

# Optical spectroscopy in materials science 7. Symmetry and selection rules in vibrational spectroscopy

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# 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:

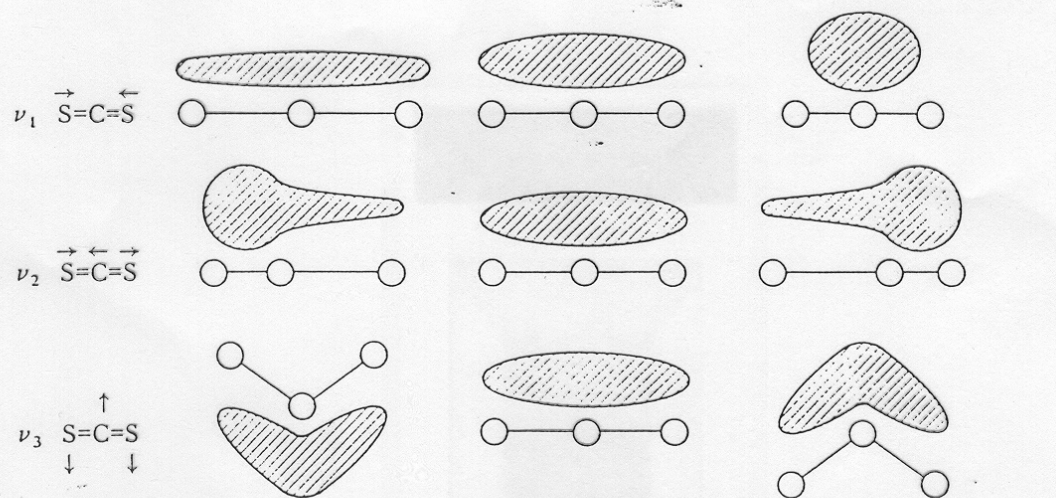
IR  $\frac{\partial \mu}{\partial Q} \neq 0$

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

Q normal coordinate, also for more complicated vibrations

Example: CS<sub>2</sub>

normal vibrations



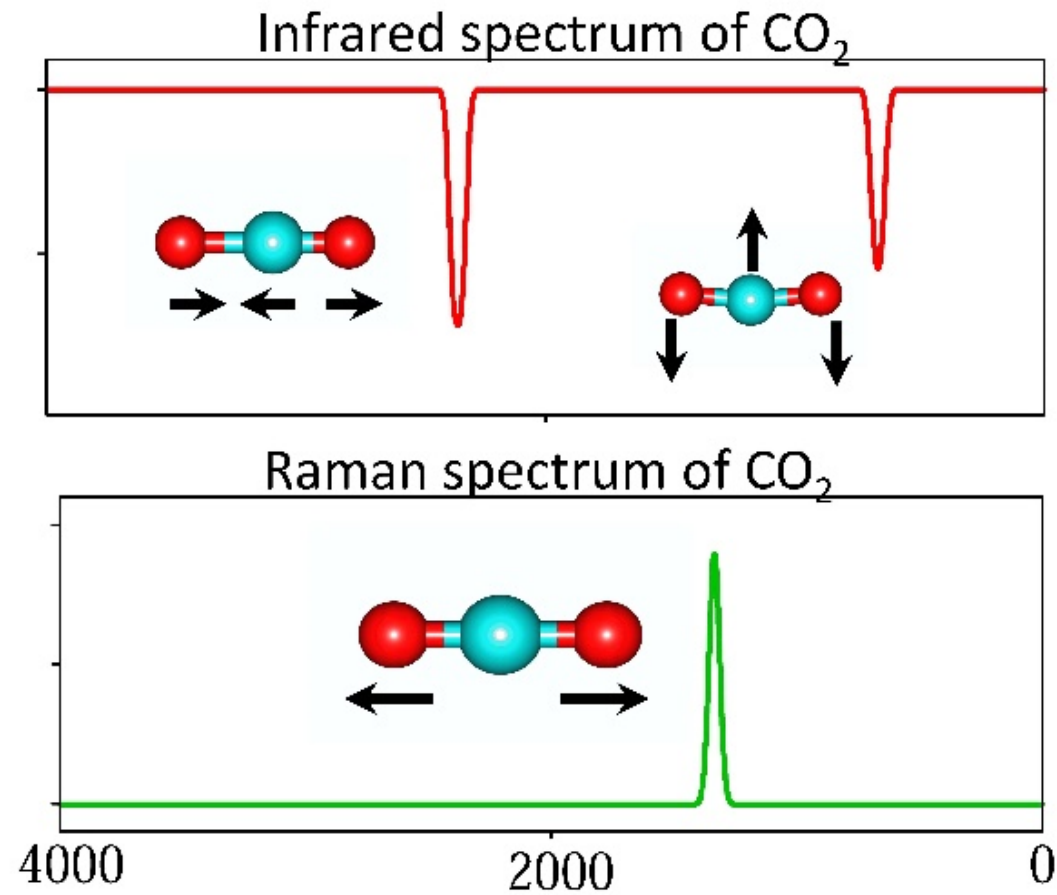
symmetric stretch

asymmetric stretch

bend

Fig. 5.2 Vibrations of carbon disulfide and accompanying changes in polarizability. Bending vibration  $\nu_3$  is degenerate, the other  $\nu_4$  being perpendicular to the paper plane.

# Vibrational spectra of CO<sub>2</sub>

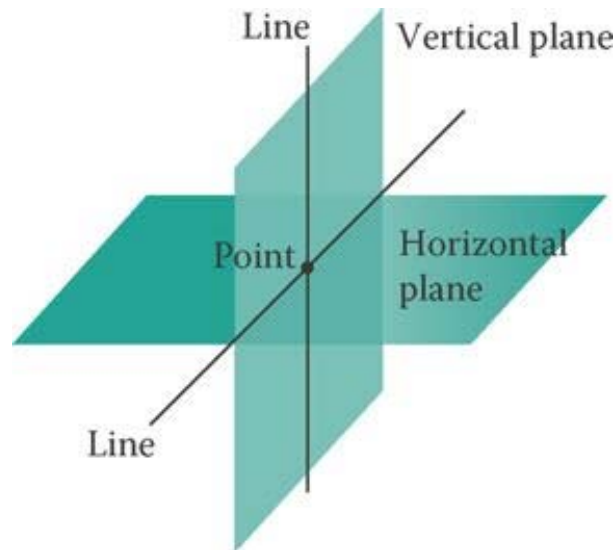


<https://scilearn.sydney.edu.au/fychemistry/chem2401/Lecture%209.pdf>

# 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

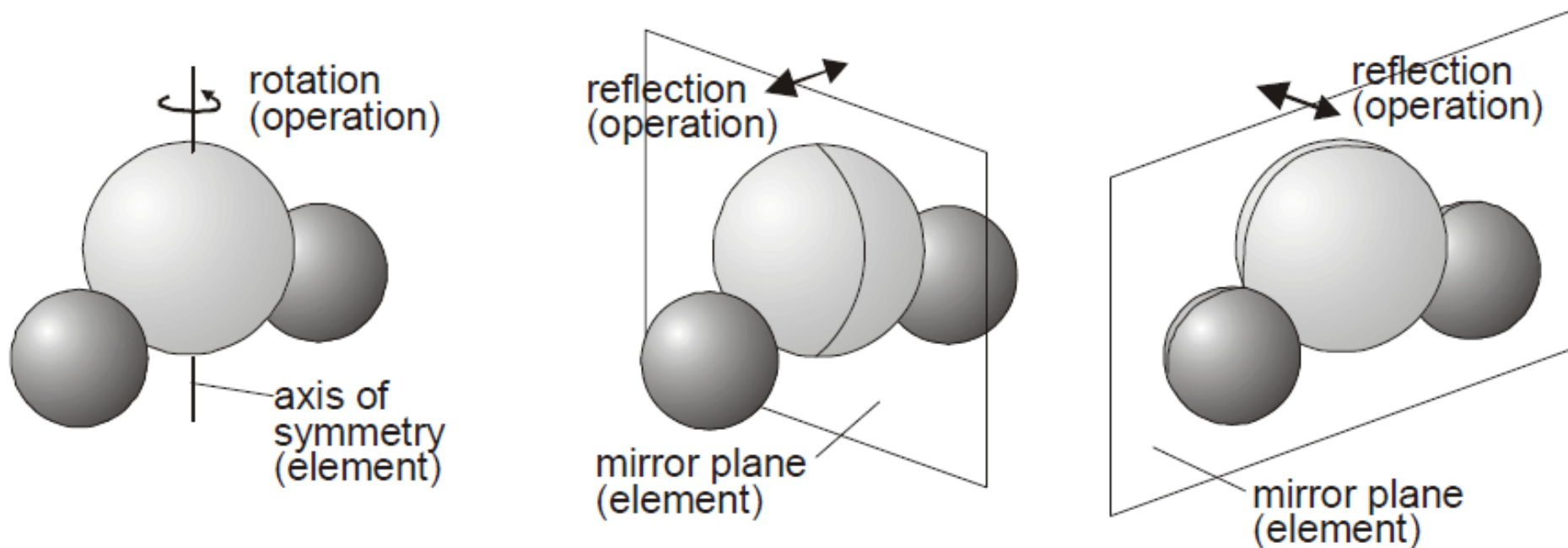
## Symmetry point group:

*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  $n$
- $\sigma$ : mirror plane
  - $\sigma_v$ : vertical
  - $\sigma_h$ : horizontal
  - $\sigma_d$ : diagonal (dihedral) vertical, bisects two  $C_2$  axes perpendicular to principal axis
- $S_n^m$ : improper rotation ( $C_n^m$ , then  $\sigma_h$ ) rotation-reflection
- $i$ : inversion center



[https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Book%3A\\_Symmetry\\_\(Vallance\)](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:**

$$AB \in G$$

$$A(BC) = (AB)C$$

$$E \in G$$

$$A^{-1}A = E, A \in G, A^{-1} \in G$$

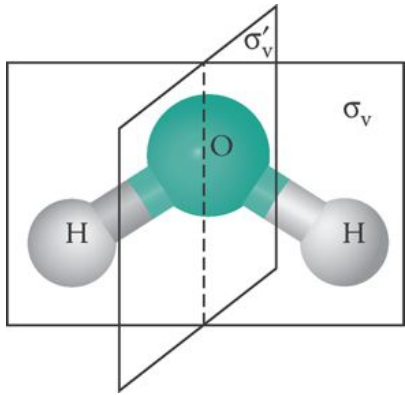
closed

associative

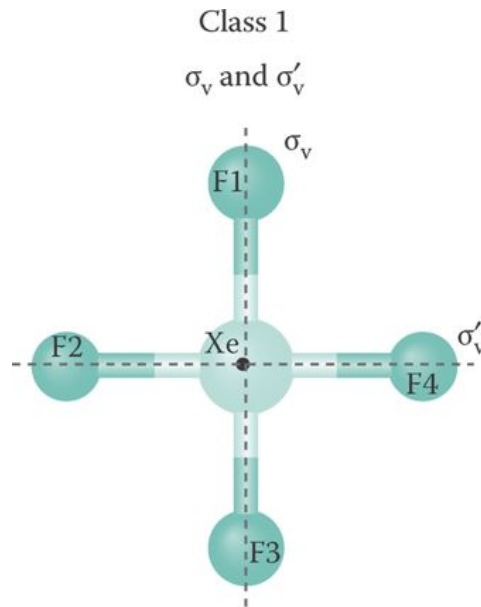
contains identity element

contains inverse element

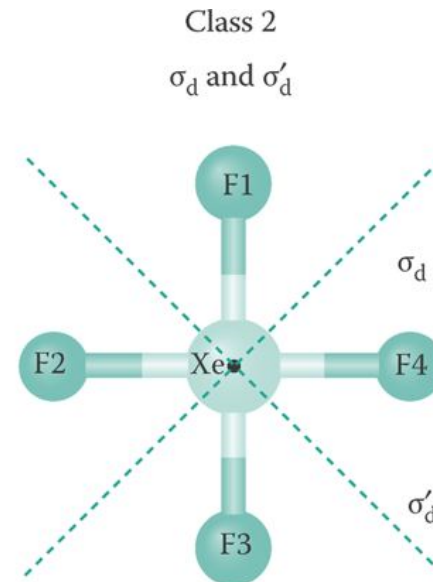
# Reflection planes



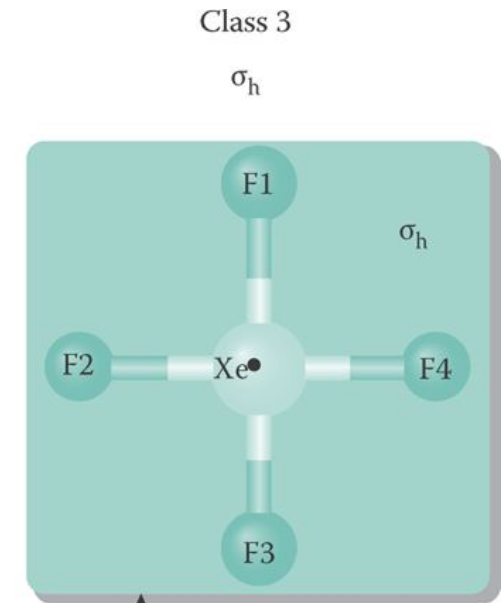
Water  
2 reflection planes



Vertical reflection planes



Dihedral reflection planes



$\sigma_h$  passes through all the atoms

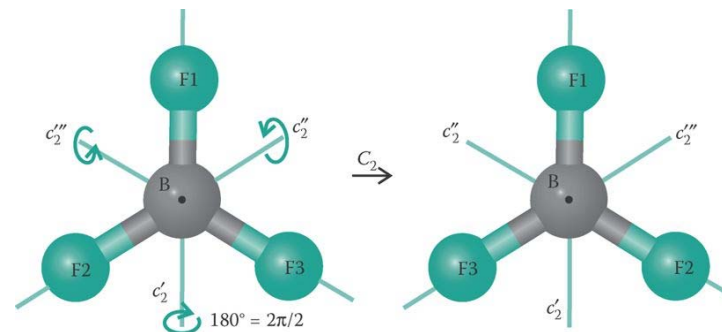
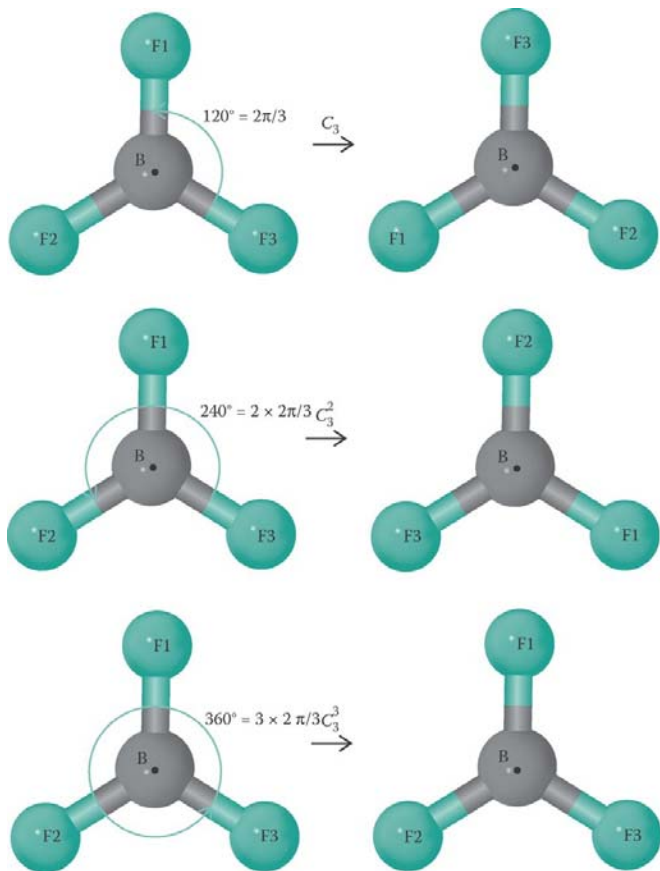
Horizontal reflection plane



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

# Proper rotations

**BF<sub>3</sub>: principal axis C<sub>3</sub>**



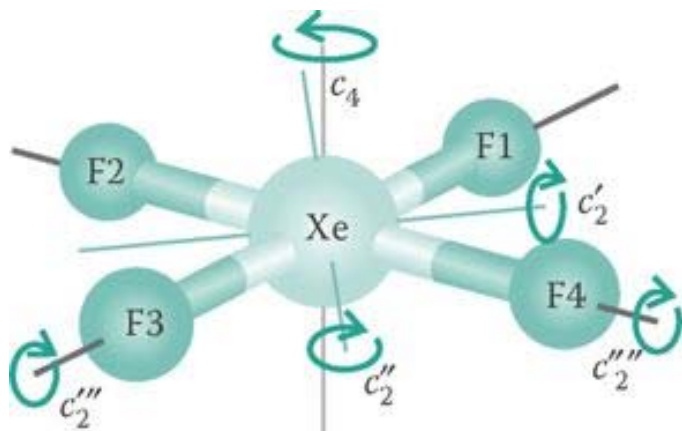
**C<sub>2</sub> axes are generated from each other by C<sub>3</sub>**



# Proper rotations for higher axes

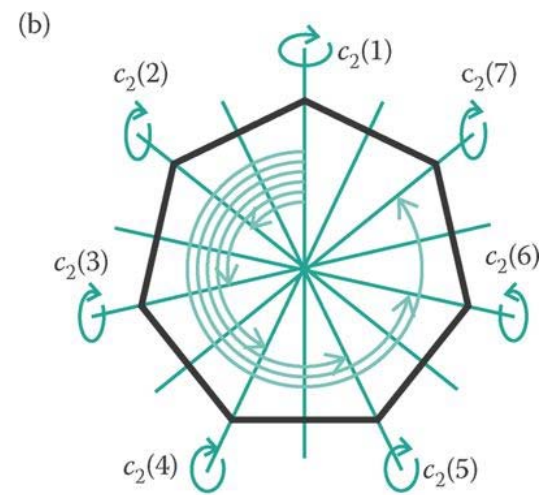
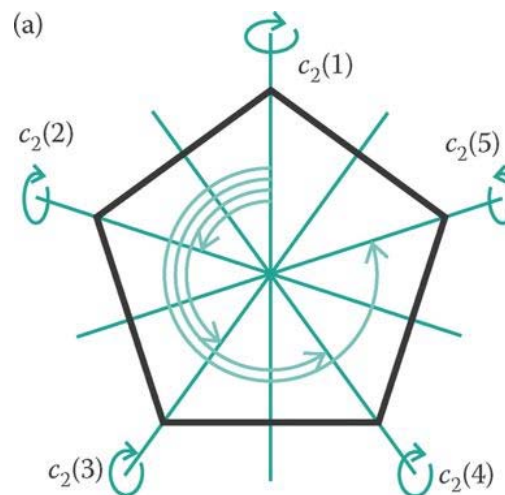
**n even**

**XeF<sub>4</sub>: principal axis C<sub>4</sub>**



**two types of C<sub>2</sub> axes**

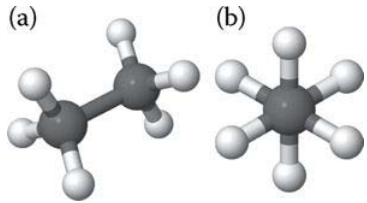
**n odd**



**one type of C<sub>2</sub> axis**

# Improper rotations

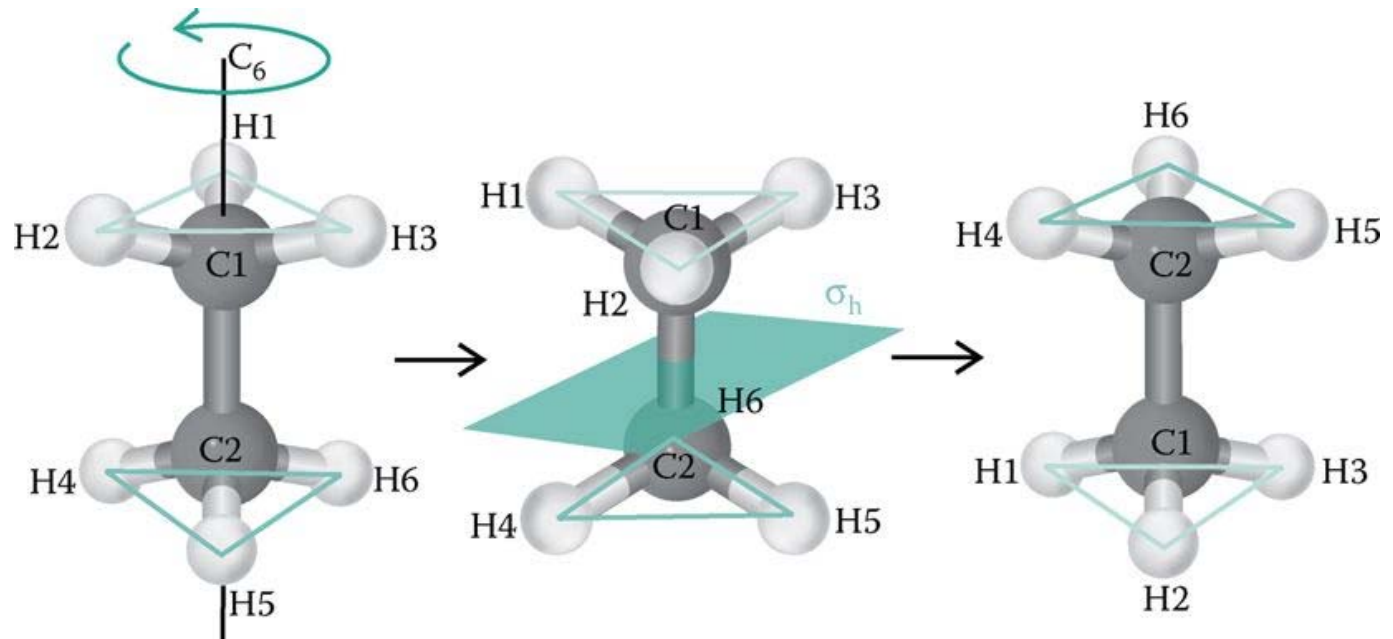
## Ethane $C_2H_6$



Side view

Top view

$S_6$



Intermediate configuration

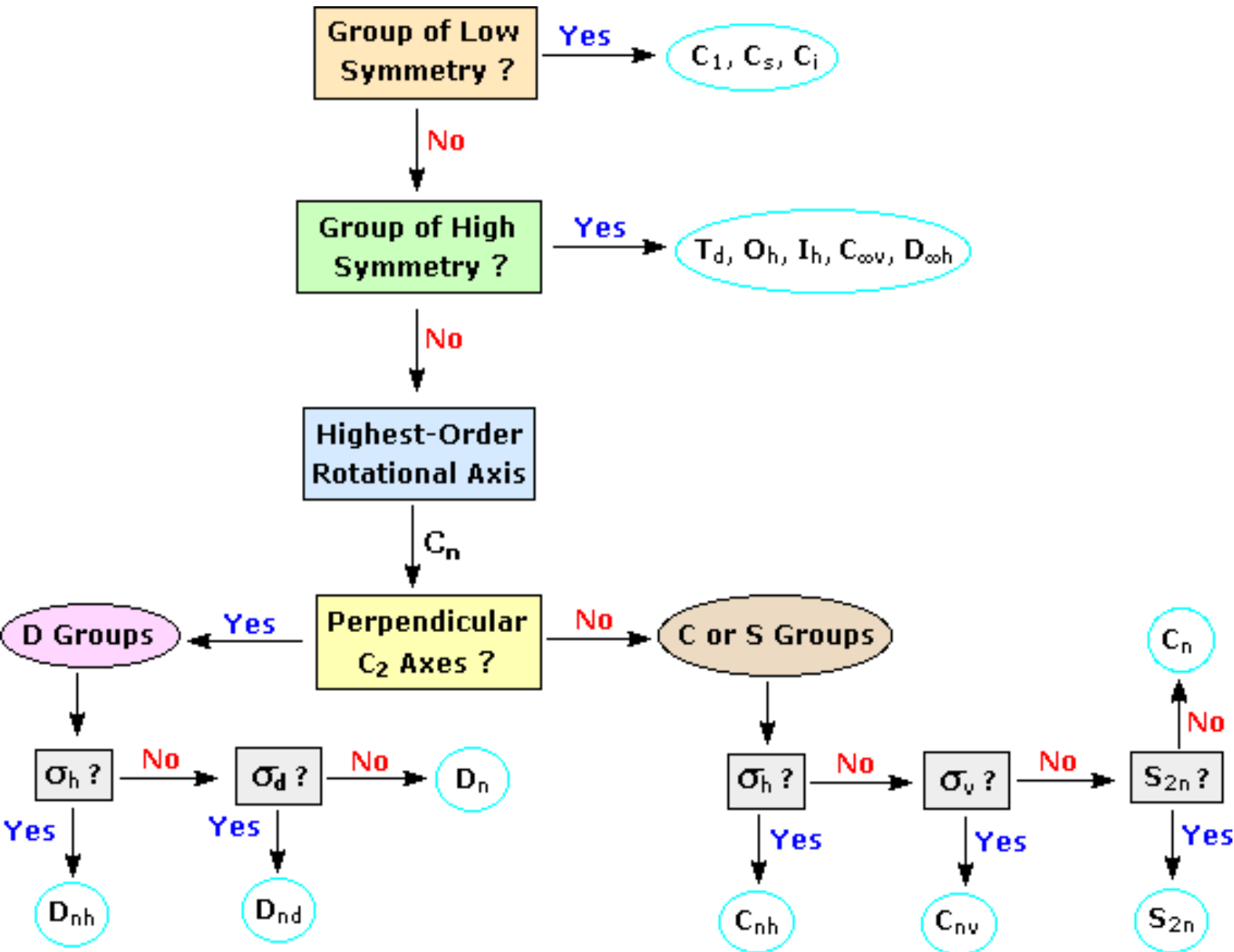
# Crystallographic point groups

	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...)

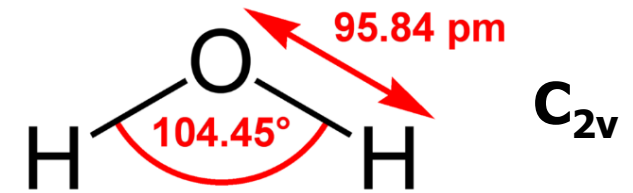
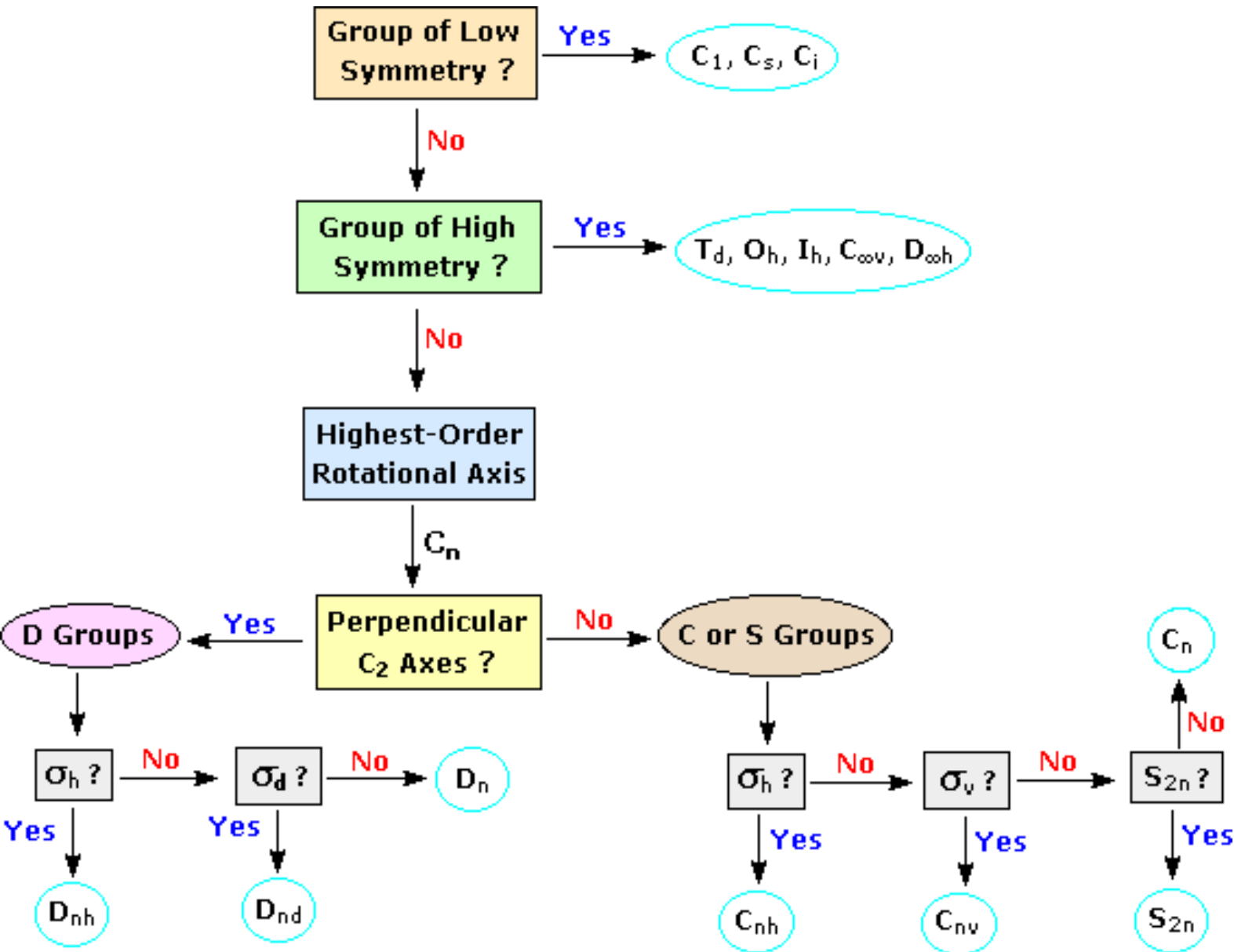
$C_{\infty v}$  (HCl),  $D_{\infty h}$  (Cl<sub>2</sub>),  $I_h$  (C<sub>60</sub>)

# Point group determination

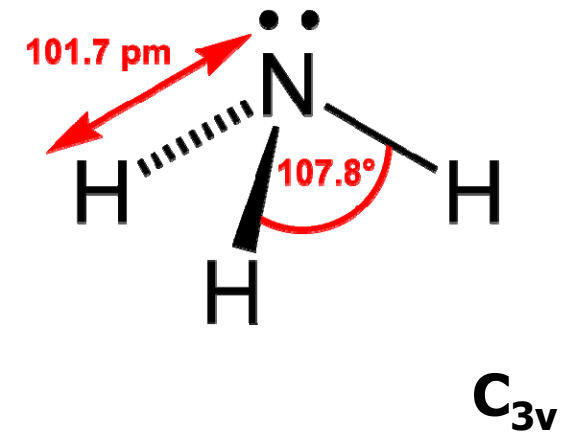
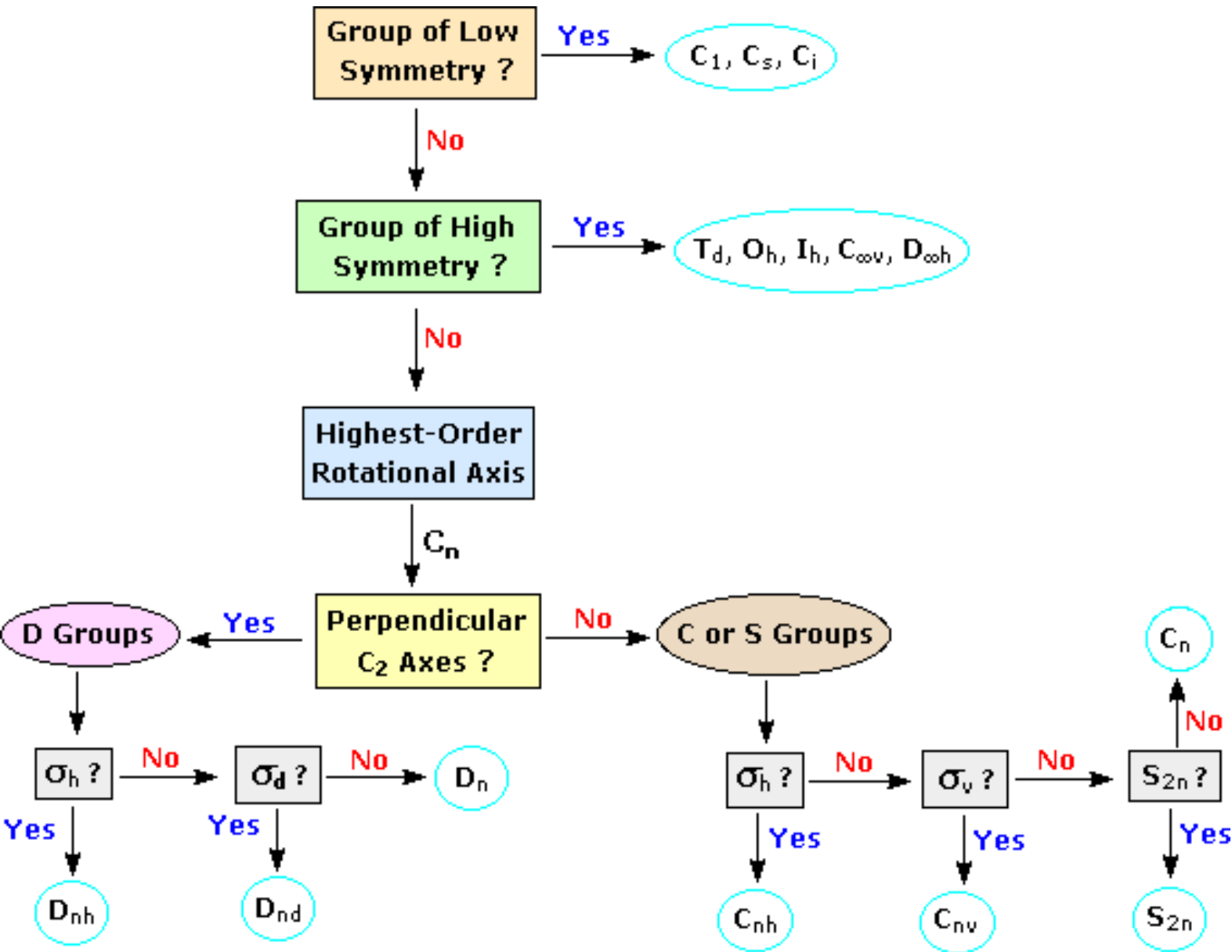


<http://www.cem.msu.edu/~reusch/VirtualText/symmetry/symmetry.htm>

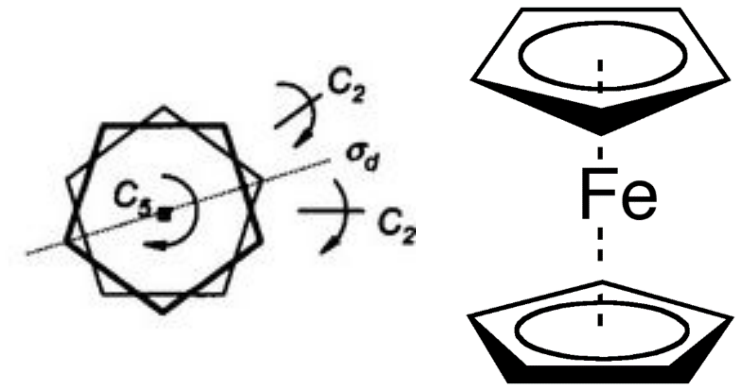
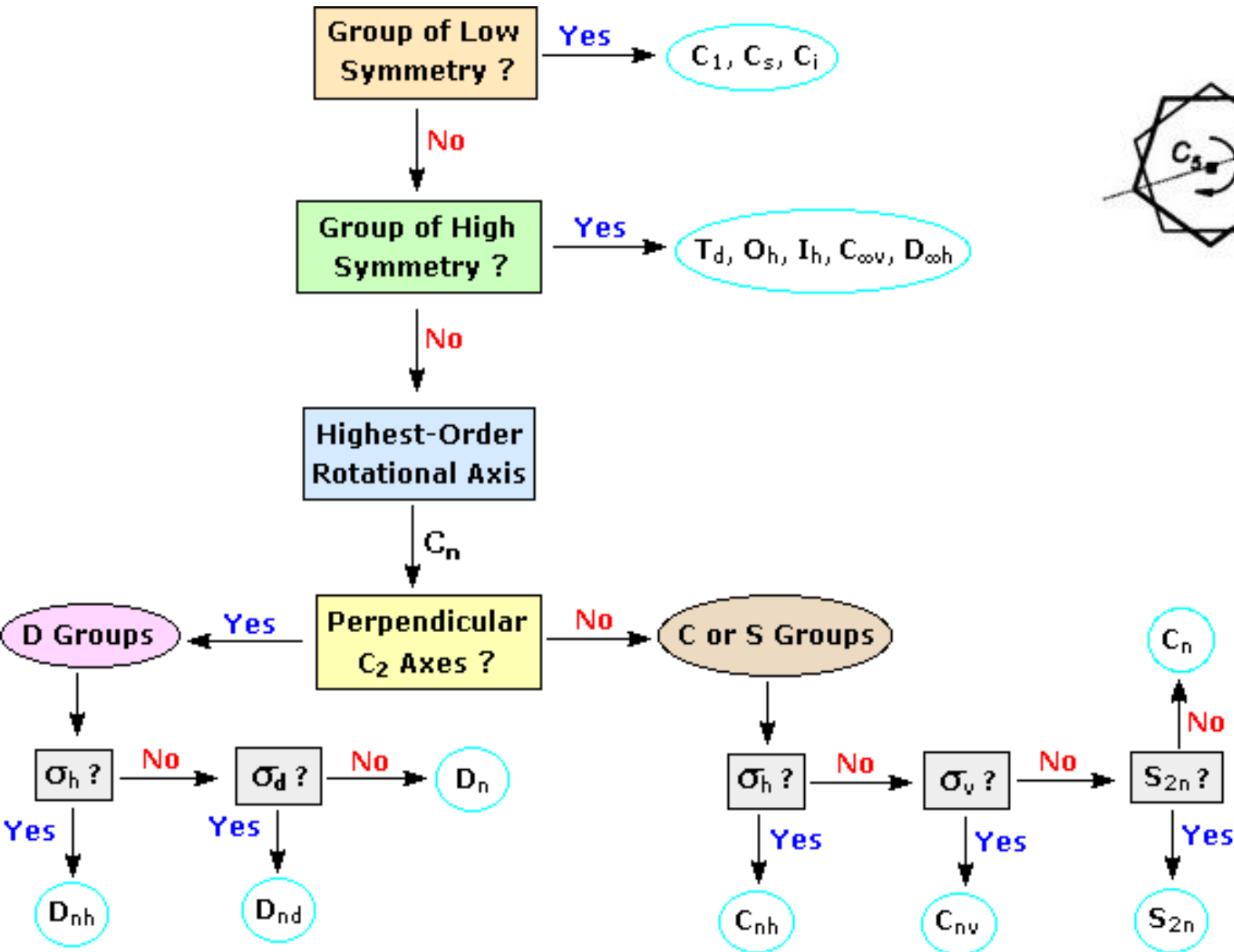
# Point group determination



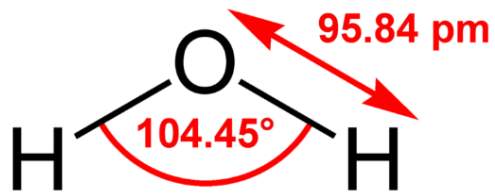
# Point group determination



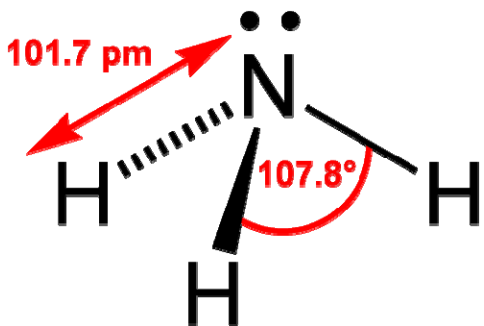
# Point group determination



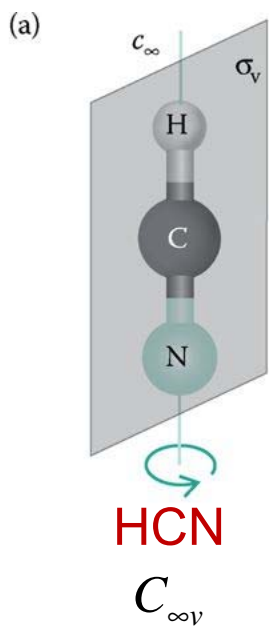
**D<sub>5d</sub>**



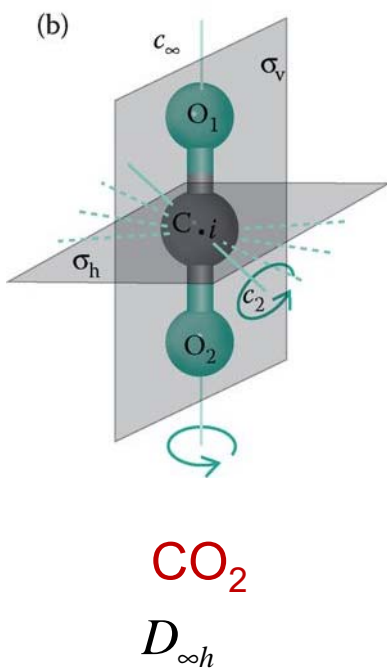
Water  
 $C_{2v}$



Ammonia  
 $C_{3v}$

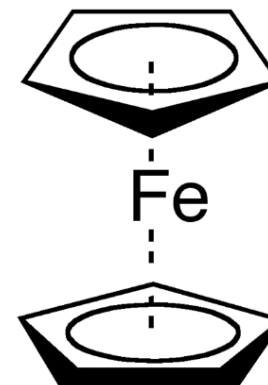
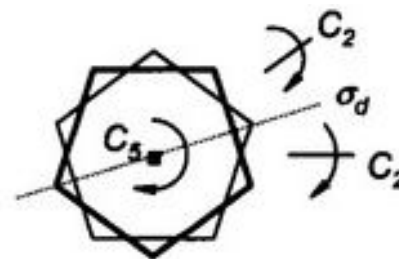


$\text{HCN}$   
 $C_{\infty v}$



$\text{CO}_2$   
 $D_{\infty h}$

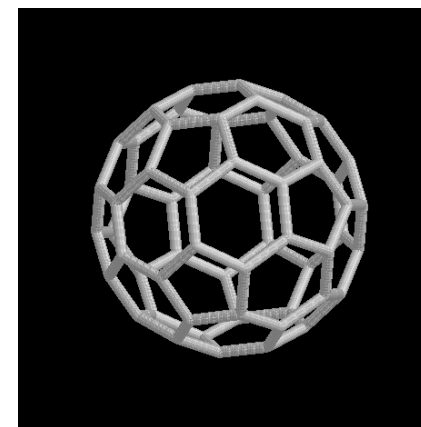
## Examples



Ferrocene  
 $D_{5d}$

Source: Wikipedia

Fullerene  $C_{60}$   
 $I_h$





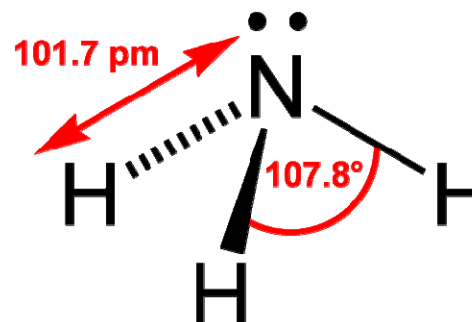
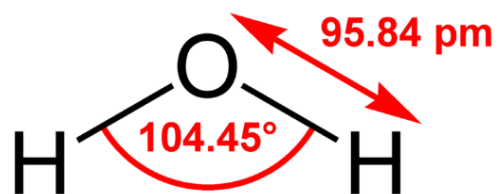
# Multiplication tables

$C_{2v}$

$C_{2v}$	$E$	$C_2$	$\sigma_v$	$\sigma_v'$
$E$	$E$	$C_2$	$\sigma_v$	$\sigma_v'$
$C_2$	$C_2$	$E$	$\sigma_v'$	$\sigma_v$
$\sigma_v$	$\sigma_v$	$\sigma_v'$	$E$	$C_2$
$\sigma_v'$	$\sigma_v'$	$\sigma_v$	$C_2$	$E$

$C_{3v}$

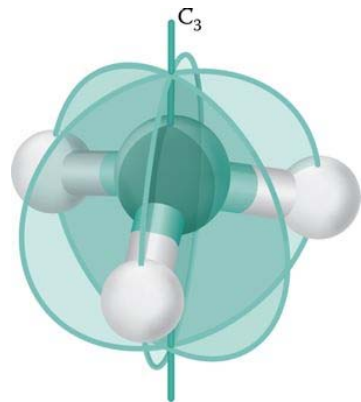
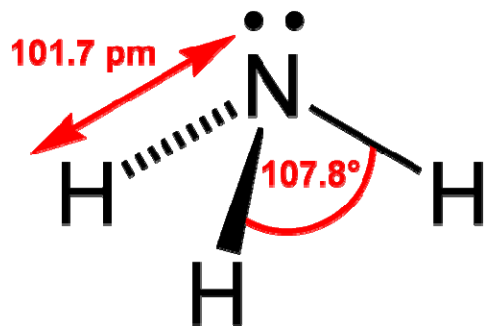
$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
$E$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
$C_3$	$C_3$	$C_3^2$	$E$	$\sigma_v''$	$\sigma_v$	$\sigma_v'$
$C_3^2$	$C_3^2$	$E$	$C_3$	$\sigma_v'$	$\sigma_v$	$\sigma_v''$
$\sigma_v$	$\sigma_v$	$\sigma_v''$	$\sigma_v'$	$E$	$C_3^2$	$C_3$
$\sigma_v'$	$\sigma_v'$	$\sigma_v$	$\sigma_v''$	$C_3$	$E$	$C_3^2$
$\sigma_v''$	$\sigma_v''$	$\sigma_v'$	$\sigma_v$	$C_3^2$	$C_3$	$E$



# 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

# Representations - example: NH<sub>3</sub>



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

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	$2C_3$	$3\sigma_v$
$\Gamma_1$	1	1	1
$\Gamma_2$	1	1	-1
$\Gamma_3$	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:

$\Gamma_i, \Gamma_j$  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

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

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

$(r_1, r_2, r_3)$

$(x, y, z)$

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

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$\Gamma_1$	1	1	1
$\Gamma_2$	1	1	-1
$\Gamma_3$	2	-1	0
$\Gamma$	3	0	1

# Vibrational modes

## Vibrational Hamiltonian:

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

$q_i$  normal coordinates  $\longrightarrow$   $\omega_i$  eigenfrequencies

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

*Neumann principle:*  $V$  and  $\omega_i$  show the symmetry of the point group

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

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

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

# Selection rules

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

$\mu_x \sim x$ ,  $\mu_y \sim y$ ,  $\mu_z \sim z$  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*

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

$\alpha_{xx} \sim x^2$ ,  $\alpha_{xy} \sim xy$ ,...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:

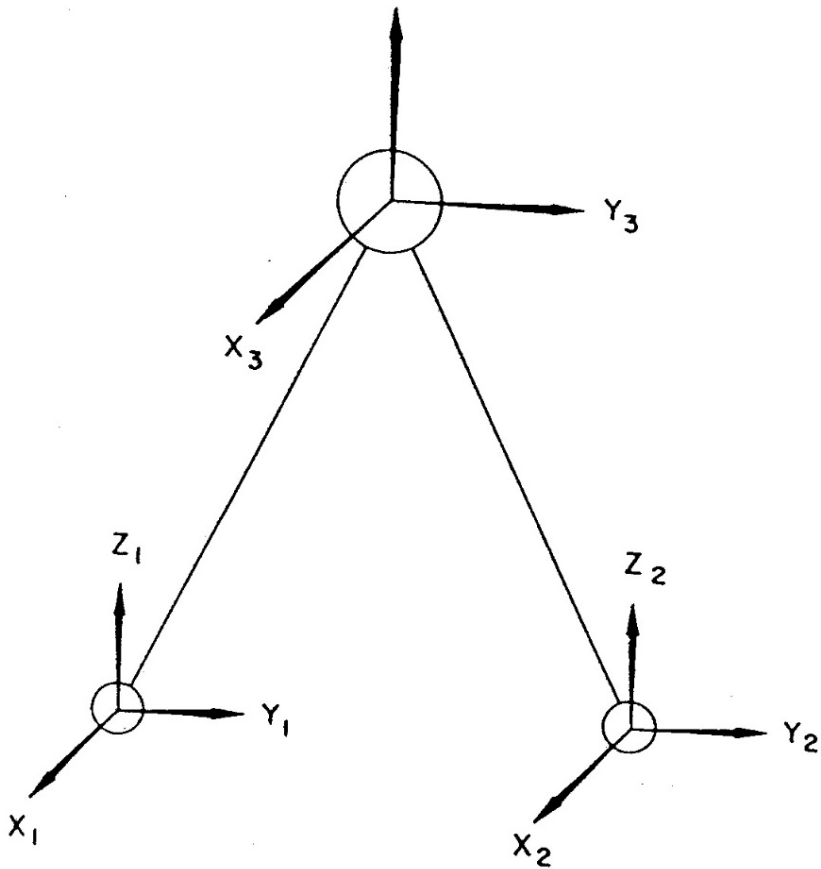
$$\chi(i) > 0 \text{ g}, \chi(i) < 0 \text{ u}$$

number in subscript is just a “serial number”



# “Counting” of vibrational modes

H<sub>2</sub>O



$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$	
$A_1$	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:

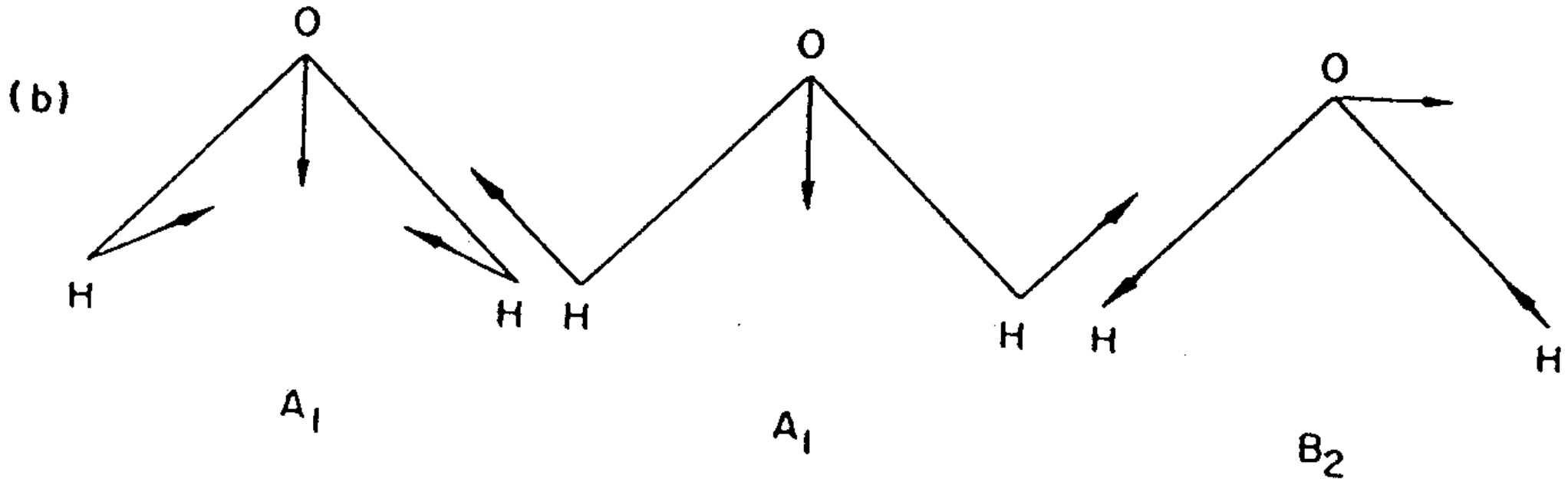
$$n(A_1) = 3, \quad n(A_2) = 1, \quad n(B_1) = 2, \quad n(B_2) = 3$$

$C_{2v}$	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	$y, R_x, yz$

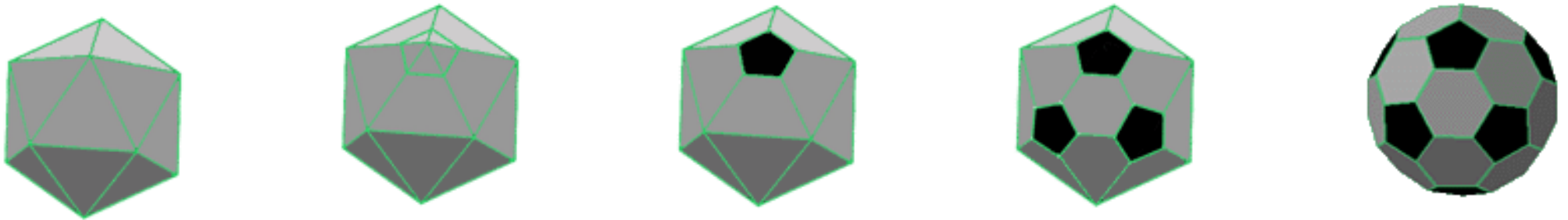
	E	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$
$n$	3	1	1	3
$\Gamma$	9	-1	1	3

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>



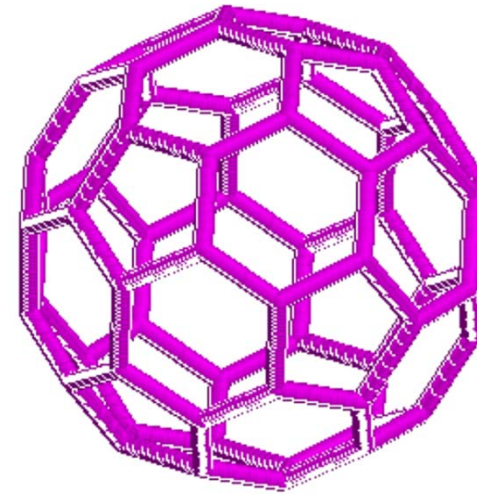
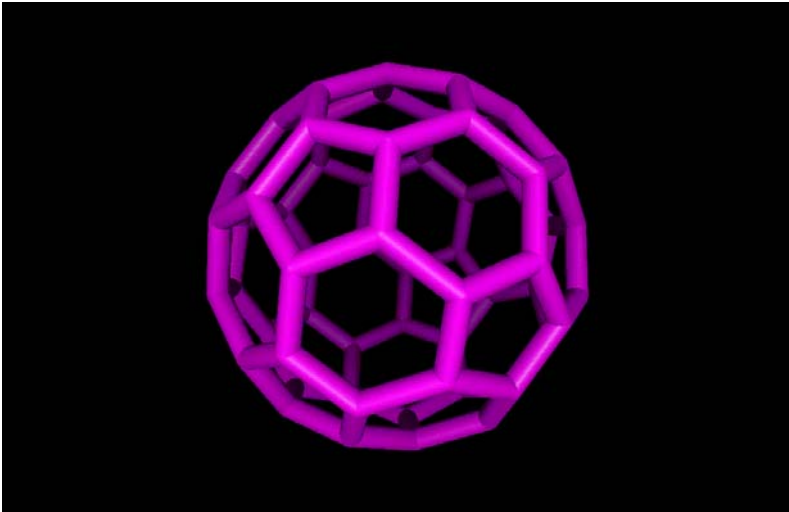
C<sub>60</sub>

## Vibrational modes of C<sub>60</sub>

Character table:

$I_h$	E	$\checkmark 12C_5$	$12C_5^2$	$20C_3$	$15C_2$	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

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

$3N - 6$  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

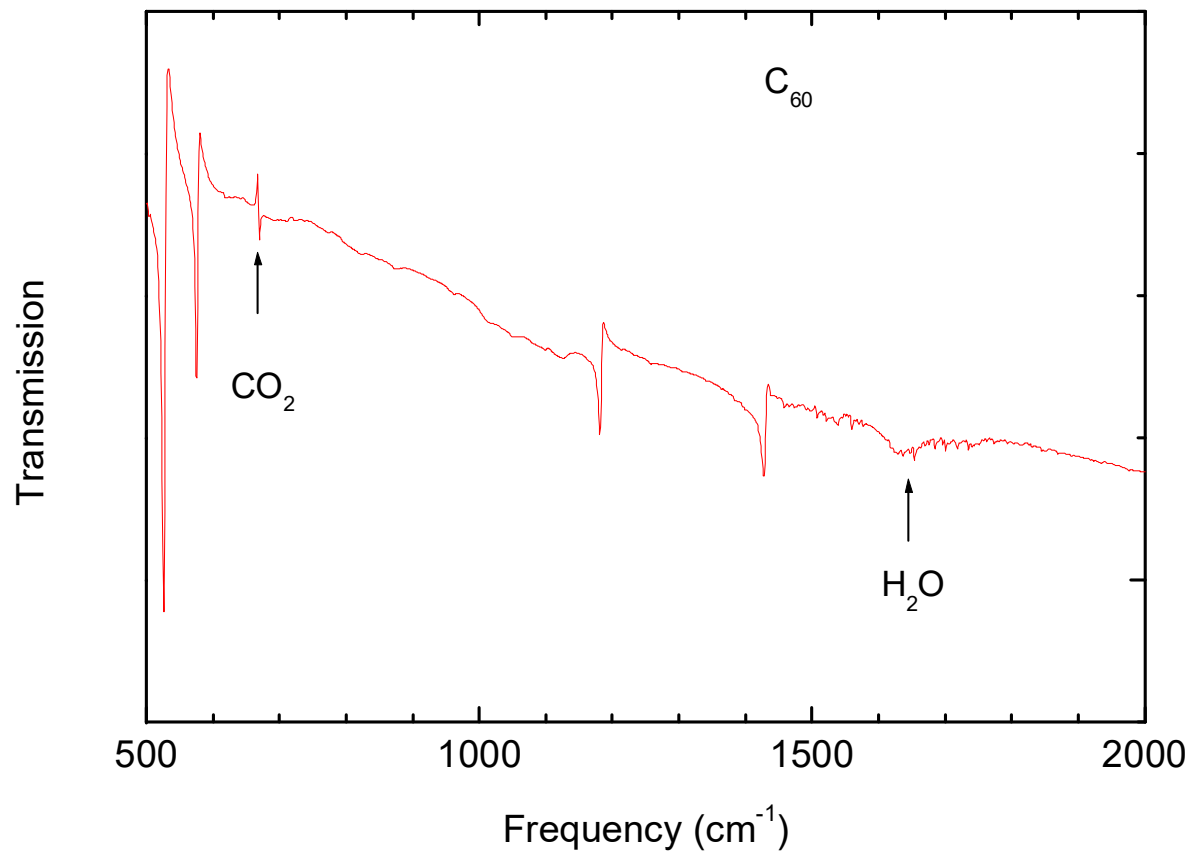
$$i: \quad \mu \rightarrow -\mu \quad (\text{u})$$

$$\alpha \rightarrow \alpha \quad (\text{g})$$

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<sub>60</sub>



# 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