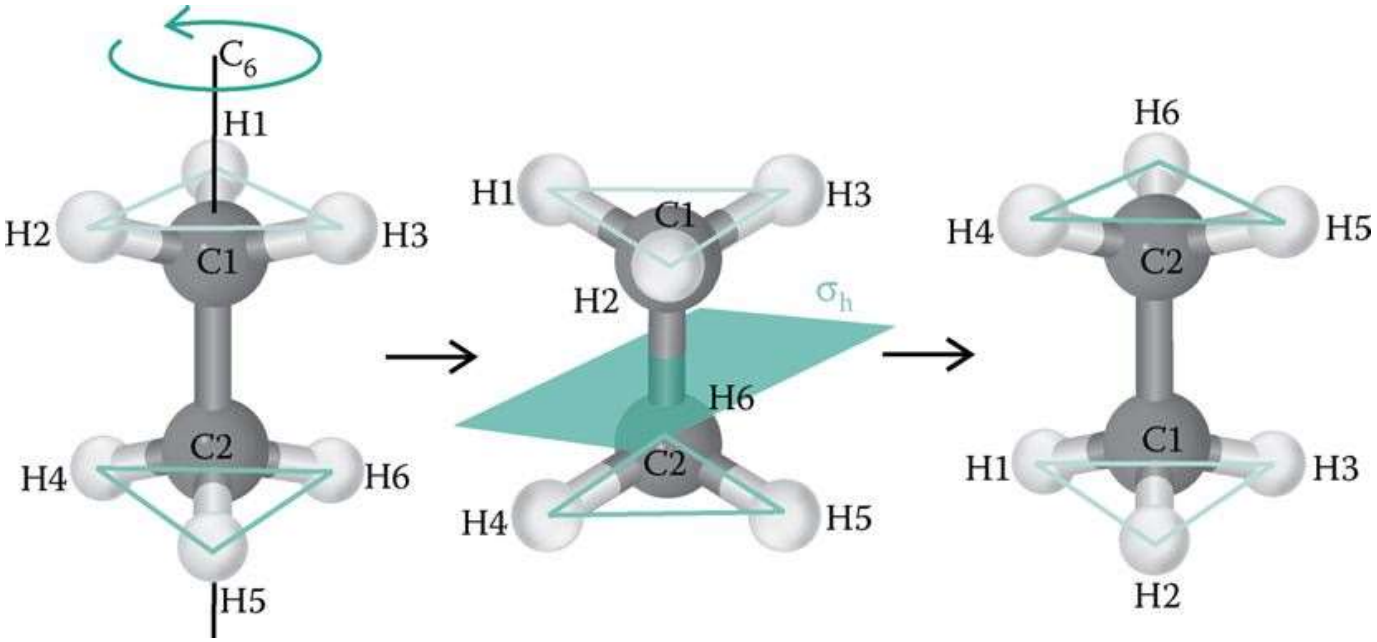
Improper rotations

Ethane C_2H_6



Side view **Top view**

S_6



Intermediate configuration

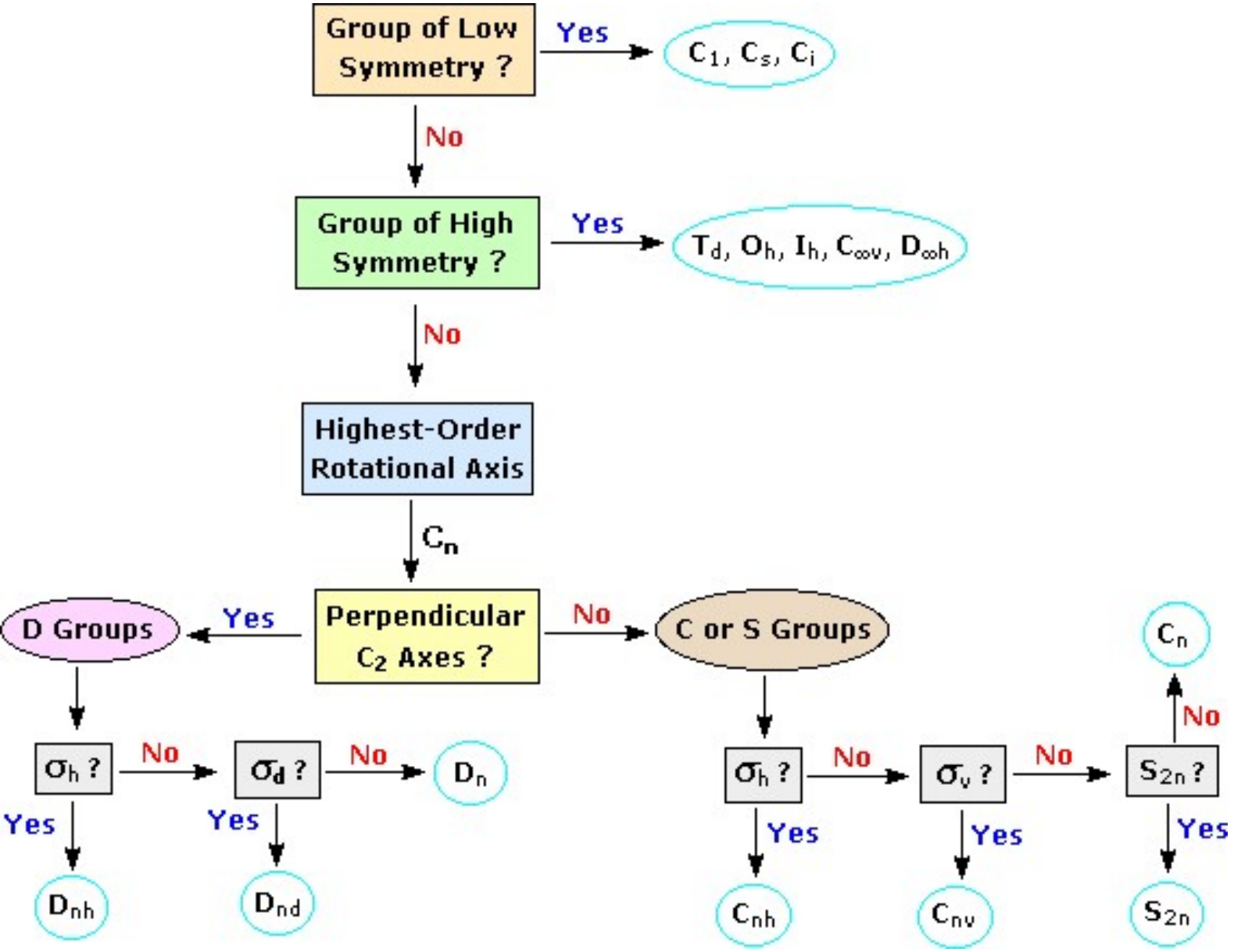
Crystallographic point groups

	notation	n	number
Rotation	C_n	1,2,3,4,6	5
$C_n+\sigma_h$	C_{nh}	1,2,3,4,6	5
$C_n+\sigma_v$	C_{nv}	2,3,4,6	4
C_n+S_n	S_n	2,4,6	3
C_n+C_2'	D_n	2,3,4,6	4
$C_{nh}+C_2'$	D_{nh}	2,3,4,6	4
S_n+C_2'	D_{nd}	2,3	2
Cubic	no principal axis	$4C_3$	5

For molecules: any n (5,7,10...)

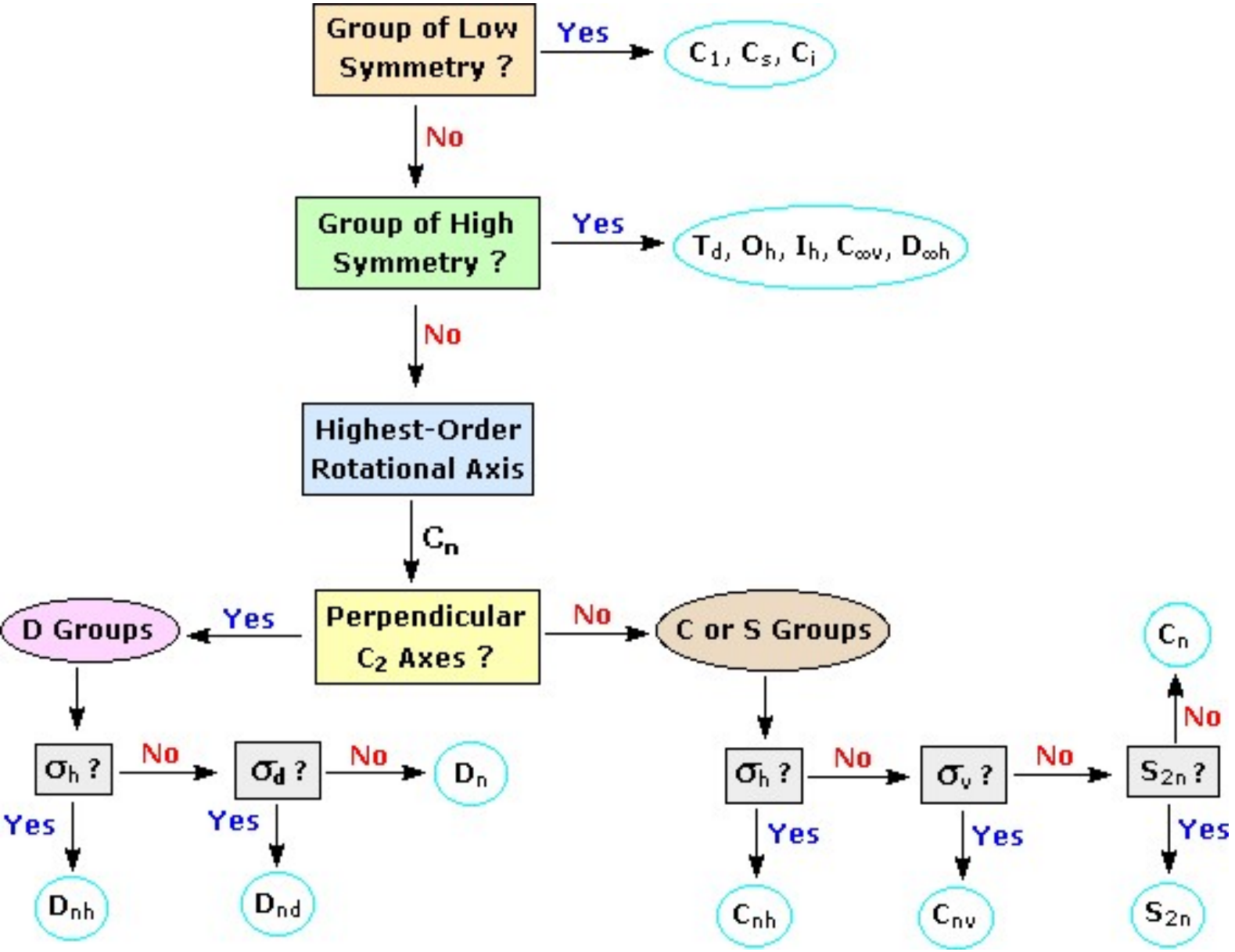
$C_{\infty v}$ (HCl), $D_{\infty h}$ (Cl_2), I_h (C_{60})

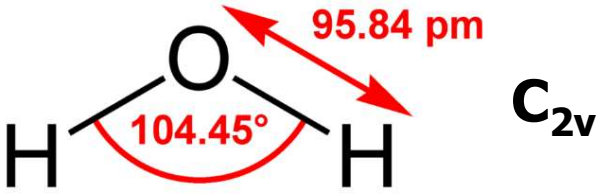
Point group determination



http://www.cem.msu.edu/~reusch/VirtualText/symmetry/symmtry.htm

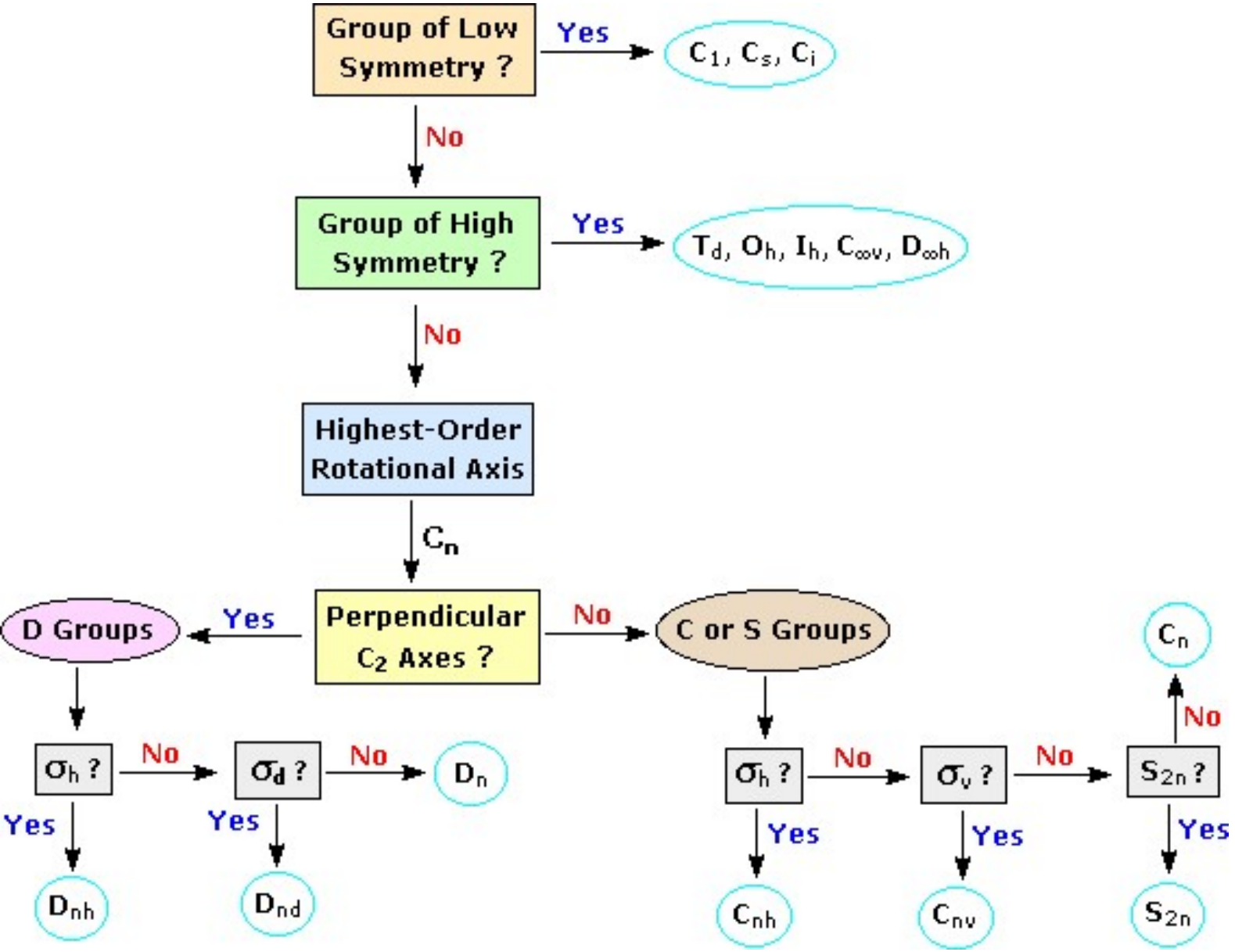
Point group determination

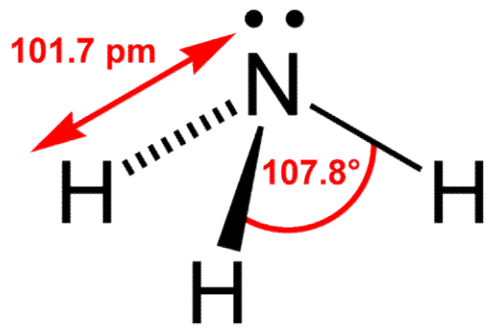




C_{2v}

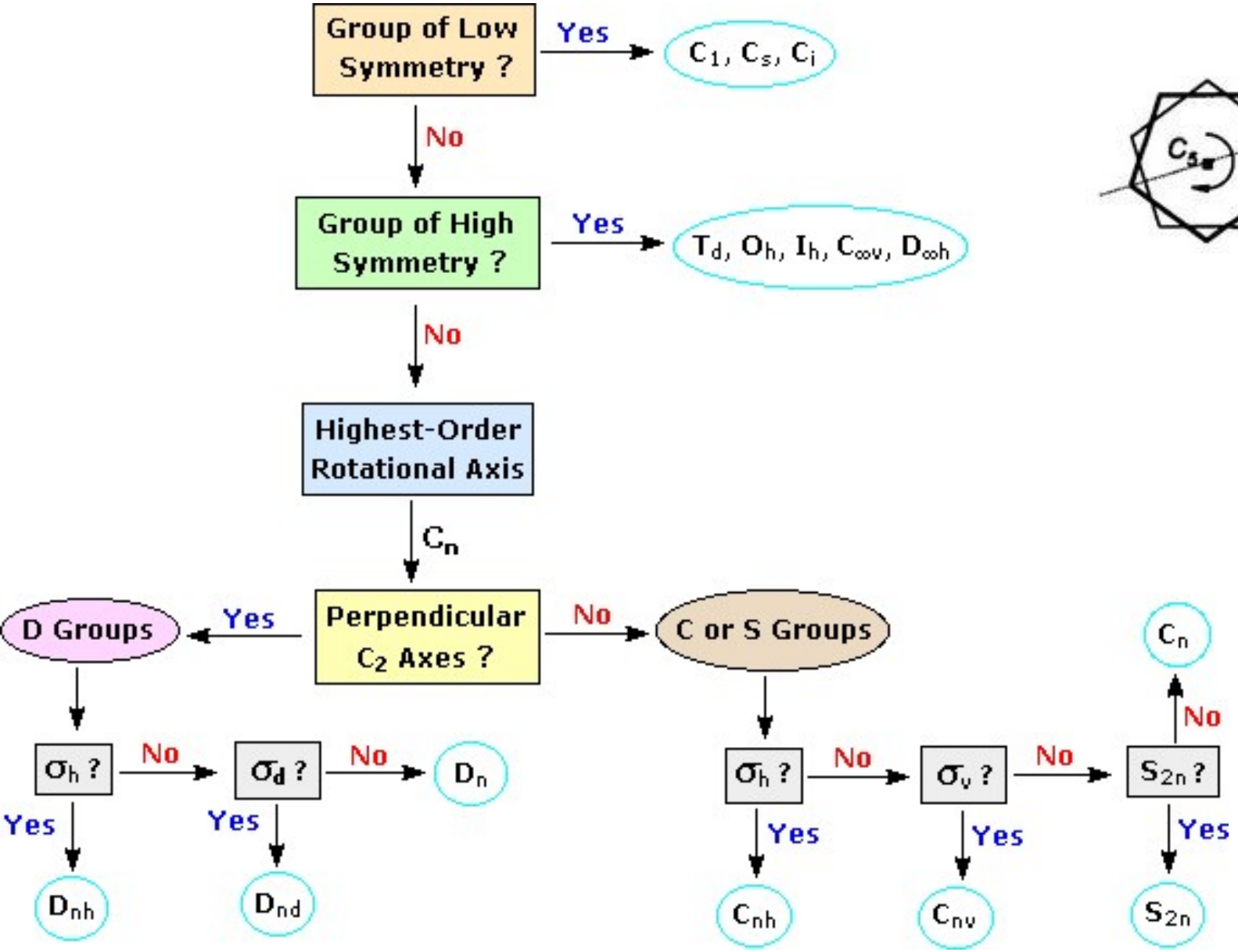
Point group determination

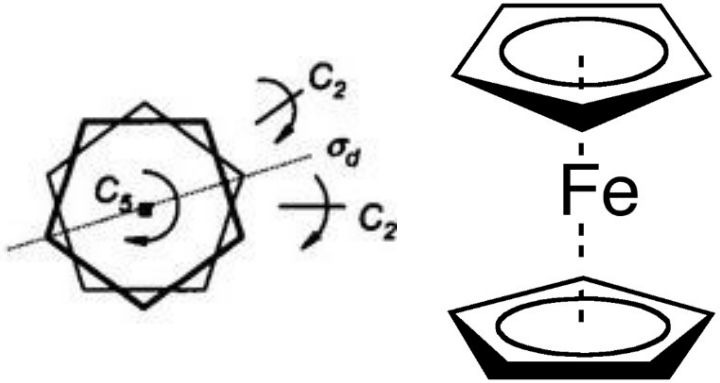




C_{3v}

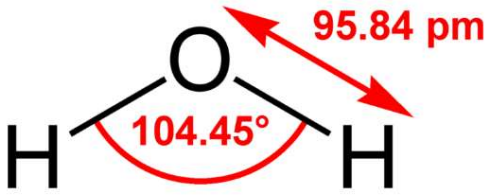
Point group determination



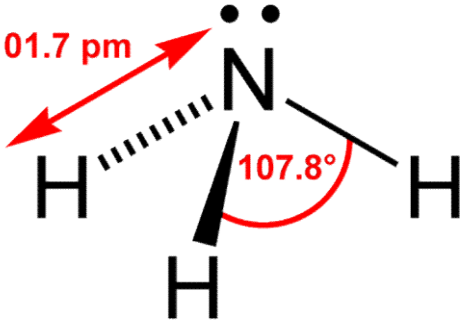


D_{5d}

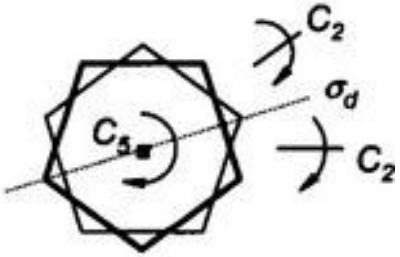
Examples

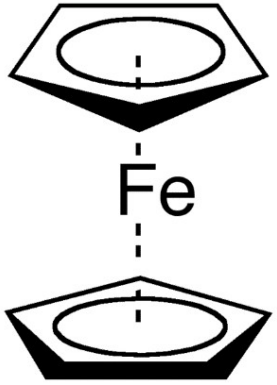


Water
C_{2v}



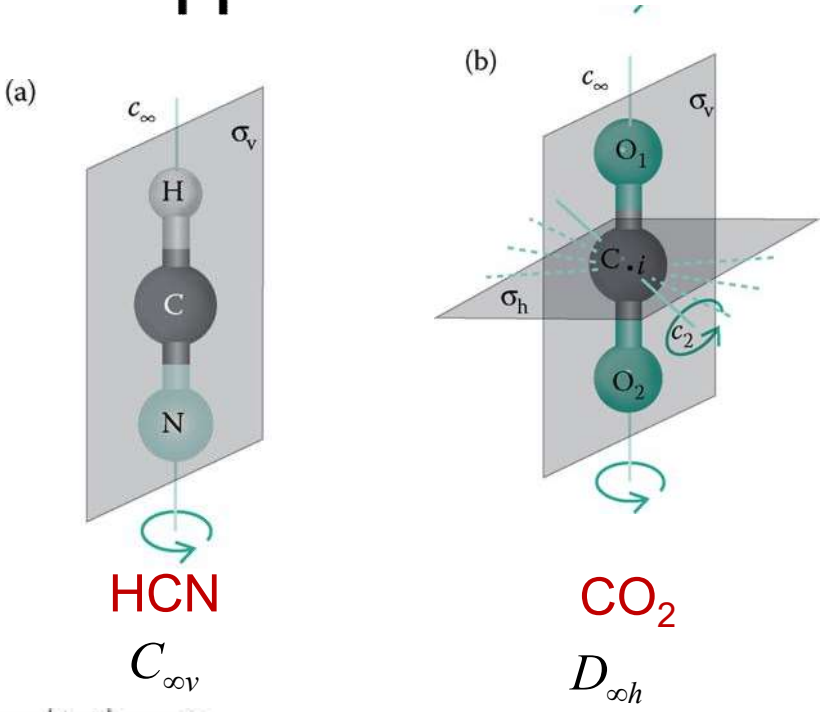
Ammonia
C_{3v}





Ferrocene
D_{5d}

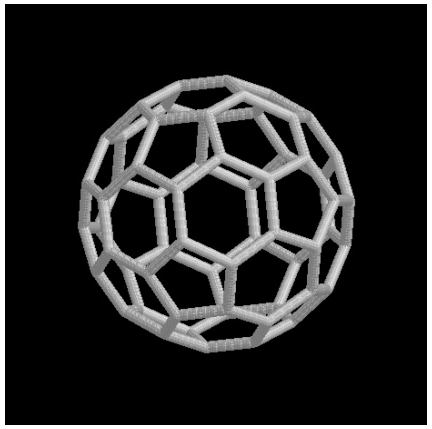
Source: Wikipedia



HCN
$C_{\infty v}$

CO_2
$D_{\infty h}$

Fullerene C_{60}
I_h



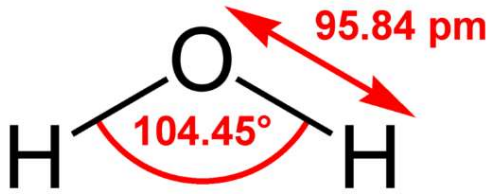
Representations

- Symmetry operations can be represented by matrices
- The trace of the matrices (*the character*) is invariant with respect to similarity transformations
- *Reducible representation:* matrices attain *block format* on a suitably chosen basis
- *Irreducible representation:* cannot be simplified (reduced) further
- *Character table:* characters of irreducible representations (*irreps*) by symmetry operation for individual point groups

Multiplication tables

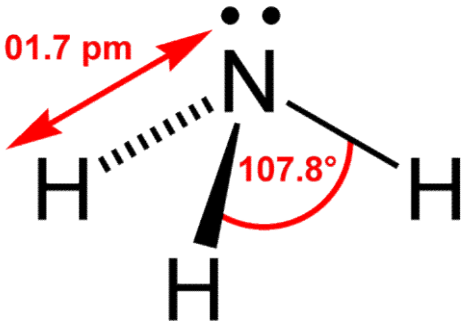
C_{2v}

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

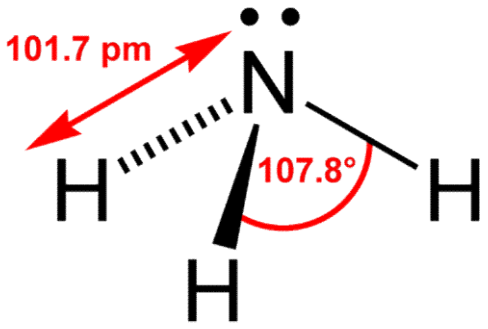


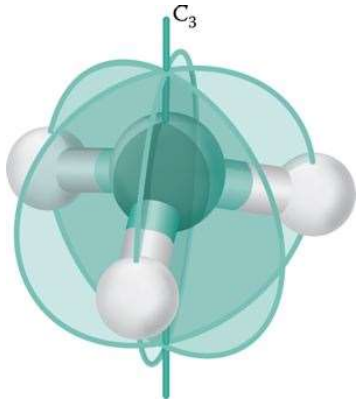
C_{3v}

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E



Representations - example: NH_3





$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Representation on r_1, r_2, r_3 basis:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} C_3^2 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\sigma_v' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \sigma_v'' = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \sigma_v''' = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Representation on Cartesian basis:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma_v'' = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma_v''' = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Character table:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

Great Orthogonality Theorem (GOT)
(Fundamentális ortogonalitási tétel (FOT))

$$\sum_R \Gamma_i(R)^*_{mn} \Gamma_j(R)_{op} = \frac{h}{l_i} \delta_{ij} \delta_{mo} \delta_{np}$$

where:
Γ_i, Γ_j are two non-equivalent irreducible representations
h is the order of the group (number of elements)
l_i is the dimension of the matrices

These relations for the characters follow from the GOT: $(\chi_R = \sum_k \Gamma_i(R)_{kk})$:

$$\sum_R \chi_i(R)^* \chi_j(R) = h \delta_{ij}$$

$$\sum_i l_i^2 = h$$

Reduction

Reduction of reducible representations: $\chi(R) = \sum_i n_i \chi_i(R)$

$\chi(R)$ being the character of the reducible representation, n_i the coefficient of the *i*th irrep

$$n_j = \frac{1}{h} \sum_R \chi_j(R)^* \chi(R)$$

$$C_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \longrightarrow C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(r_1, r_2, r_3) (x, y, z)

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ	3	0	1

$$\Gamma = \Gamma_1 \oplus \Gamma_3$$

Vibrational modes

Vibrational Hamiltonian:

$$H_{vib} = \sum_i H_i = \frac{1}{2}(-\hbar^2 \frac{\partial}{\partial q_i^2}) + \omega_i q_i^2)$$

q_i normal coordinates ⟶ ω_i eigenfrequencies

$$V = \frac{1}{2}\sum_i \omega_i^2 q_i^2$$

Neumann principle: V and ω_i show the symmetry of the point group

• non-degenerate case: $V \sim q_i^2, \qquad Rq_i = \pm q_i$

•degenerate case: $V \sim (q_j^2 + q_k^2 + q_l^2) \qquad R|q_j, q_k, q_l| \Rightarrow |\pm q_j, \pm q_k, \pm q_l|$

The normal coordinates form bases of the irreps of the point group; the dimension of the representation equals the degeneracy

Selection rules

IR: $\frac{\partial \mu}{\partial q} \neq 0$

$\mu_x \sim x$, $\mu_y \sim y$, $\mu_z \sim z$ are always basis functions for an irrep of the point group

Since basis functions of inequivalent representations are orthogonal, this selection rule means:
those vibrations are IR active, whose normal coordinate belongs to the same irrep as one of the x,y,z coordinates

Raman: $\frac{\partial \alpha}{\partial q} \neq 0$

$\alpha_{xx} \sim x^2$, $\alpha_{xy} \sim xy$,...and the products of the coordinates are also always basis functions for an irrep of the point group, this selection rule means:
those vibrations are Raman active whose normal coordinate belongs to the same irrep as one of the binary products of the x,y,z coordinates

Notation of irreps

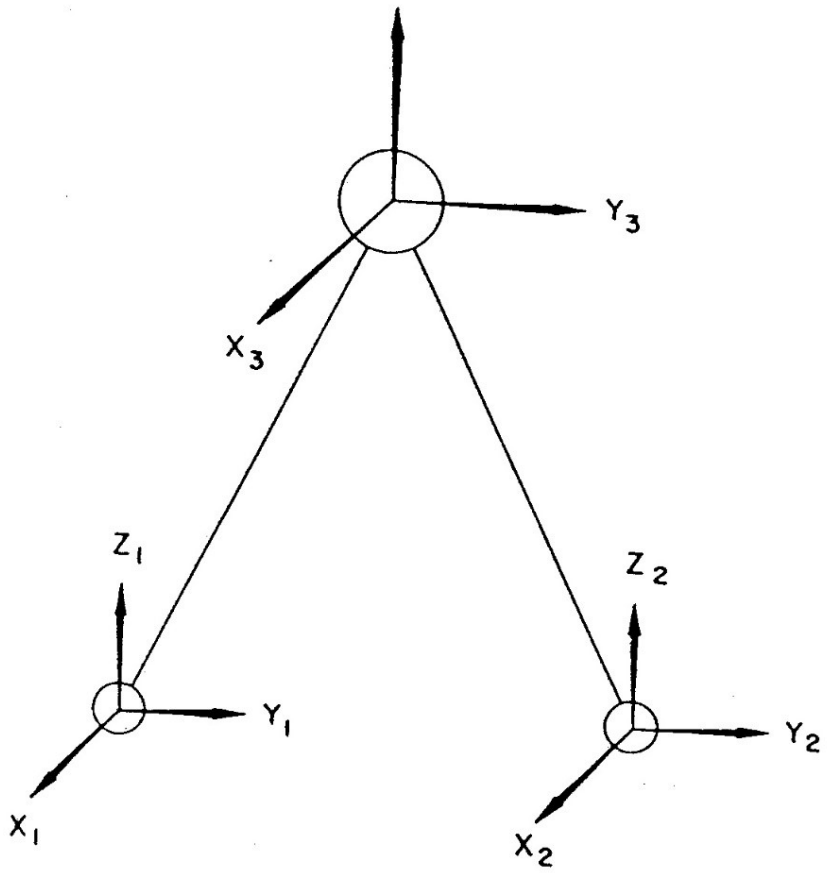
A, B 1-dimensional
E 2-dimensional
T (F) 3-dimensional
G 4-dimensional
H 5-dimensional

In point groups containing inversion:
Subscript g (gerade = even) or u (ungerade = odd)
refers to the character of *i* in the given irrep:
$\chi(i) > 0$ **g**, $\chi(i) < 0$ **u**

number in subscript is just a “serial number”

“Counting” of vibrational modes

H_2O



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_x, xy
B_1	1	-1	1	-1	x, R_x, xz
B_2	1	-1	-1	1	y, R_z, yz

Representation on a 3N-dimensional basis

$$C_2\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

$$\sigma_v(yz)\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

Character contributions of atoms situated on symmetry elements

R	$\chi(R)$	R	$\chi(R)$
C_n^k	$1+2\cos(2\pi k/n)$	S_n^k	$-1+2\cos(2\pi k/n)$
$E=C_1^k$	3	$\sigma=S_1^1$	1
C_2^1	-1	$i=S_2^1$	-3
C_3^1, C_3^2	0	S_3^1, S_3^5	-2
C_4^1, C_4^3	1	S_4^1, S_4^3	-1
C_6^1, C_6^5	2	S_6^1, S_6^5	0

Reduction

$$n_j = \frac{1}{h}\sum_R \chi_j(R)^* \chi(R)$$

For water, $\chi_r(E) = 9$, $\chi_r(C_2) = -1$, $\chi_r(\sigma_{xz}) = 1$, $\chi_r(\sigma_{yz}) = 3$.
Applying the reduction formula and using the character table:

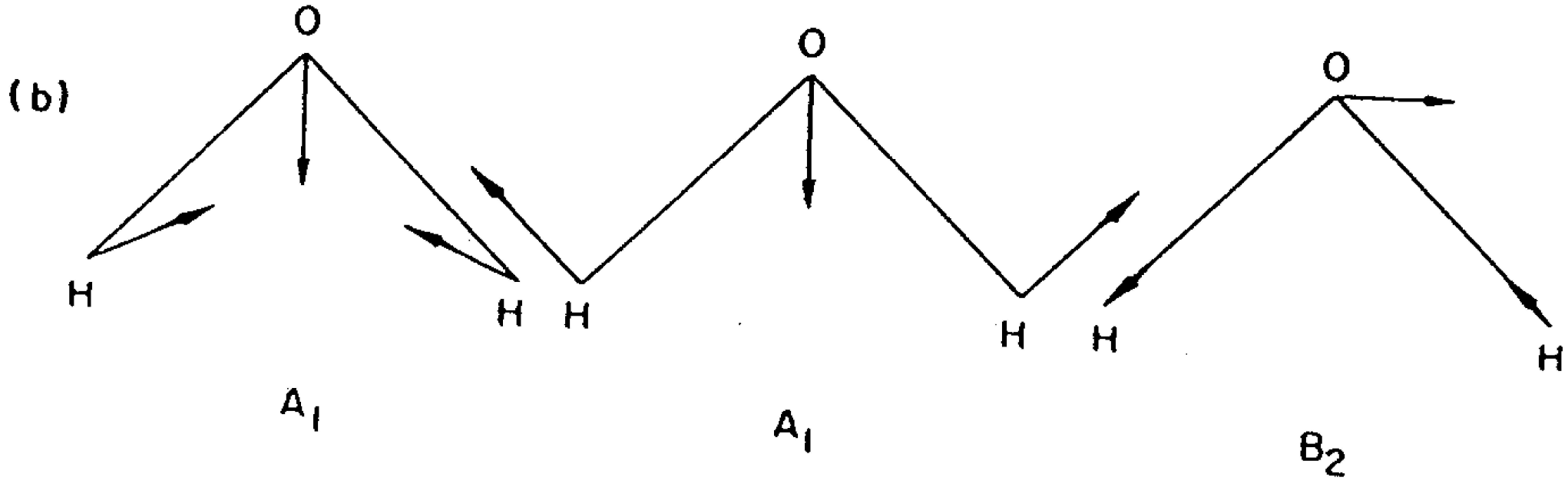
$n(A_1) = 3$, $n(A_2) = 1$, $n(B_1) = 2$, $n(B_2) = 3$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
n	3	1	1	3
Γ	9	-1	1	3

Vibrational modes: $\Gamma = 2A_1 \oplus B_2$

Normal vibrations of the water molecule



C_{60}, the truncated icosahedron

http://www.seed.slb.com/en/scictr/watch/fullerenes2/saved.htm

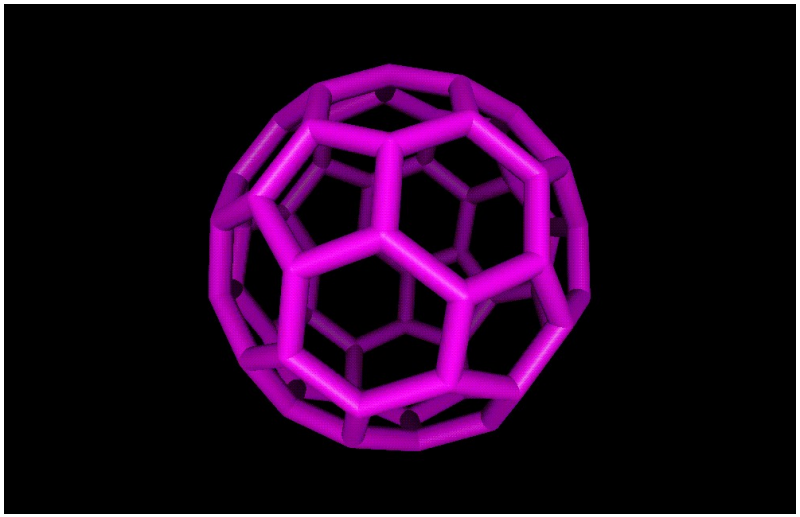
Vibrational modes of C_{60}

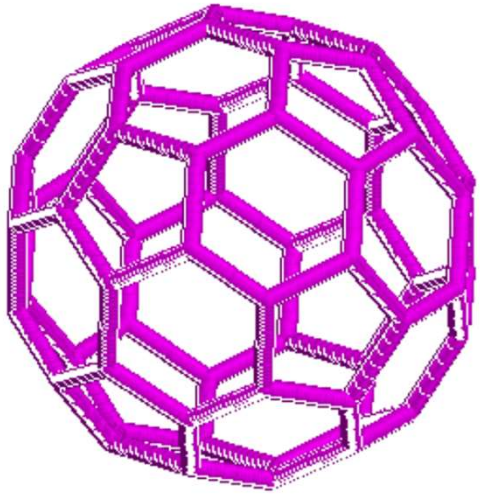
C_{60}

Character table:

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma_d$	
A_g	1	1	1	1	1	1	1	1	1	1	Raman
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
F_{1g}	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	rot
F_{1u}	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	-3	$-\frac{(1-\sqrt{5})}{2}$	$-\frac{(1+\sqrt{5})}{2}$	0	1	IR
F_{2g}	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	
F_{2u}	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	-3	$-\frac{(1+\sqrt{5})}{2}$	$-\frac{(1-\sqrt{5})}{2}$	0	1	
G_{1g}	4	-1	-1	1	0	4	-1	-1	1	0	
G_{1u}	4	-1	-1	1	0	-4	1	1	-1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	Raman
H_u	5	0	0	-1	1	-5	0	0	1	-1	

How many atoms are left in place?





Characters and reduction of 3N dimensional representation

Counting of C_{60} vibrational modes:

Characters of representation defined by Cartesian unit vectors on atoms:

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma_d$
$\chi_\Gamma(R)$	180	0	0	0	0	0	0	0	0	4

From here, using the reduction formula, we get for the A_g mode:

$n(A_g) = 1/120(1*180) - 12(1*0) + 12(1*0) + 20(1*0) + 15(1*0) + 1*0 + 12(1*0) + 20(1*0) + 15(1*4) = 2$

The final result of the reduction is:

$$\Gamma = 2A_g \oplus 4T_{1g} \oplus 4T_{2g} \oplus 6G_g \oplus 8H_g \oplus 1A_u \oplus 5T_{1u} \oplus 5T_{2u} \oplus 6G_u \oplus 7H_u$$

Estimation of the number of vibrations

IR $\frac{\partial \mu}{\partial Q} \neq 0$ Raman $\frac{\partial \alpha}{\partial Q} \neq 0$

3N – 6 degrees of freedom

↓

degeneration

↓

selection rules ⇔ IR, Raman, silent

Principle of mutual exclusion:
if the molecule possesses an inversion center, IR-active modes are not Raman active and vice versa

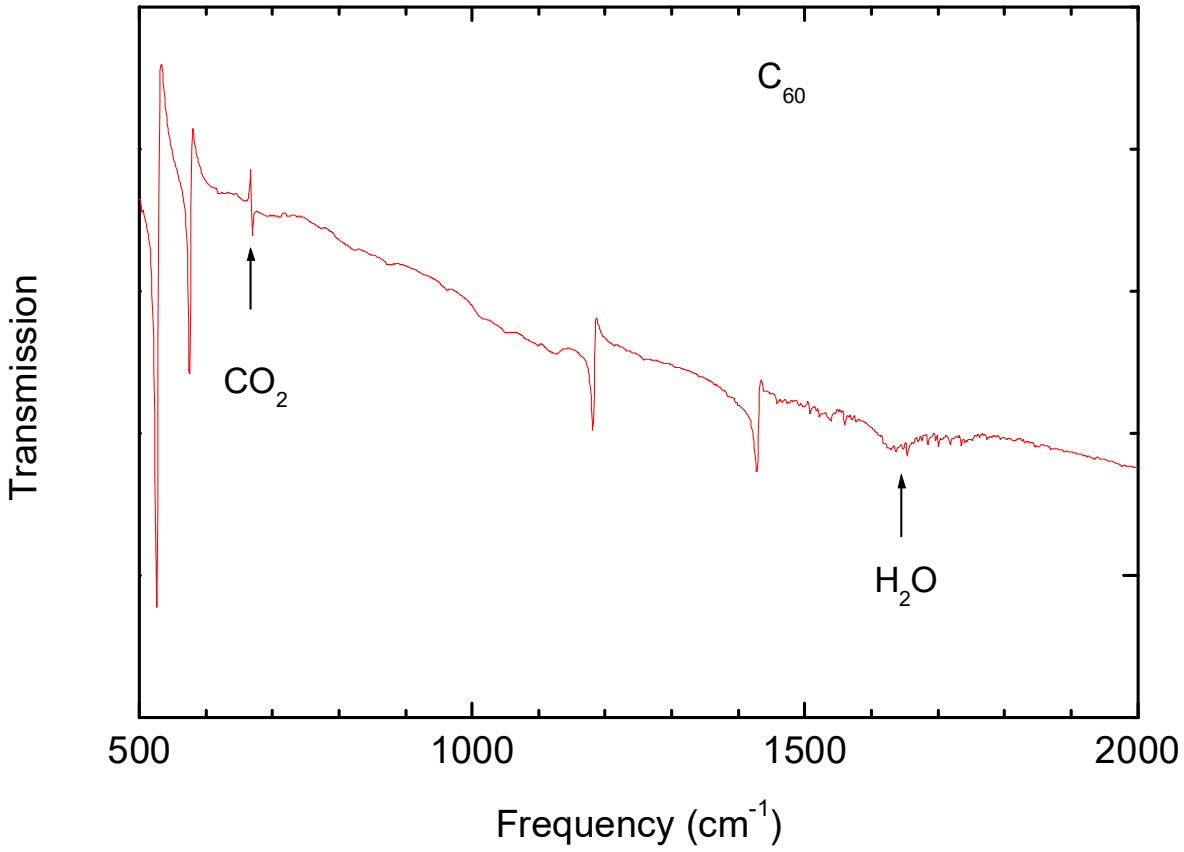
i: $\mu \rightarrow -\mu$ (u)

$\alpha \rightarrow \alpha$ (g)

odd *(ungerade)* and even *(gerade)* modes are orthogonal

Symmetry analysis gives the maximum number of spectral lines
(it can decrease by incidental degeneration, intensity below detection threshold)

Infrared spectrum of C_{60}



Take-home message

- Point group: set of symmetry operations leaving at least one point in the object fixed
- Symmetry operations form a group in the mathematical sense
- Matrix representations – reducible, irreducible
- Starting from the molecular structure, using the character tables and the reduction formula, the number of vibrational modes can be predicted
- IR and Raman activity:
  symmetry analysis – selection rules – principle of mutual exclusion

Összefoglalás

- Pontcsoport: azon szimmetriaműveletek halmaza, amik egy objektumban legalább egy pontot mozdulatlanul hagynak
- A szimmetriaműveletek matematikai értelemben csoportot alkotnak
- A szimmetriaműveletek mátrixokkal ábrázolhatók – reducibilis, irreducibilis
- A szerkezetből kiindulva, a karaktertáblák és a redukciós formula alkalmazásával a rezgési módusok száma meghatározható
- IR és Raman-aktív módusok:
  szimmetria-analízis – kiválasztási szabályok – kölcsönös kizárás elve