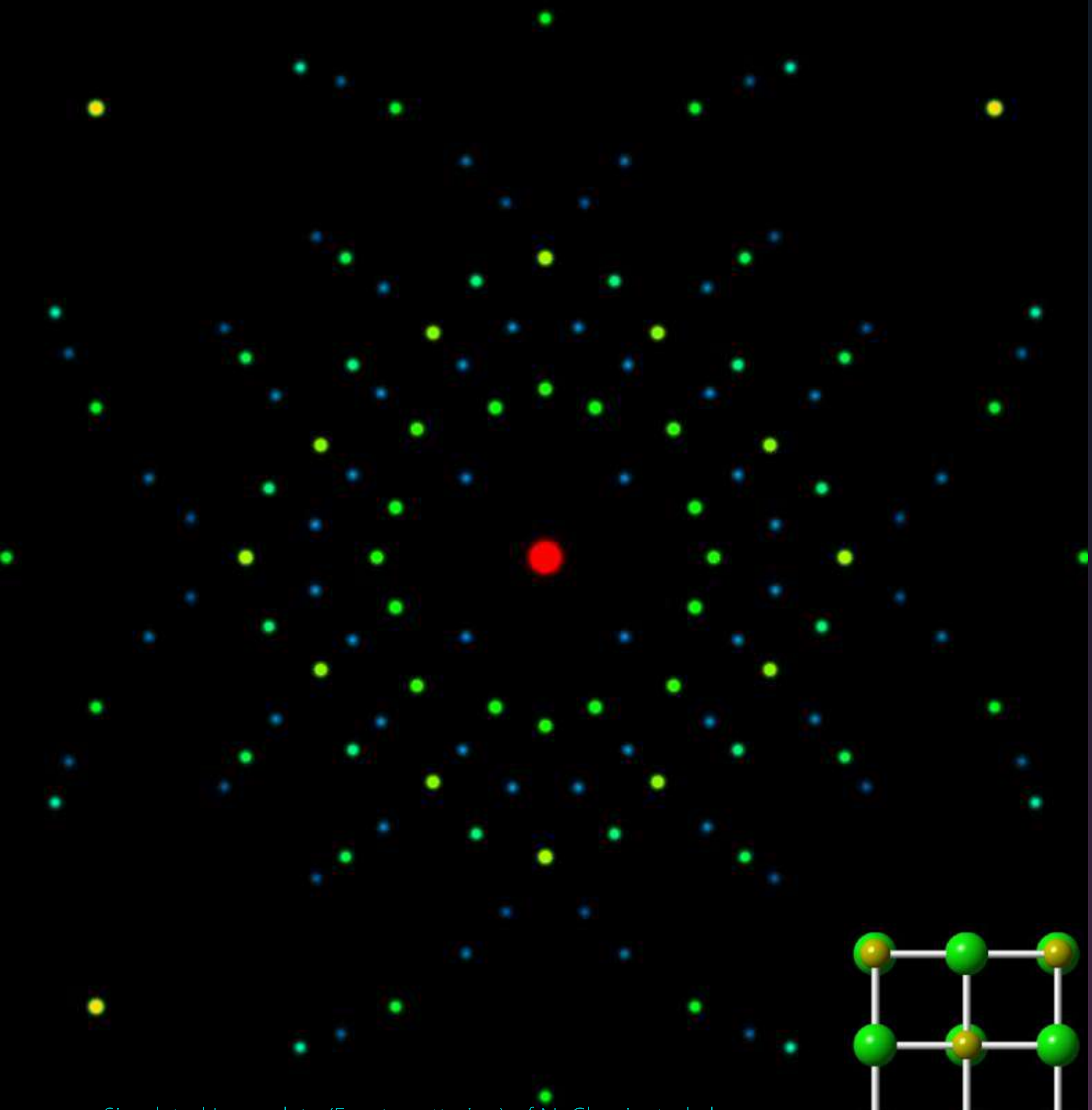
Crystal structure simulation methods, theory and practical examples in biomineralogy

Gianfranco Ulian, PhD

Outline

- Fundamentals of Crystallography
- Infrared and Raman spectroscopy
- Theoretical methods in crystallography
- Examples in biomineralogy and mineralogy

Source: Wikipedia



Simulated Laue plate (Front-scattering) of NaCl, oriented along the [001] direction

Fundamentals of Crystallography

Just some notes…
… and a little bit of history!

01/03/2022

Nobel Prizes

Associated to Crystallography

http://www.iucr.org/people/nobel-prize

M. von Laue

1914 – Diffraction of X-rays by crystals

W.H. Bragg

1915 – Use of X-rays to determine crystal structure

W.L. Bragg

1915 – Use of X-rays to determine crystal structure

C.J. Davisson

1937 – Diffraction of electrons by crystals

G. Thomson

1937 – Diffraction of electrons by crystals

D. Hodgkin

1964 – Structure of many biochemical substances including Vitamin B12

Nobel Prizes

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http://www.iucr.org/people/nobel-prize

F. Crick

1962 – The helical structure of DNA

J. D. Watson

1962 – The helical structure of DNA

M. Wilkins

1962 – The helical structure of DNA

C. Shull

1994 – Neutron diffraction

L. C. Pauling

1954 – For his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances

D. Shechtman

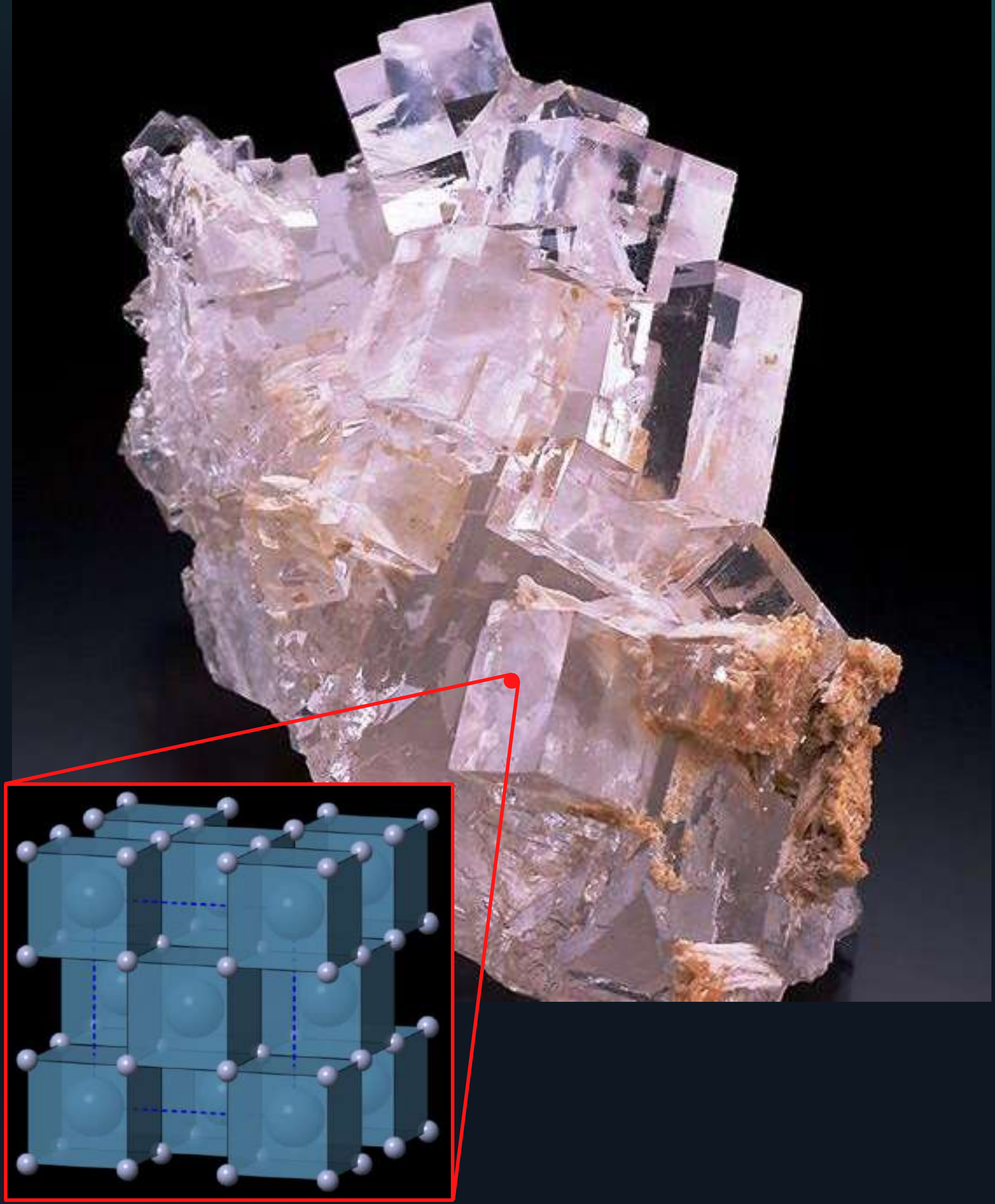
2011 – For the discovery of quasicrystals

What is a crystal?

A crystal is:

- a solid material,
- with a determined chemical composition,
- that presents a regularly repeating internal arrangement of its atoms (high internal order)
- and often external (macroscopic) faces oriented in specific directions.

In this context, minerals, natural solids formed as a result of the certain geological processes, the largest source of naturally formed crystalline solids



Polyhedron geometry

As you noted from the previous pictures, some minerals may develop well defined polyhedral shapes. They are made of:

- Faces (f)

Polyhedron geometry

As you noted from the previous pictures, some minerals may develop well defined polyhedral shapes. They are made of:

- Faces (f)
- Edges (e)
- Vertices (v)
- Dihedral angles (angles described by faces)

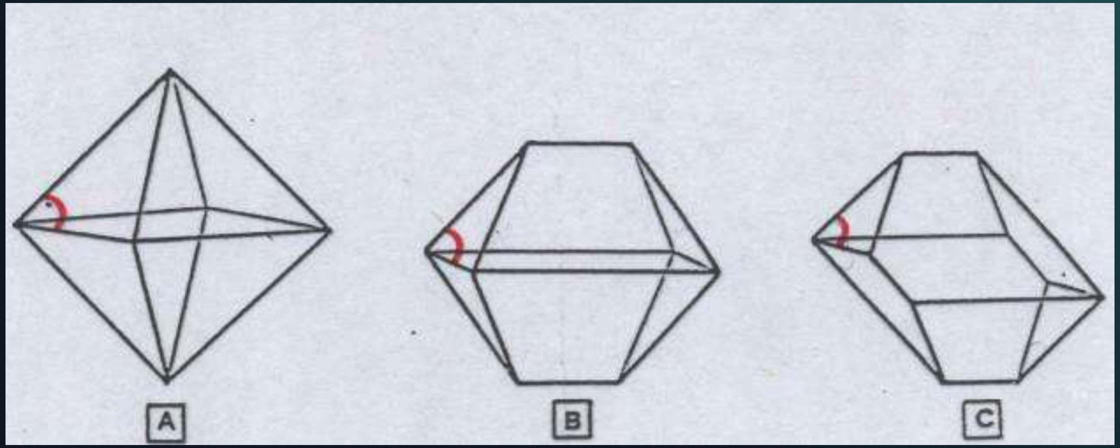
Euler rule

$$f + v = e + 2$$

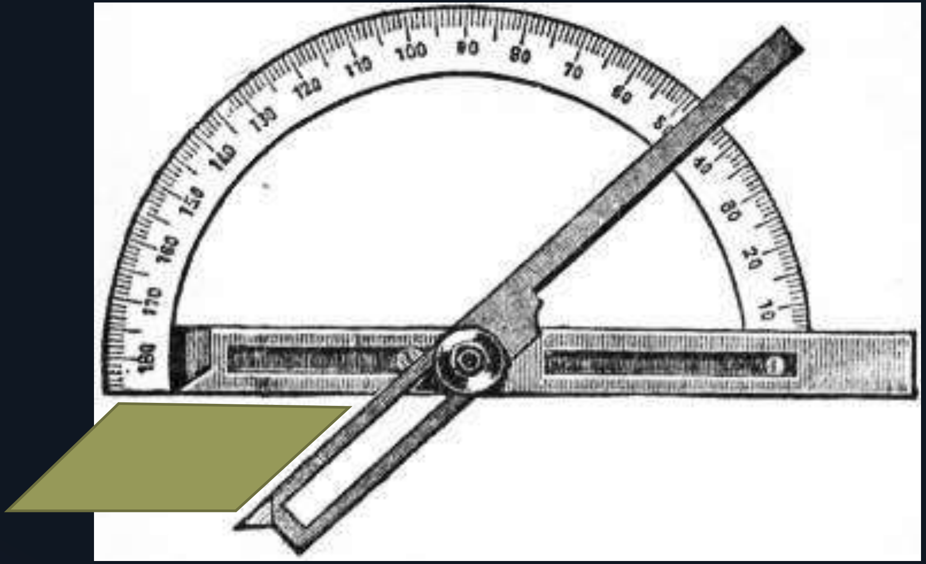
Steno's law (1669)

Law of the constancy of the interfacial angles

- The angles between two corresponding faces on the crystals of any solid chemical or mineral species are constant and are characteristic of the species.
- The law holds for any two crystals, regardless of size, locality of occurrence, or whether they are natural or man-made.
- Confirmed in 1772 by Jean-Baptiste L. Romé de l'Isle.



A: perfect crystal; B & C: disproportioned crystals



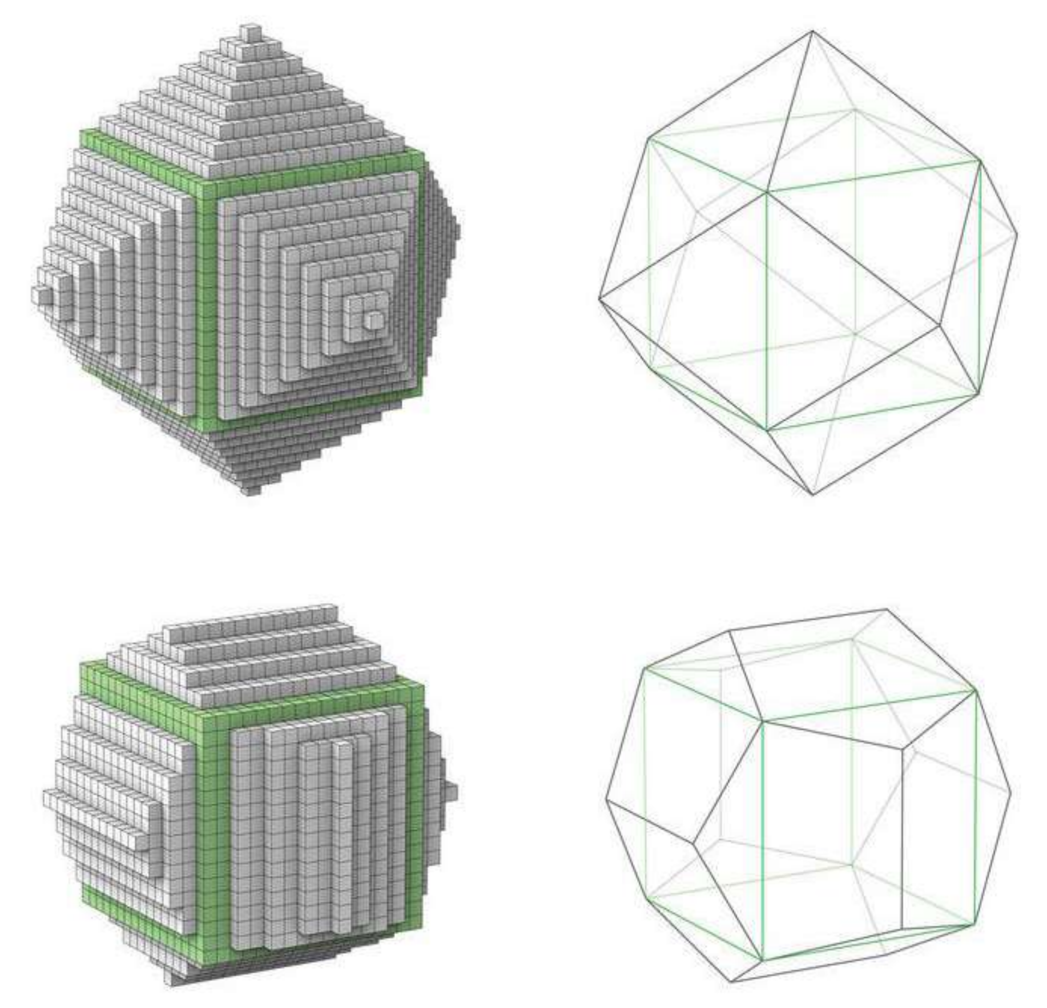
Carangeot's (contact) goniometer

Haüy’s law (XVIII century)

Law of the rational indices

- For the given crystal species, it is always possible to choose three vectors, a, b and c so that all the natural faces of this crystal cut the lengths proportional to the three integer numbers.
- The idea is that crystals are formed by stacking elementary building blocks (e.g., cubes). This stacking procedure leads to the formation of the natural faces of crystals.

First idea of «periodicity»!

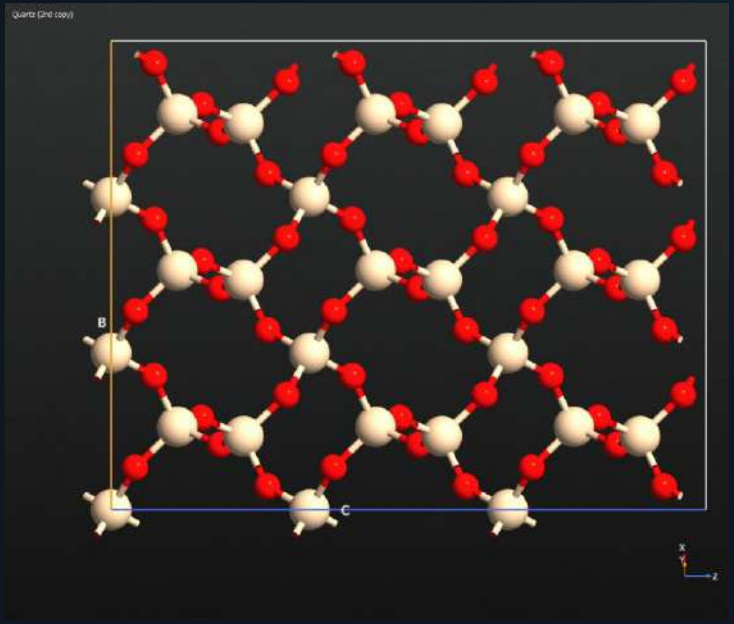


Crystal geometry

Morphology – Crystal habit

External shape of the crystal

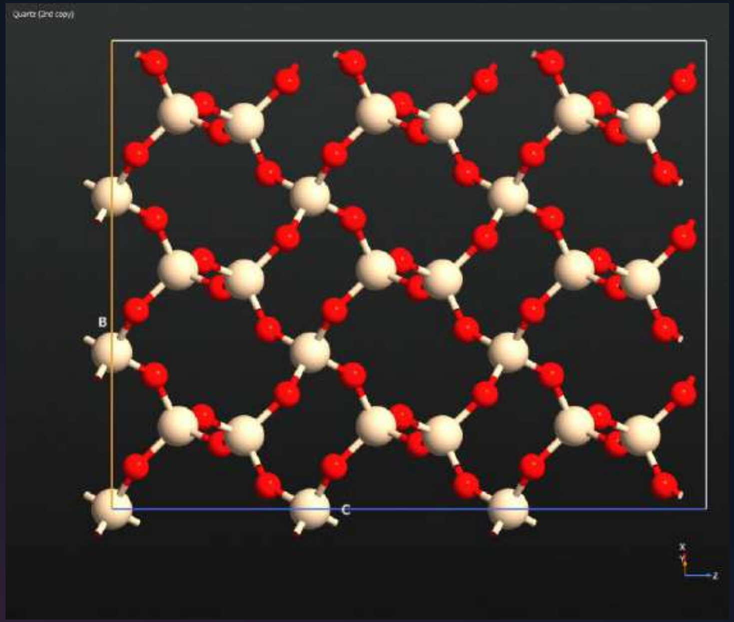
Crystal structure



Ordered repetition of atoms, ions and molecules

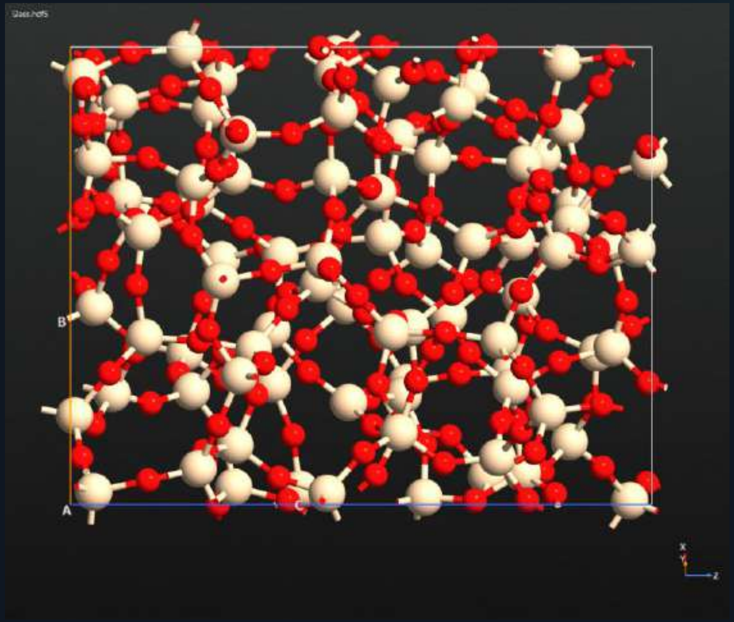
Crystalline vs Amorphous

Quartz – crystalline SiO_2

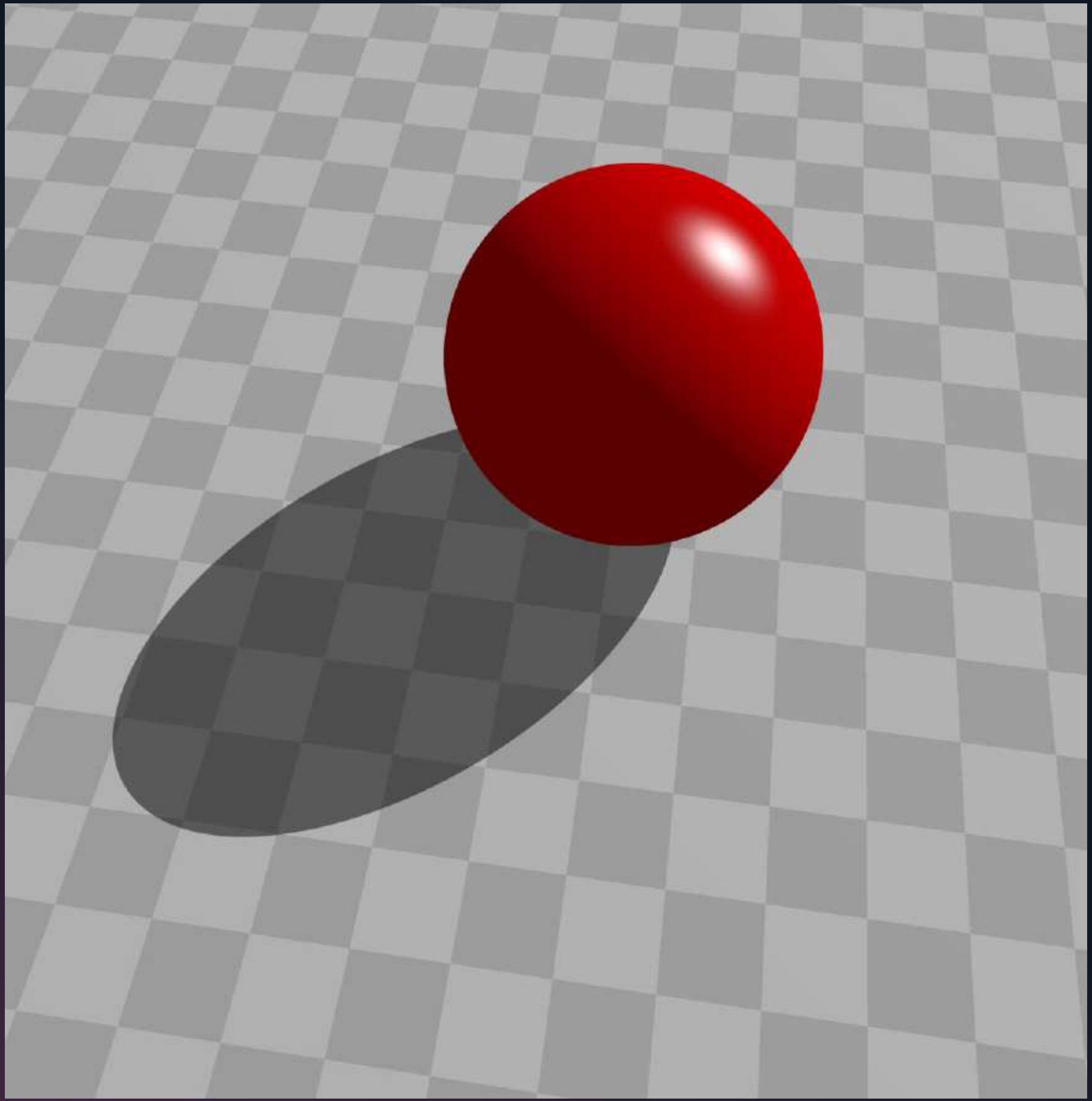


Long-range order

Glass – non-crystalline SiO_2



Short-range order



Symmetry

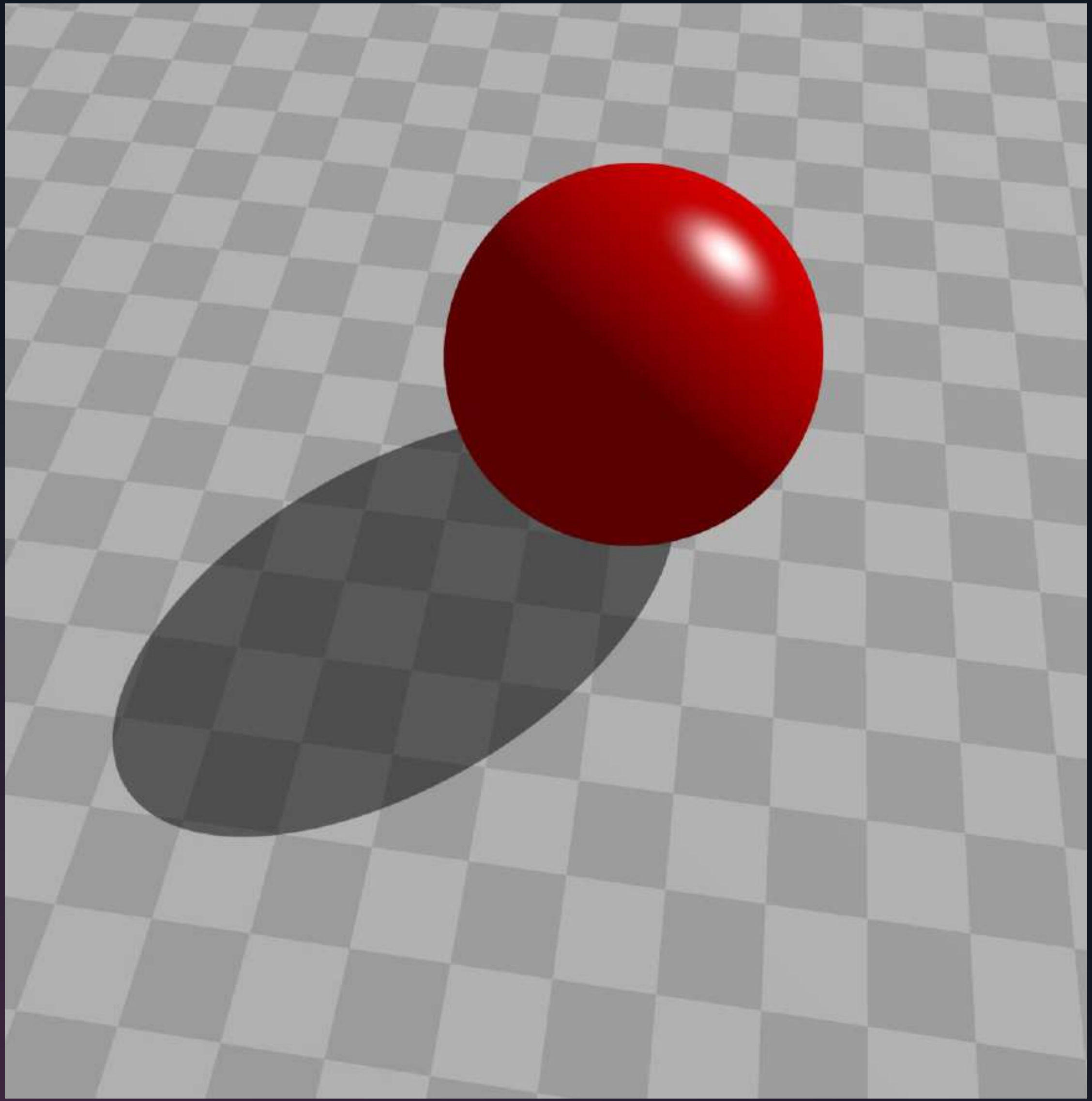
From Greek *symmetria*, «agreement in dimensions, due proportion, arrangement»

Symmetry is a set of mathematical rules that describe the shape of an object. We can express these rules with

- algebraic formulae, and/or
- matrix representation

What is the object with the highest symmetry?

The sphere



Symmetry

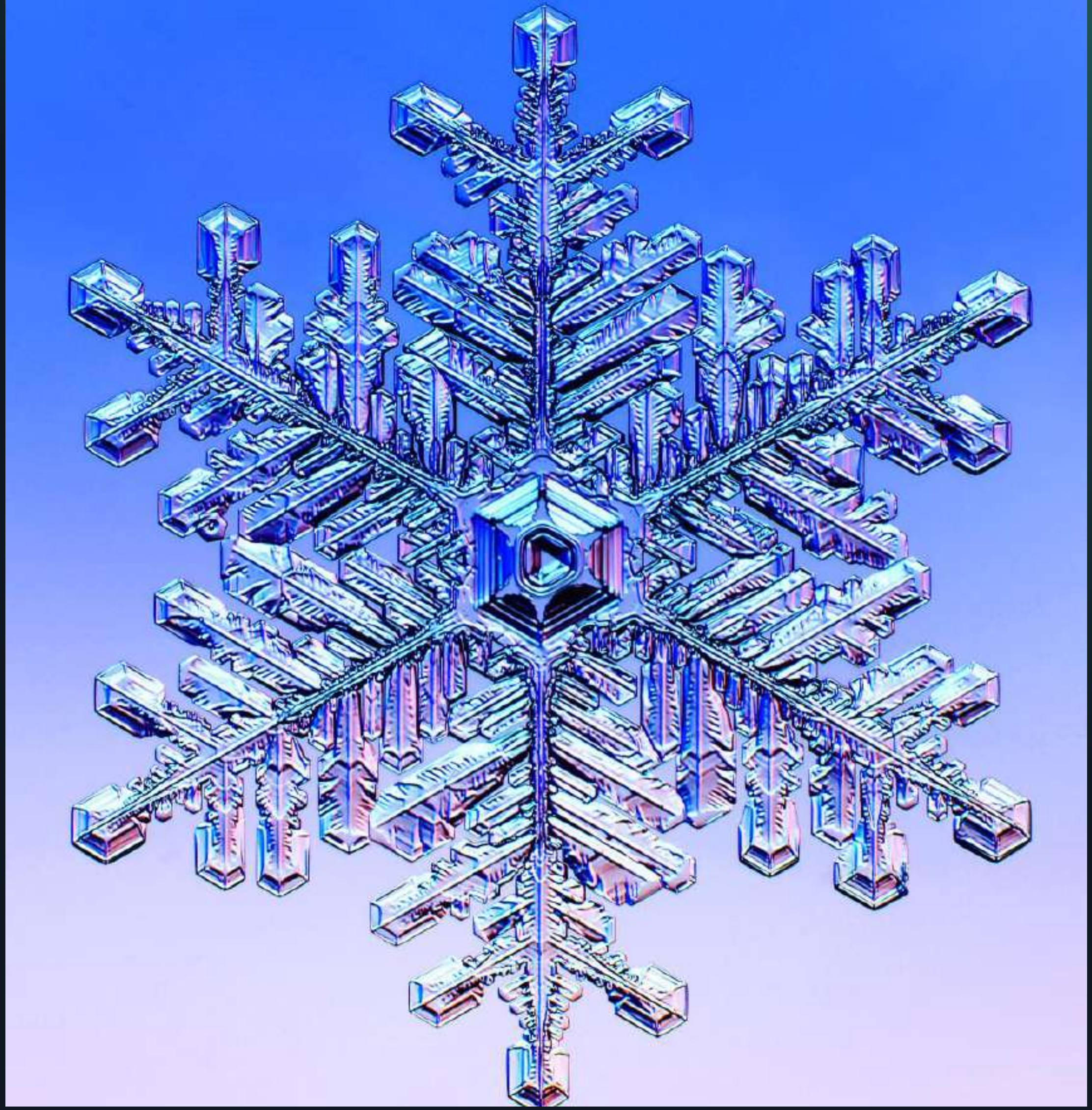
From Greek *symmetria*, «agreement in dimensions, due proportion, arrangement»

- A body is said to be symmetrical when it can be divided into parts that are related to each other in certain ways. The operation of transferring one part to the position of a symmetrically related part is termed a symmetry operation, the result of which is to leave the final state of the body indistinguishable from its original state.
- In general, successive application of the symmetry operation must ultimately bring the body into its original state again.

Lipson, H., and W. Cochran. The Determination of Crystal Structures. Ithaca, NY: Cornell University Press, 1966. ISBN: 080140276X.

Some examples

- A snowflake



Source: http://www.snowcrystals.com

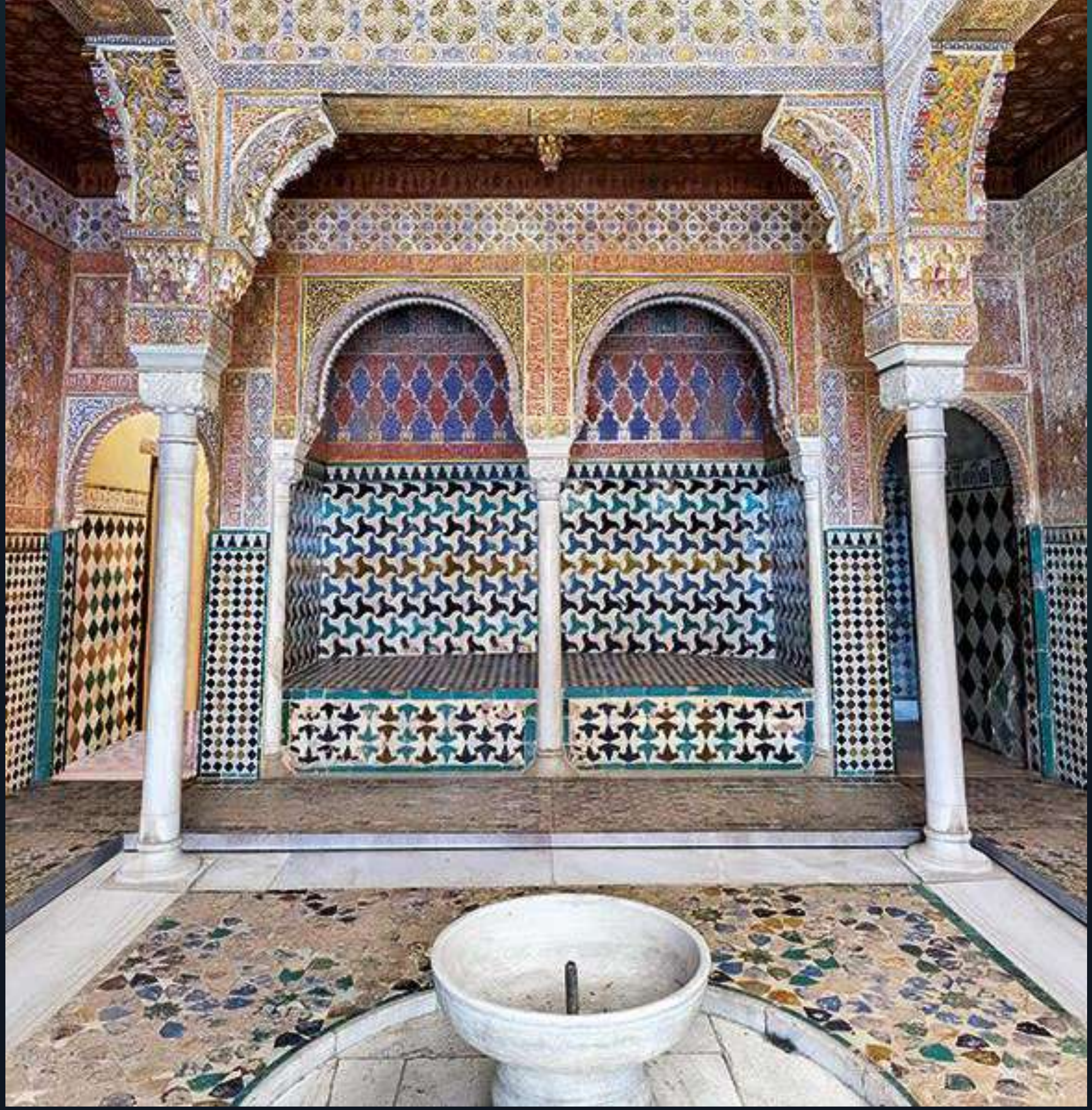
Some examples

- A snowflake
- The octagonal ceiling of Ely Cathedral (England)

Source: https://smarthistory.org/ely-cathedral/

Some examples

- A snowflake
- The octagonal ceiling of Ely Cathedral (England)
- The tilework and mosaic in La Alhambra (Granada, Spain)



Source: https://www.dosde.com/discover/en/tilework-in-the-alhambra/

Some examples

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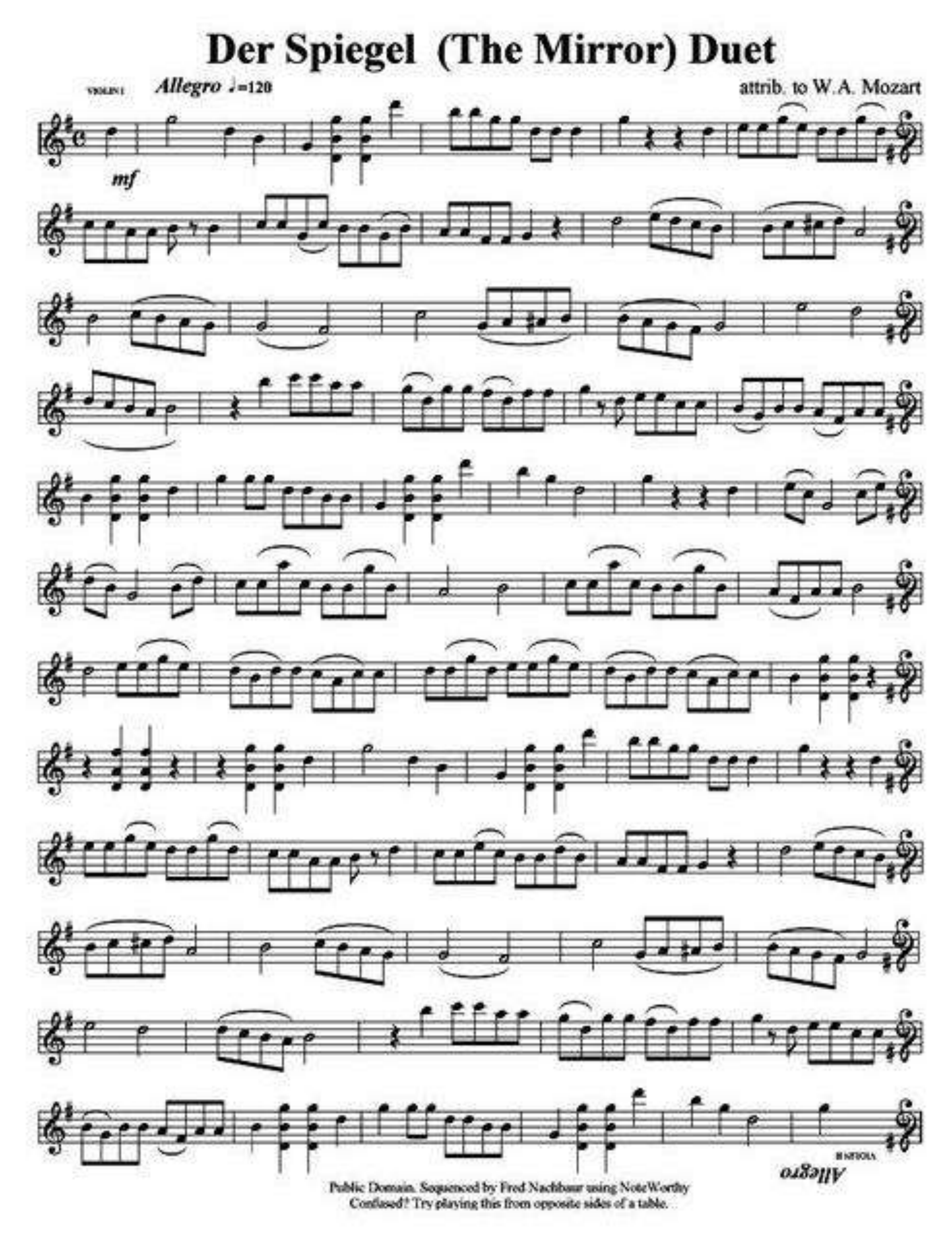
- The tilework and mosaic in Alhambra (Granada, Spain)
- A music score (attributed to Mozart)

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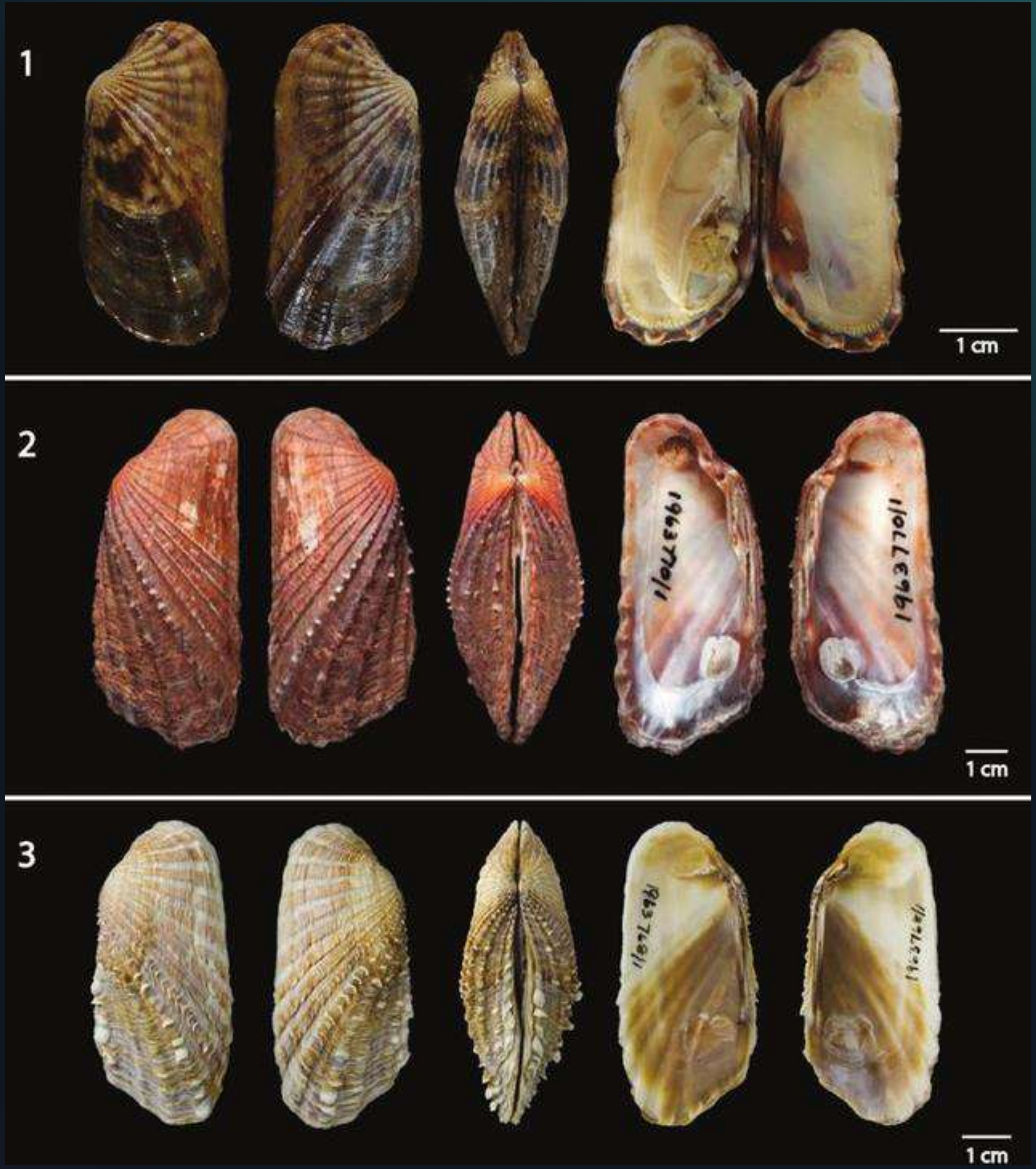
- Bivalve mollusk shells



Source: Gonzalez V. L., Giribet G., «A New Cryptic Species of Carditid Bivalve from the Gulf of California (Mollusca, Bivalvia, Archiheterodonta, Carditidae)", *Malacologia*, 55(2), 235-250

Some examples

- A snowflake
- The octagonal ceiling of Ely Cathedral (England)
- The tilework and mosaic in Alhambra (Granada, Spain)
- A music score (attributed to Mozart)
- Bivalve mollusk shells
- A mineral (pyrite, FeS_2)

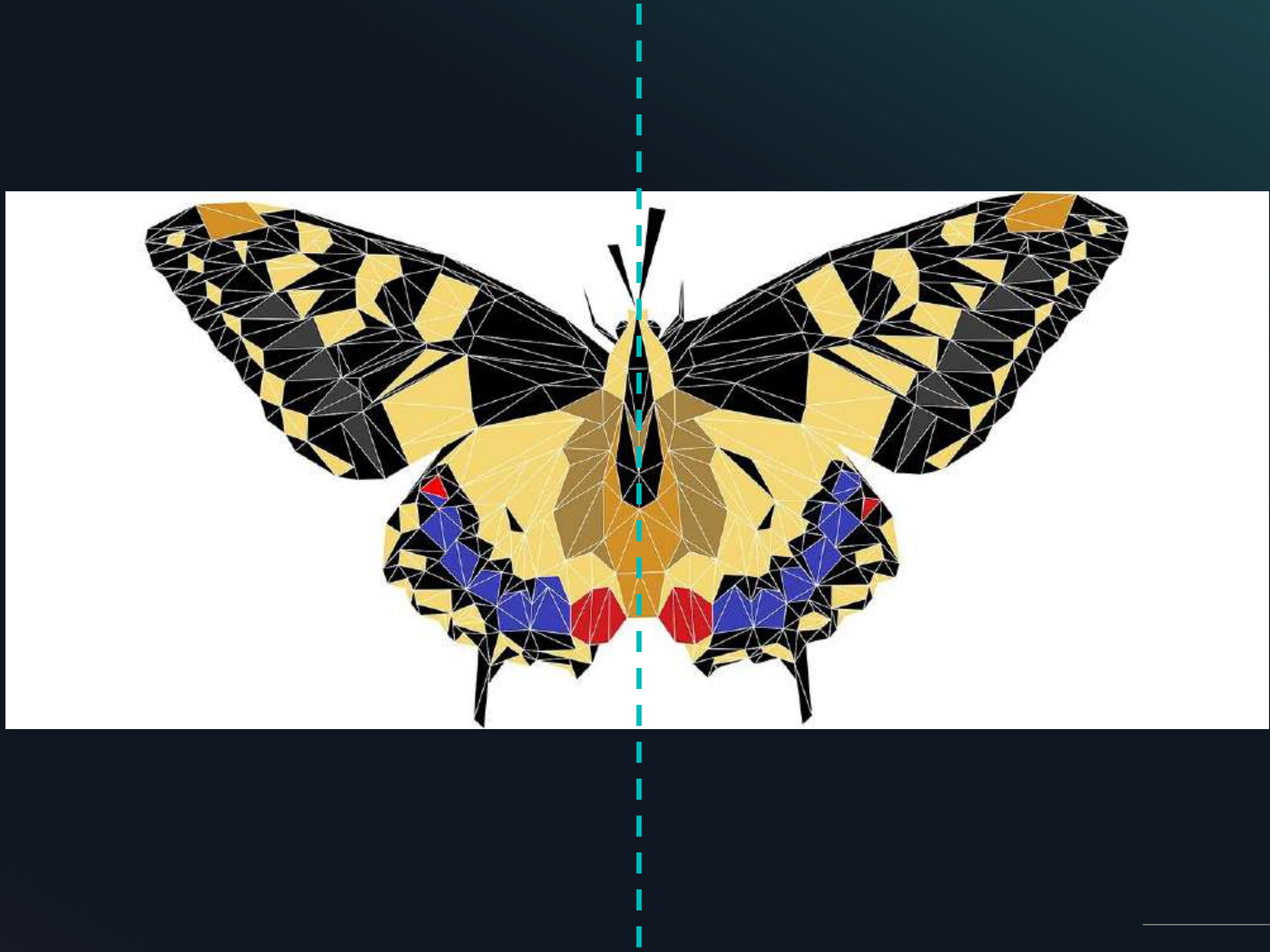
Source: https://www.mindat.org/

Symmetry

Mathematical definition of symmetry

An object has symmetry if there is an operation or transformation, such as translation, rotation or reflection, which maps the figure/object onto itself.

In other words, the object has an invariance under the transform.

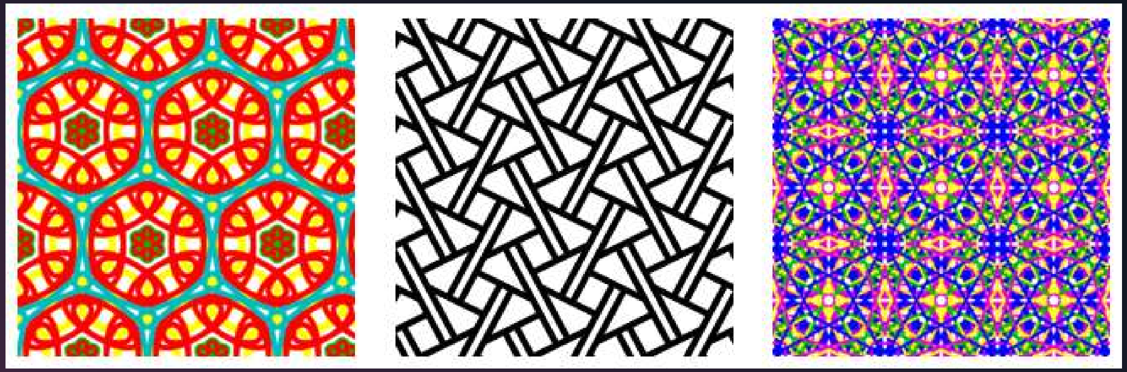


Crystals and symmetry

The symmetry of crystals is described by the so-called *Space Group*, which considers two types of symmetry

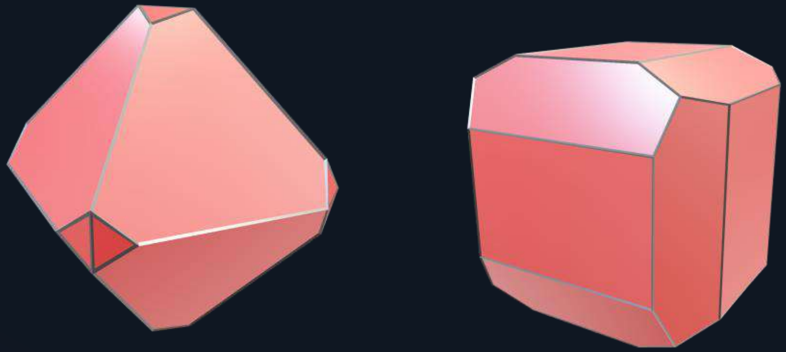
Translation symmetry

- Shifting movements along one, two, three, …, *n* directions for a certain specified distance, such that the operation does not result in any change of the shifted pattern. In crystals, we are interested in 3D patterns.



Point symmetry

- Mathematical group of isometries (macroscopically visible symmetry operations) that keep at least one point of the object fixed (invariant)



Aristov, M. M., Geng, H., Pavelic, A. & Berry, J. F. (2022). *Journal of Applied Crystallography* **55**, 172-179.

Translation symmetry

The «invisible» operator by the naked eye

Crystal, lattice and basis

- An ideal crystal is constructed by the infinite repetition in (3D) space (lattice) of identical structural units (basis)

Crystal = lattice + basis

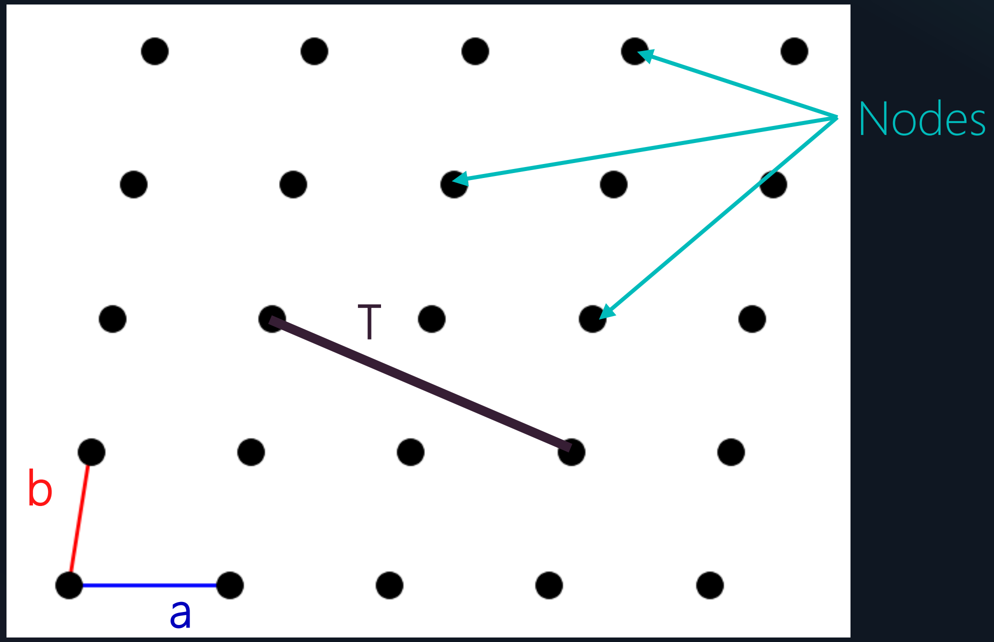
- The lattice is defined by three translation vectors *a*, *b* and *c*, and any point (node) in such a lattice may be described by the vector *r* as:

$$\boldsymbol{r} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

- where *u*, *v* and *w* are arbitrary integers.
- The crystal axes *a*, *b* and *c* form three adjacent edges of a parallelepiped.
- A lattice translation operation is defined as:

$$\boldsymbol{T} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

Example of lattice (in 2D)



Translation symmetry

The «invisible» operator by the naked eye

Basis and crystal structure

Attached to every lattice point (aka, node) there is a basis of atoms, which is characterized by the same:

- composition,
- arrangement,
- orientation.

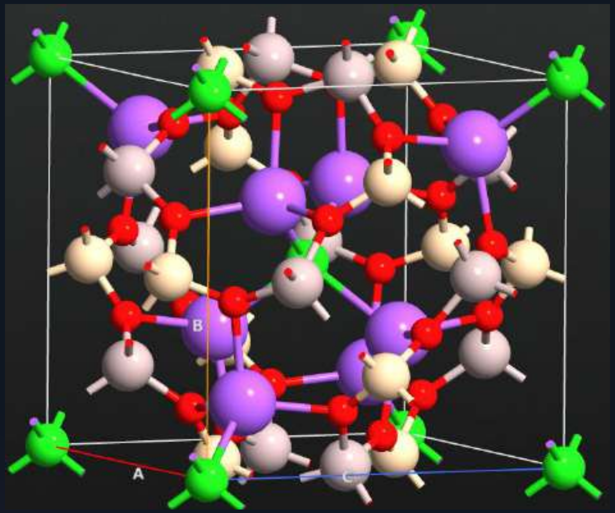
The number of atoms could be as low as 1 (e.g., metals) or higher than 1000 (e.g., proteins)

The position (center) of each atom *j* can be written as:

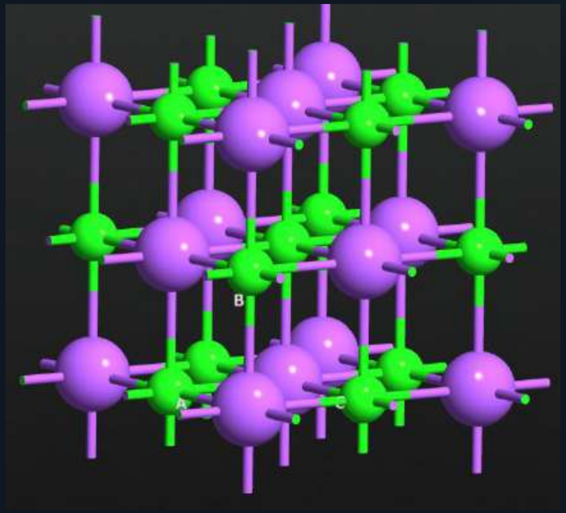
$$\boldsymbol{r} = x_j\boldsymbol{a} + y_j\boldsymbol{b} + z_j\boldsymbol{c}$$

with the factors $0 \leq x_j, y_j, z_j \leq 1$ called fractional coordinates.

Example



Sodalite ($Na_8Al_6Si_6O_{24}Cl_2$)

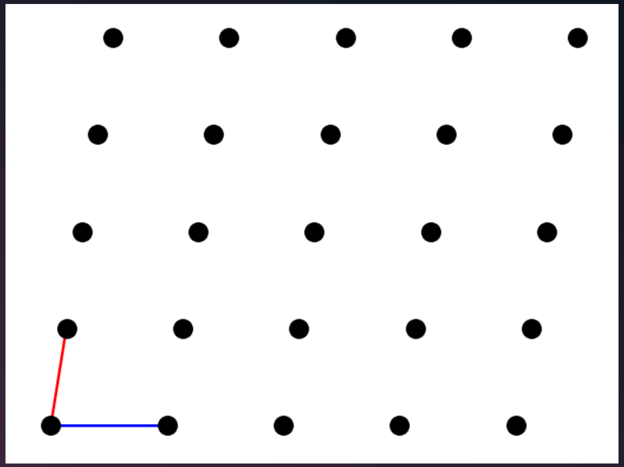


Halite (NaCl)

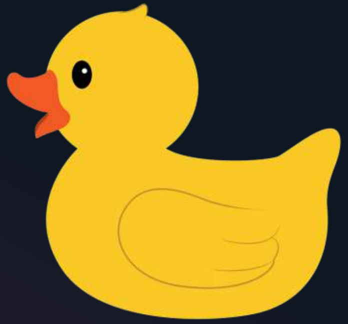
Translation symmetry

The «invisible» operator by the naked eye

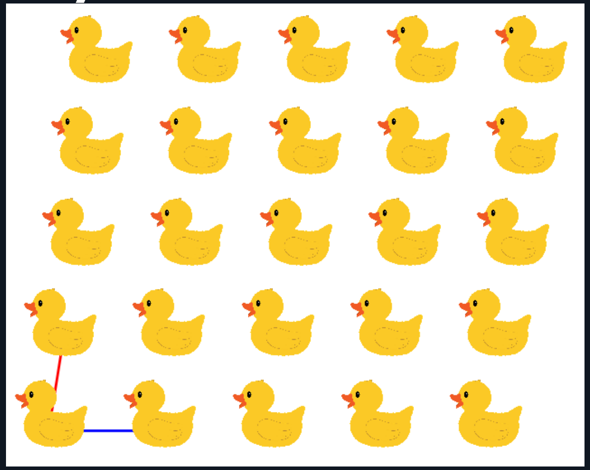
Lattice



Basis



Crystal



Translation symmetry

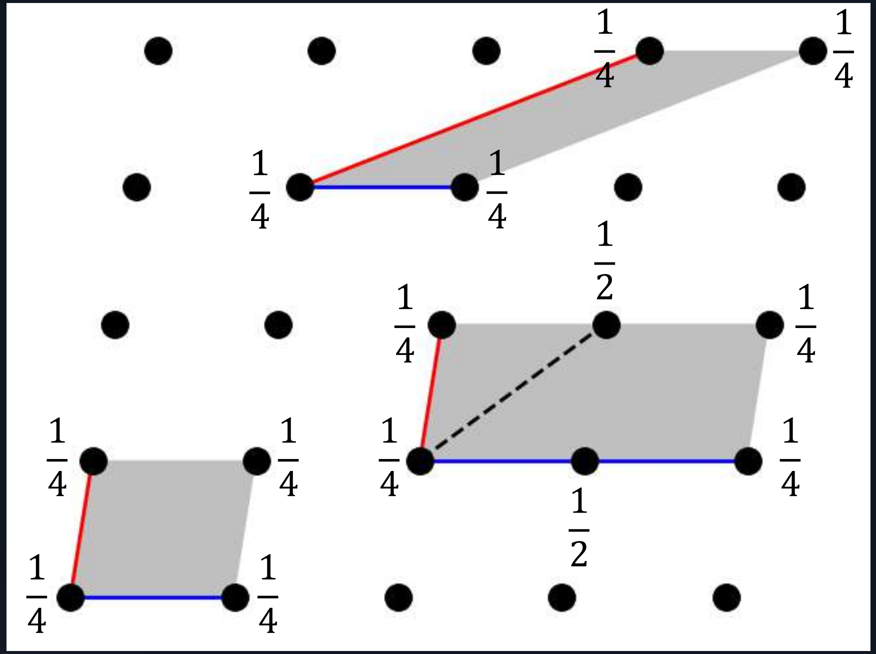
The «invisible» operator by the naked eye

Primitive cell

- By definition, a primitive cell is a unit cell that contains exactly one lattice point.
- Lattice points at the edges of the cell are shared with other cells, thus they count as a fraction.
  - $1/2$ in 1D lattices (edges of a line);
  - $1/4$ in 2D lattices (edges of a parallelogram);
  - $1/8$ in 3D lattices (edges of a parallelepiped);
- No basis contains fewer atoms than a primitive basis contains.
- By elementary vector analysis, the volume of a cell is given by

$$V_c = |\boldsymbol{a} \times \boldsymbol{b} \cdot \boldsymbol{c}|$$

Example



Translation symmetry

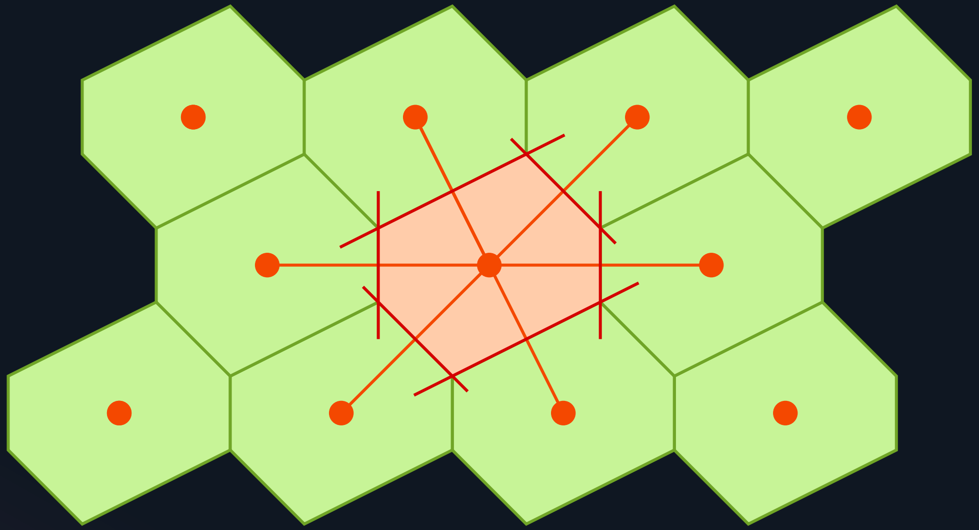
The «invisible» operator by the naked eye

Wigner-Seitz cell

It is a special type of primitive cell.

- The Wigner-Seitz cell of a lattice point is defined as the volume that encloses all points in space which are closer to this particular lattice point than to any other.
- It can be constructed as depicted on the right picture and explained below:
  1. One chooses any lattice point and draws connecting lines to its closest neighbours.
  2. In a second step one constructs the perpendicular bisectors of the connecting lines.
  3. The enclosed area is the Wigner-Seitz cell.
- The Wigner-Seitz is a unit cell, i.e., it forms the whole lattice without gaps.

Example



Point symmetry

In point symmetry, a symmetry operation is performed by a symmetry element, leaving the object unaltered.

It was the first analysis performed by natural scientists and mineralogists on crystals (more precisely, minerals) since the ancient times (see the *Naturalis Historia* by Plinius, for one of the first examples).

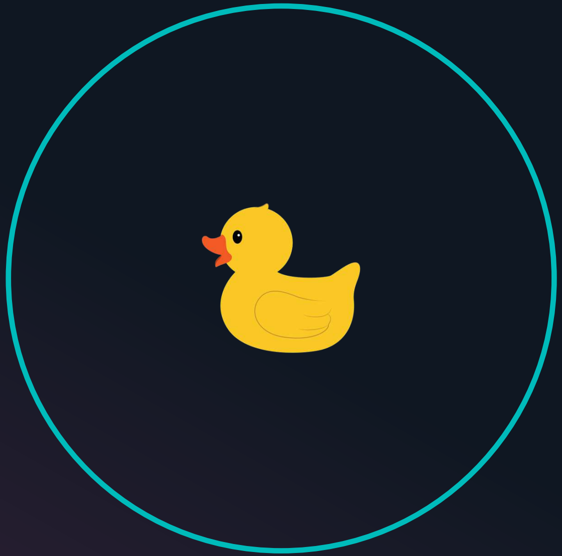
We call **lattice point group** a collection of the symmetry operations that, when applied about a lattice point, leave the lattice invariant.

Symmetry elements

- Point
- Line
- Plane

Symmetry operators

- Identity
- Rotation
- Reflection
- Inversion



Identity

The identity operation is the simplest symmetry element of all: it does nothing!

But it is important because all objects at the very least have the identity element, and there are many objects that have no other symmetry elements

Rotation

The rotation operations (both proper and improper) occur with respect to a line called rotation axis.

- A proper rotation is performed by rotating the object by 360°/*n*, where ***n*** is the order of the axis.
- An improper rotation is performed by rotating the object 360°/n followed by a reflection through a plane perpendicular to the rotation axis. The resulting object can be distinguishable or indistinguishable from the original, normally distinguishable, as they cannot be superimposed. If the resulting object is indistinguishable from the original, is because the improper rotation axis is passing through the object.

C_2 = 180°

C_3 = 120°

C_4 = 90°

C_6 = 60°

Rotation

The rotation operations (both proper and improper) occur with respect to a line called rotation axis.

The only rotations allowed in crystals are:

- Unary rotation (C_1)
- Binary rotation (C_2) – symbol ⬮
- Ternary rotation (C_3) – symbol ▲
- Quaternary rot. (C_4) – symbol ■
- Senary rotation (C_6) – symbol ⬢


C_2 = 180°


C_3 = 120°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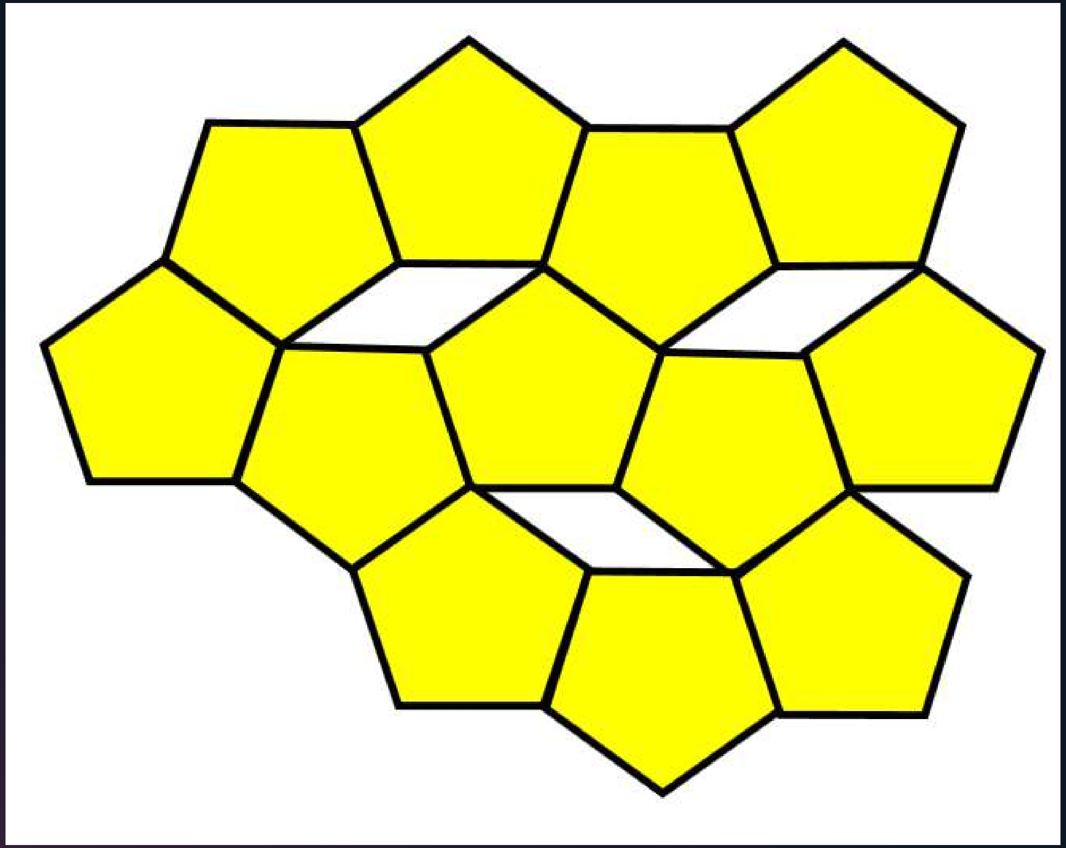
C_6 = 60°



Example: five-fold rotation

Rotation

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Unary rotation	(C_1)	
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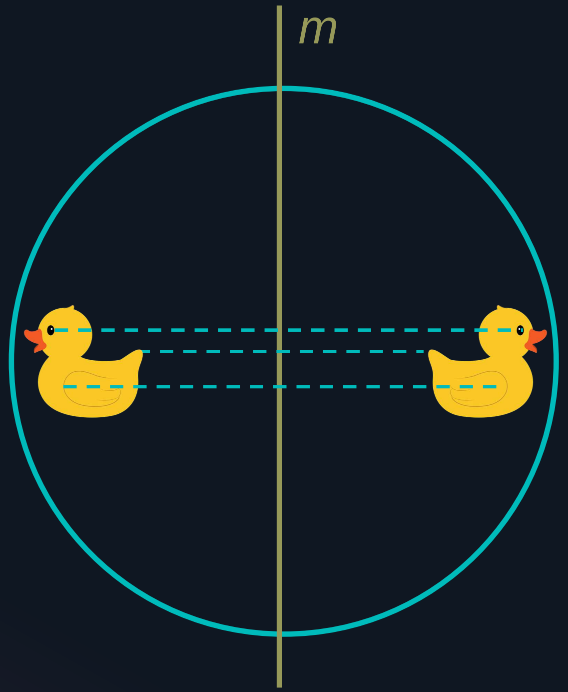
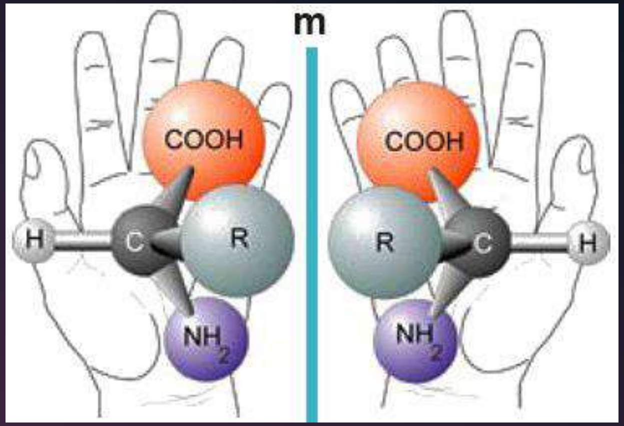
Ternary rotation	(C_3) – symbol	▲
Quaternary rot.	(C_4) – symbol	■
Senary rotation	(C_6) – symbol	⬢

Other rotation are not allowed because of the impossibility to completely fill all the available space.

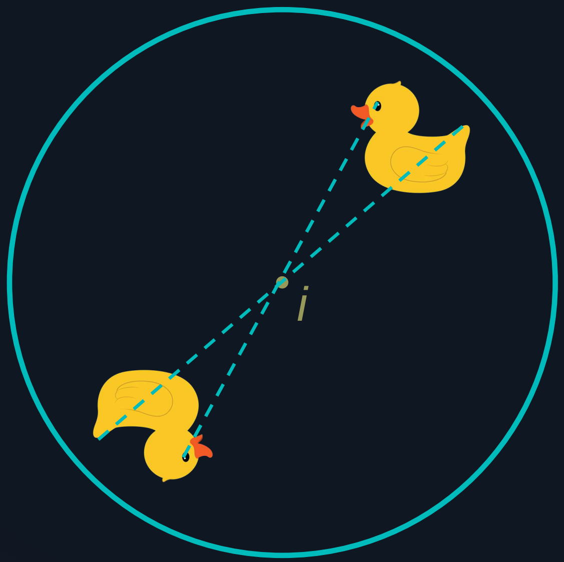


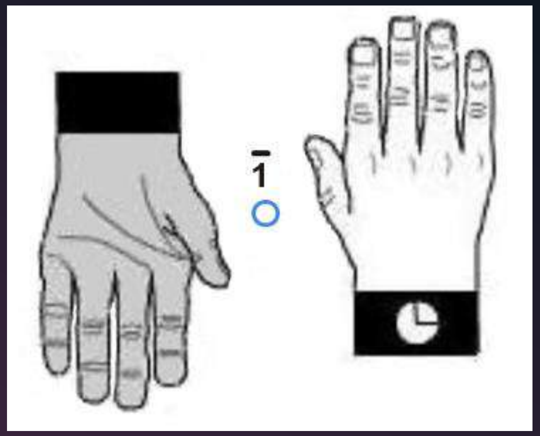


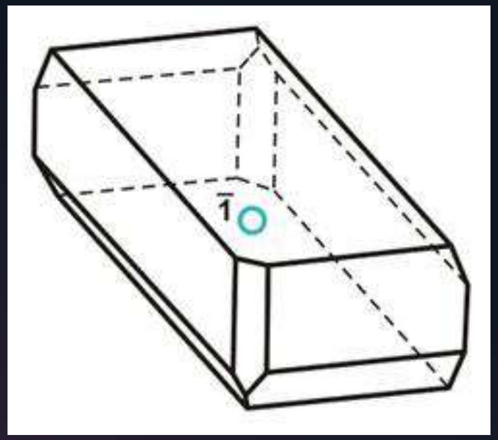
Reflection

It is the symmetry operation that occurs when we put an object in front of a mirror.

- The object is found perpendicular to the reflection plane (called *m*) and equidistant from that plane, on the opposite side of the plane.
- The resulting object can be distinguishable or indistinguishable from the original, normally distinguishable, as they cannot be superimposed.
- If the resulting object is indistinguishable from the original, is because the reflection plane is passing through the object.



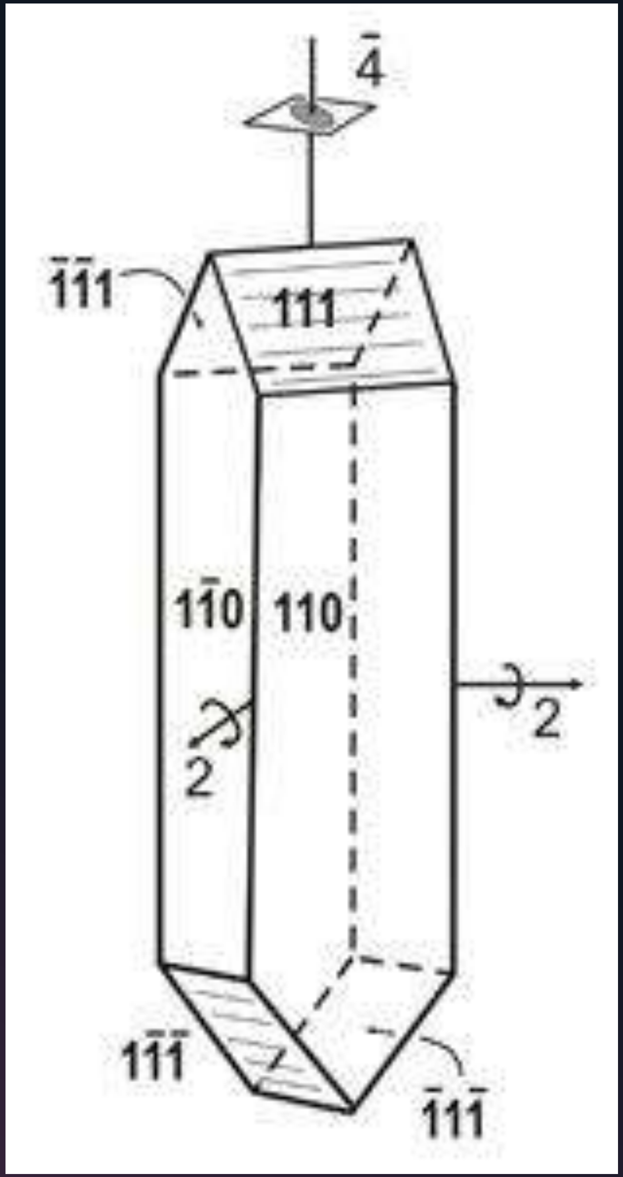




Inversion

It is the operation that occurs through a single point called the inversion center.

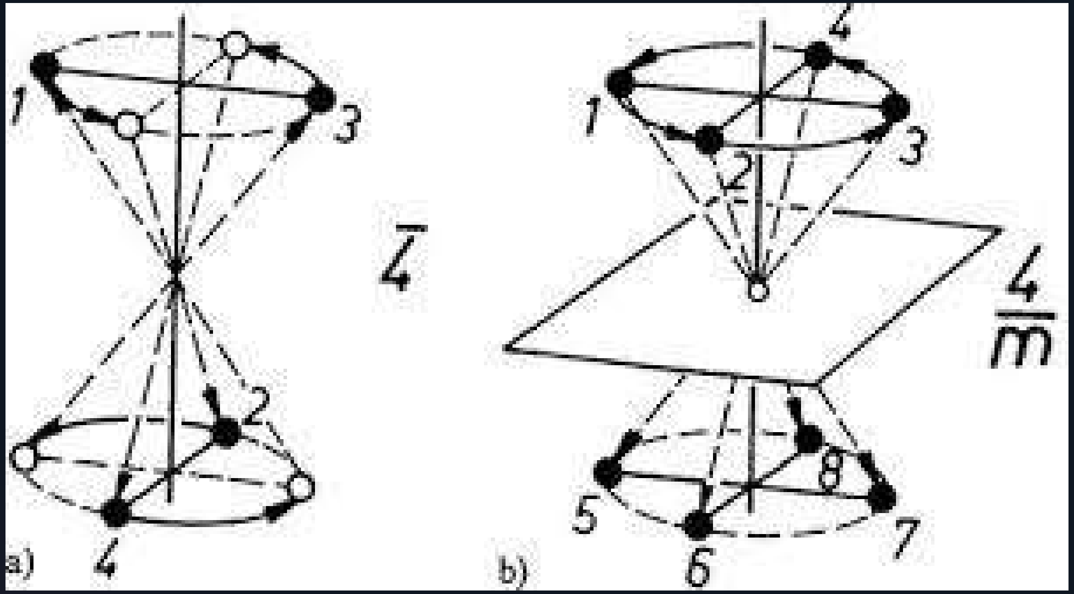
- Each part of the object is moved along a straight line through the inversion center, called *i* or $\bar{1}$, to a point at an equal distance from the inversion center.
- The resulting object can be distinguishable or indistinguishable from the original, normally distinguishable, as they cannot be superimposed.
- If the resulting object is indistinguishable from the original, is because the inversion center is inside the object.



Roto-inversion and Roto-reflection

They are improper rotation, given by the combination of a rotation, followed by either an inversion or a reflection.

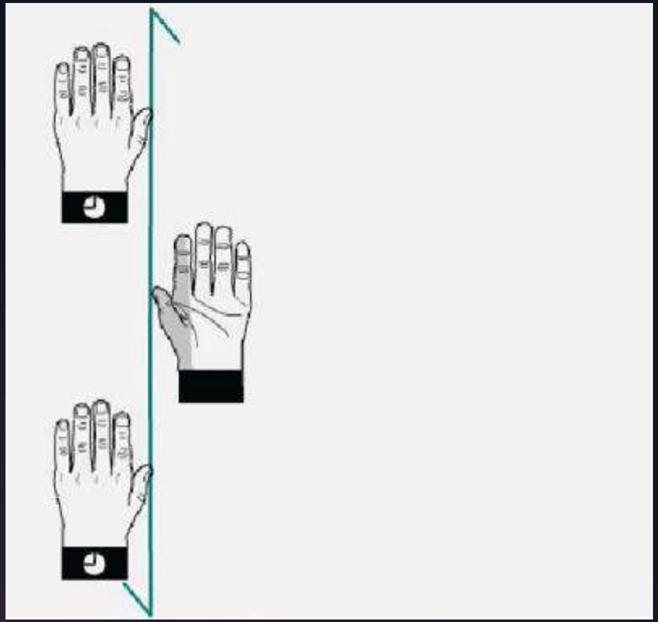
- The roto-inversion is labelled as $\bar{n}$, with n the order of the rotation axis.
- The roto-reflection is called S_n, or n/m.



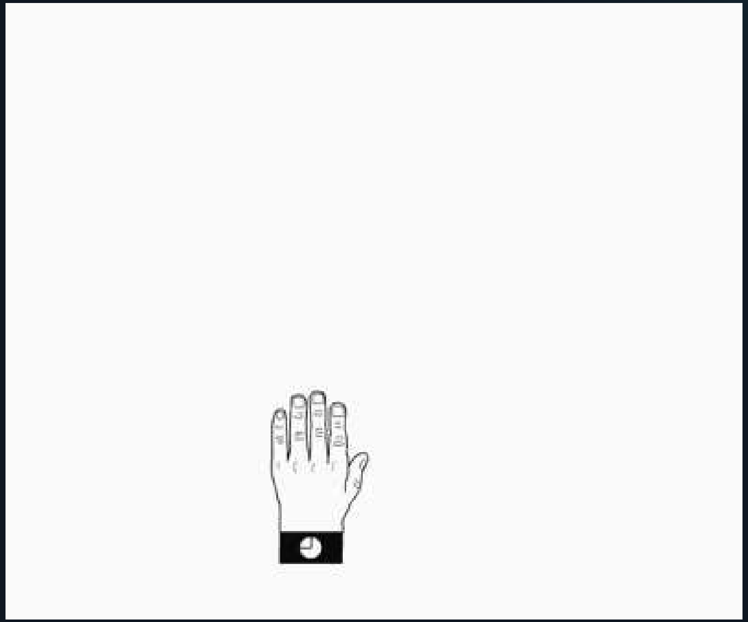
Screw axis and glide plane

Combinations of a rotation and a mirror plane with a translation.

Screw-axis: translation + rotation



Glide plane: translation + mirror

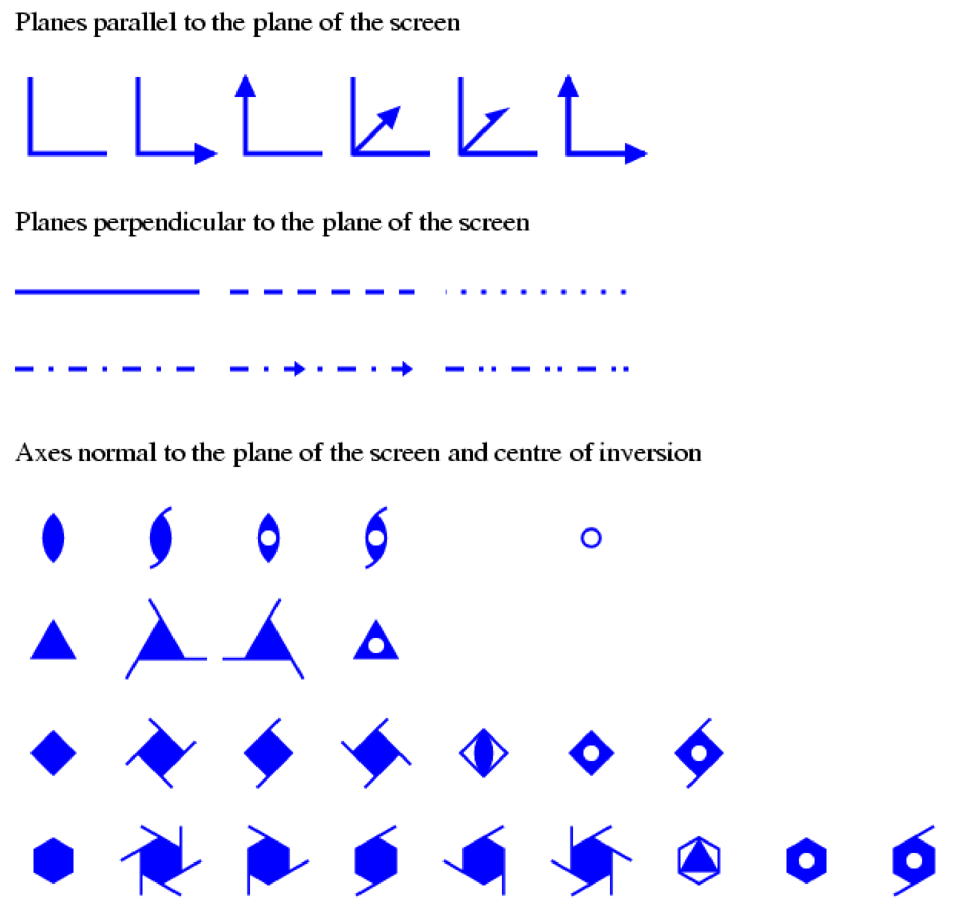


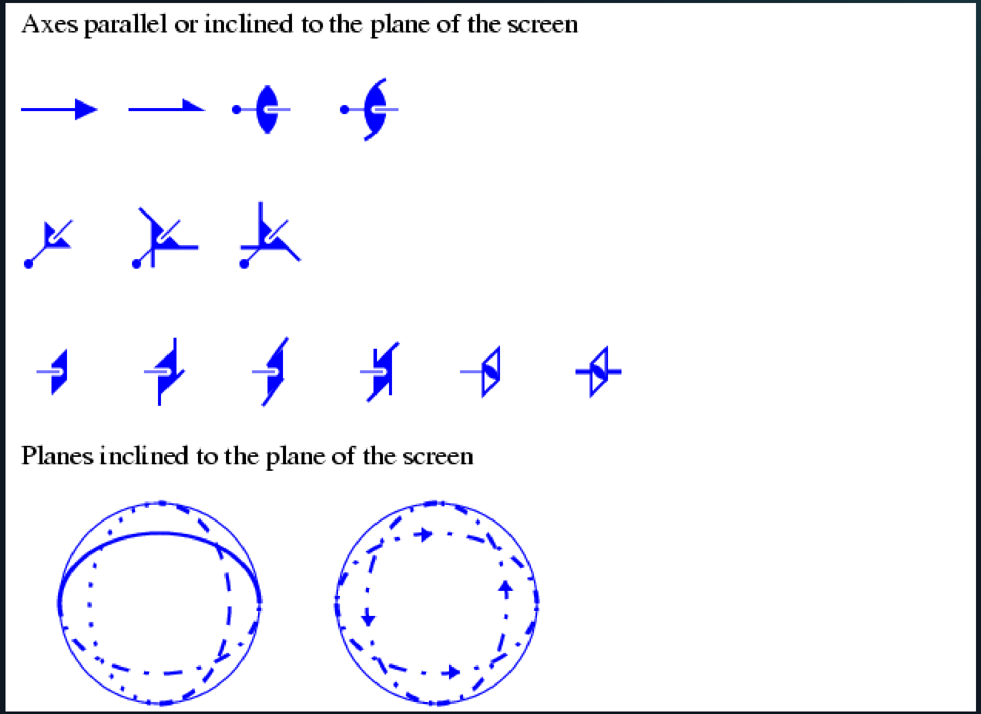
Symmetry notation

	Symmetry operation	Hermann-Mauguin symbol[a]	Schönflies symbol[b]
Point symmetry	Mirror plane	m	σ_v, σ_h
	Rotation axis	$n = 2, 3, 4, 6$	C_n (C_2, C_3, ecc.)
	Roto-inversion axis	$\bar{n}$ (= 1, 2, ecc.)	–
	Roto-reflection axis	–	S_n (S_2, S_3, ecc.)
	Inversion centre	$\bar{1}$	i
Space symmetry	Glide plane	a, b, c, d, n	–
	Screw axis	$2_1, 3_1$, ecc.	–

a) Hermann-Mauguin symbols are employed in crystallography
b) Schönflies symbols are used un spectroscopy

Symmetry symbols



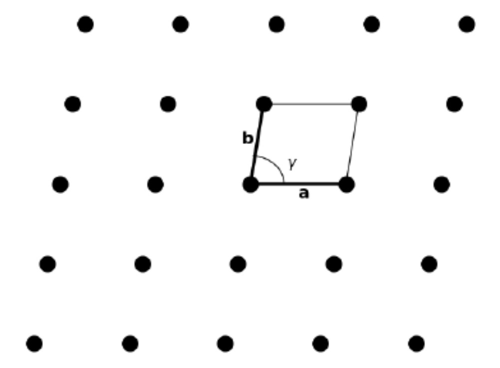


Source: http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

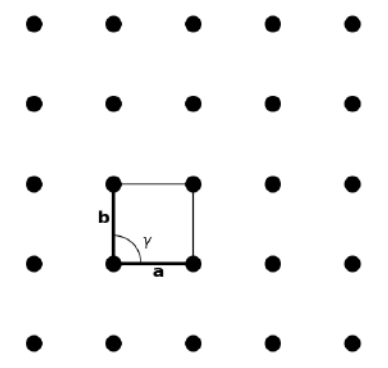
Bravais lattice (2D)

- A unit cell is defined by the two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, or, equivalently, by the lengths of the vectors, $a = |\boldsymbol{a}|$ and $b = |\boldsymbol{b}|$, and the angle γ described by them (2D cell parameters).
- Infinite number of possible lattices, because there is no restriction on the choice of the cell parameters → oblique lattice.
- Oblique lattice is invariant only under rotation of 180° and 360°
- Other rotations (60°, 90°, 120°) and the mirror plane require restrictions of the $\boldsymbol{a}$ and $\boldsymbol{b}$ vectors.
- Overall, 5 possible choices of lattice parameters → the Bravais lattices in two dimensions.

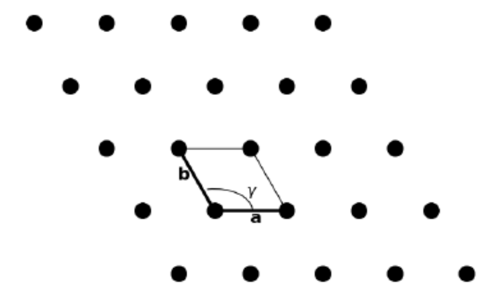
Oblique $|\boldsymbol{a}| \neq |\boldsymbol{b}|, \gamma \neq 90°$



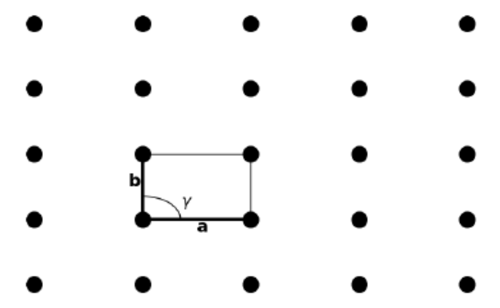
Square $|\boldsymbol{a}| = |\boldsymbol{b}|, \gamma = 90°$



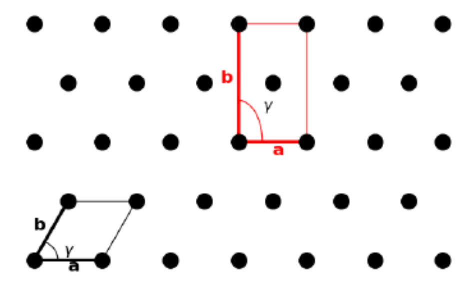
Hexagonal $|\boldsymbol{a}| \neq |\boldsymbol{b}|, \gamma \neq 90°$



Rectangular $|\boldsymbol{a}| = |\boldsymbol{b}|, \gamma = 90°$

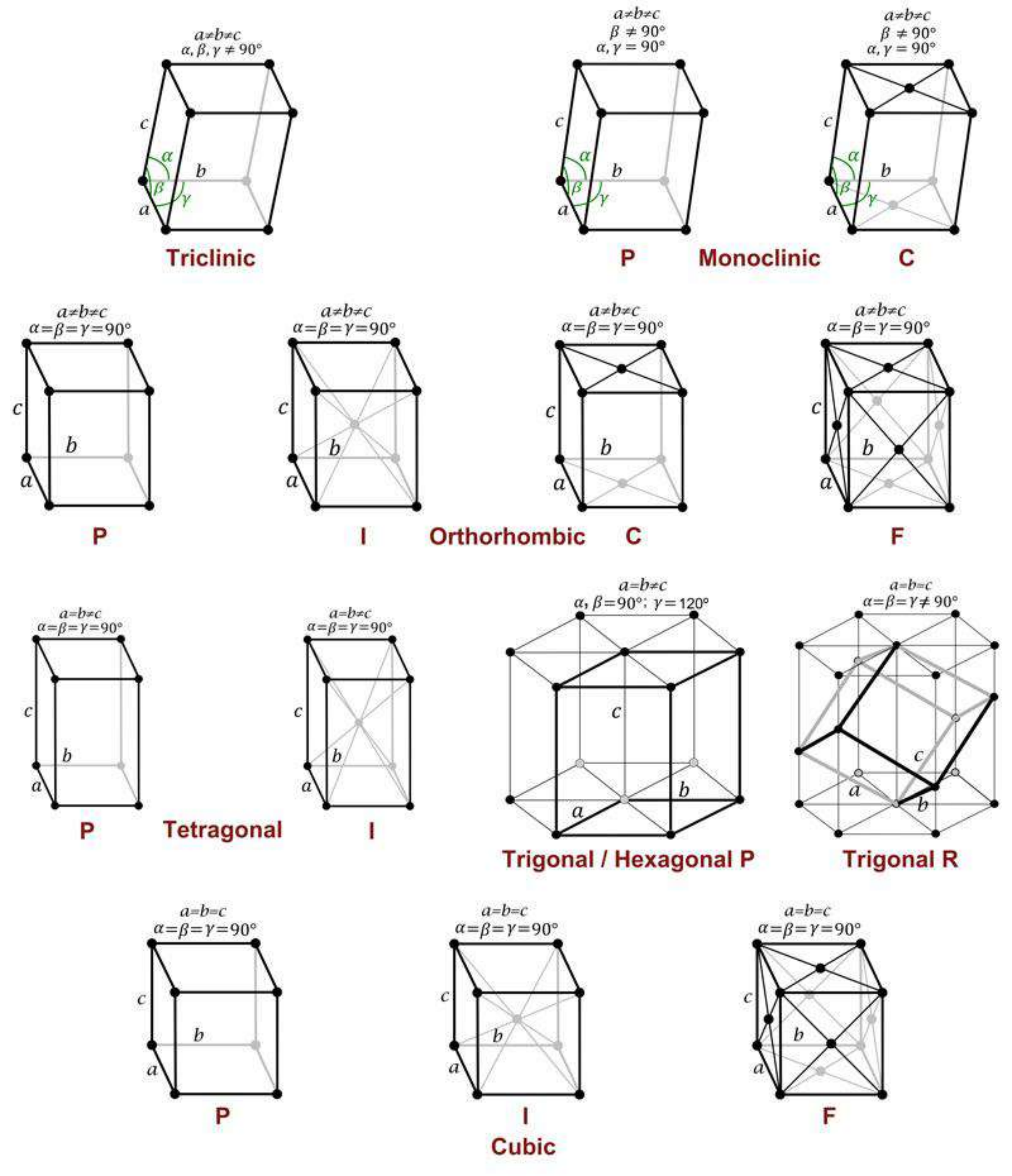


Centred rect. $|\boldsymbol{a}| \neq |\boldsymbol{b}|, \gamma = 90°$

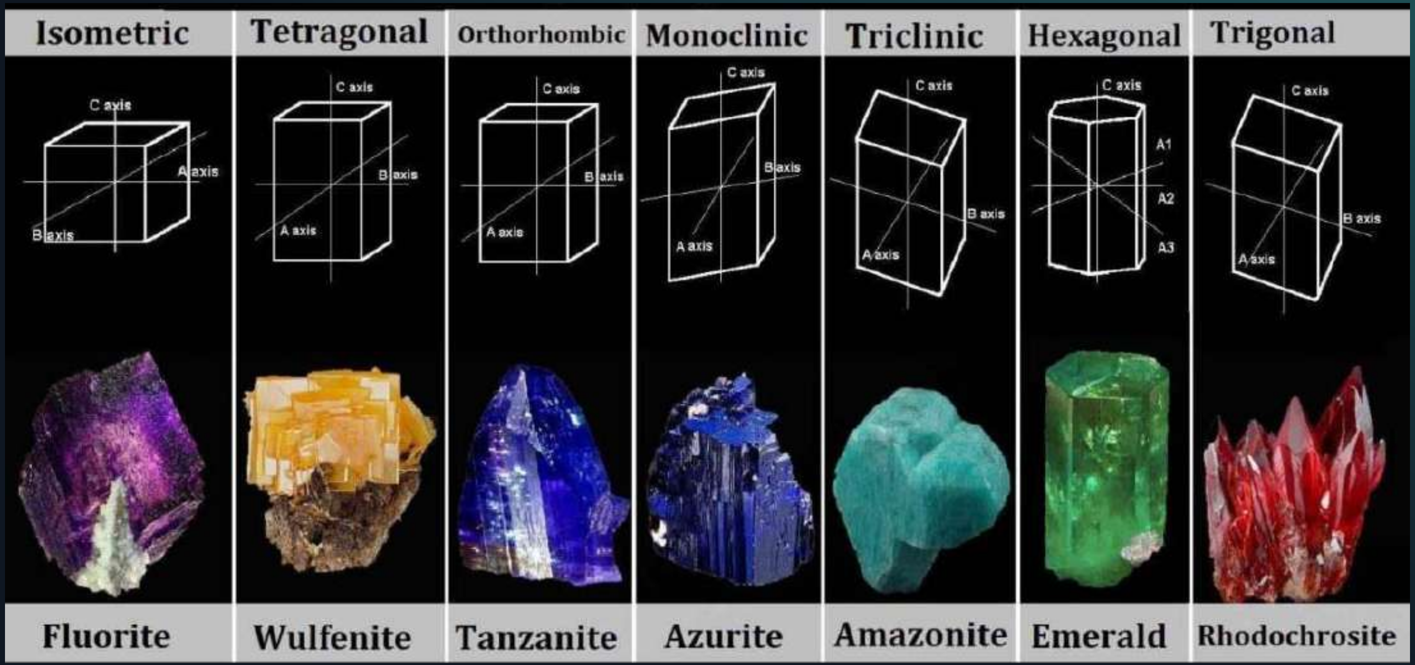


14 Bravais lattices

- P = primitive (1 lattice point)
- C = centered on the two faces perpendicular to the *c* axis (2 lattice points)
- I = centered in the body of the unit cell (2 lattice points)
- F = centered in all faces of the unit cell (4 lattice points)
- R = primitive, identical cell axes and angles (1 lattice points)



7 crystal systems



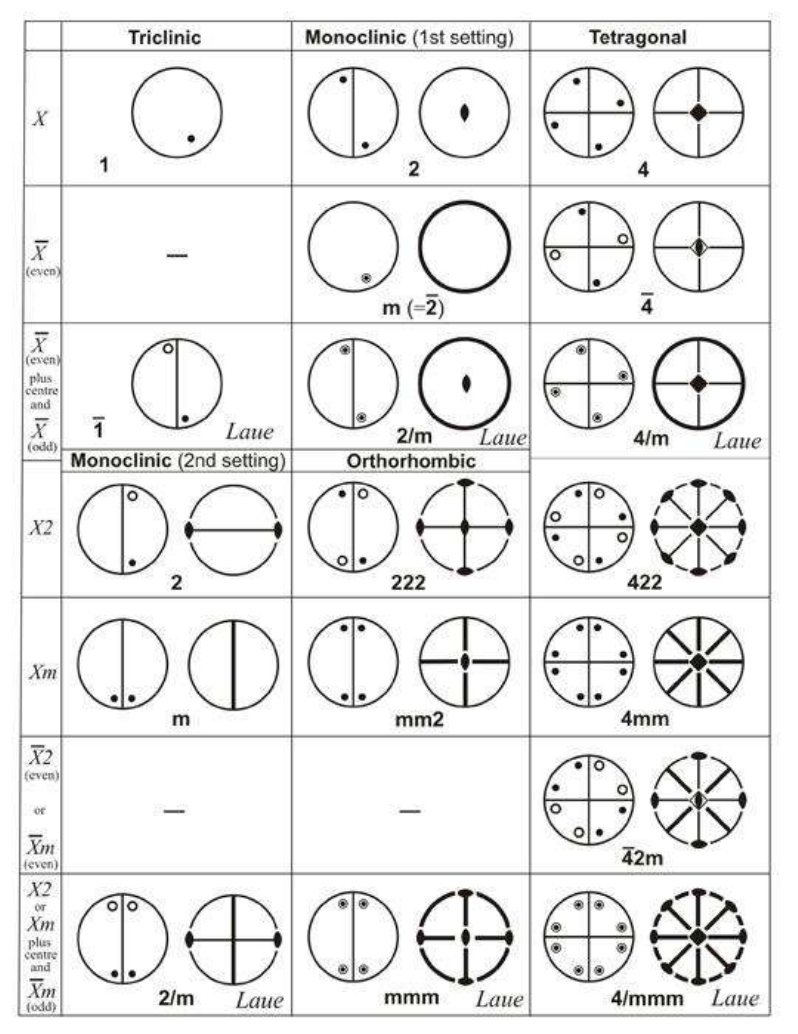
Group	Crystal system	Axis system	Crystal classes
Isometric	Cubic	$\lvert\boldsymbol{a}\rvert = \lvert\boldsymbol{b}\rvert = \lvert\boldsymbol{c}\rvert, \alpha = \beta = \gamma = 90°$	5
Dimetric	Tetragonal	$\lvert\boldsymbol{a}\rvert = \lvert\boldsymbol{b}\rvert \neq \lvert\boldsymbol{c}\rvert, \alpha = \beta = \gamma = 90°$	7
	Hexagonal	$\lvert\boldsymbol{a}\rvert = \lvert\boldsymbol{b}\rvert \neq \lvert\boldsymbol{c}\rvert, \alpha = \beta = 90°, \gamma = 120°$	7
	Rhombohedral (Trigonal)	$\lvert\boldsymbol{a}\rvert = \lvert\boldsymbol{b}\rvert = \lvert\boldsymbol{c}\rvert, \alpha = \beta = \gamma \neq 90°$	5
Trimetric	Orthorhombic	$\lvert\boldsymbol{a}\rvert \neq \lvert\boldsymbol{b}\rvert \neq \lvert\boldsymbol{c}\rvert, \alpha = \beta = \gamma = 90°$	3
	Monoclinic	$\lvert\boldsymbol{a}\rvert \neq \lvert\boldsymbol{b}\rvert \neq \lvert\boldsymbol{c}\rvert, \alpha = \gamma = 90°, \beta \neq 90°$	3
	Triclinic	$\lvert\boldsymbol{a}\rvert \neq \lvert\boldsymbol{b}\rvert \neq \lvert\boldsymbol{c}\rvert, \alpha \neq \beta \neq \gamma \neq 90°$	2

32 crystal classes (point groups)

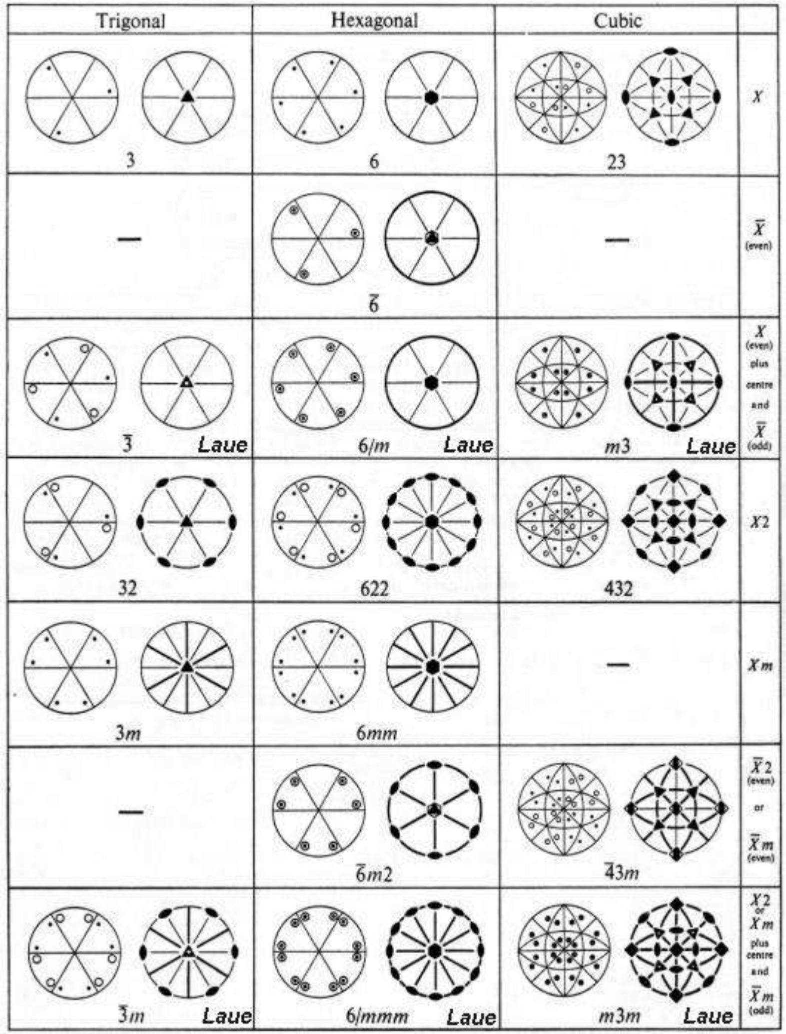
- Derived from the crystallographic (symmetry) analysis of macroscopic crystals (no translations!).
- The Laue group column lists the holoedric group, i.e., the crystal system class with the maximum number of combinations of symmetry elements.
- The point groups column lists the meroedric groups, i.e., the other classes of the system having a lower number of combinations of symmetry operations than the holoedric one.

Crystal system	Point groups	Laue group
Triclinic	1	$\bar{1}$
Monoclinic	2, m	2/m
Orthorhombic	222, mm2	mmm
Tetragonal low	4, $\bar{4}$	4/m
Tetragonal high	422, 4mm, $\bar{4}$2m	4/mmm
Trigonal low	3	$\bar{3}$
Trigonal high	312, 31m	$\bar{3}$1m
Hexagonal low	6, $\bar{6}$	6/m
Hexagonal high	622, 6mm, $\bar{6}$m2	6/mmm
Rhombohedral low	R3	R$\bar{3}$
Rhombohedral high	R32, R3m	R$\bar{3}$m
Cubic low	23	m3
Cubic high	432, $\bar{4}$3m	m3m

32 crystal classes (point groups)



Representations of the 32 symmetry classes as stereograms of poles



Symmetry & translation

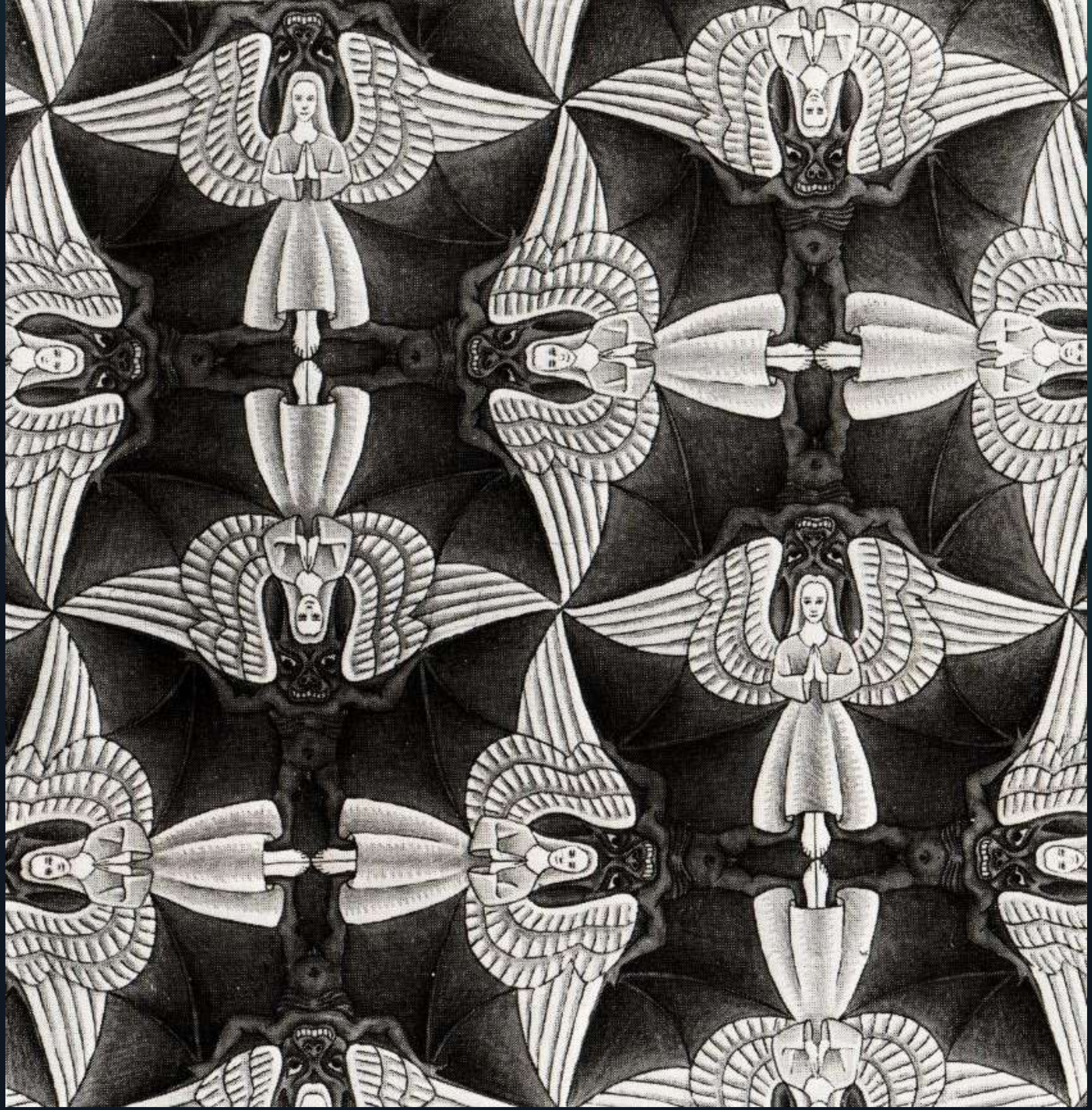
The space groups

Dimensionality	Bravais lattices	Groups of symmetry operations		
1D	1	2	…	
2D	5	10	17	PLANAR GROUPS
3D	14	32	230	SPACE GROUPS

Symmetry & translation

In a two-dimensional design, such as that of a wall-paper, a unit of pattern is repeated at regular intervals. Let us chose some representative point in the unit of pattern, and mark the position of similar points in all the other units. If these points be considered alone, the pattern being for the moment disregarded, it will be seen that they form a regular network. By drawing lines through them, the area can be divided into a series of cells each of which contains a unit of the pattern. It is immaterial which point of the design is chosen as representative, for a similar network of points will always be obtained

Bragg, Sir Lawrence, et al. The Crystalline State, Volumes I-IV. Ithaca, NY: Cornell University Press, 1965

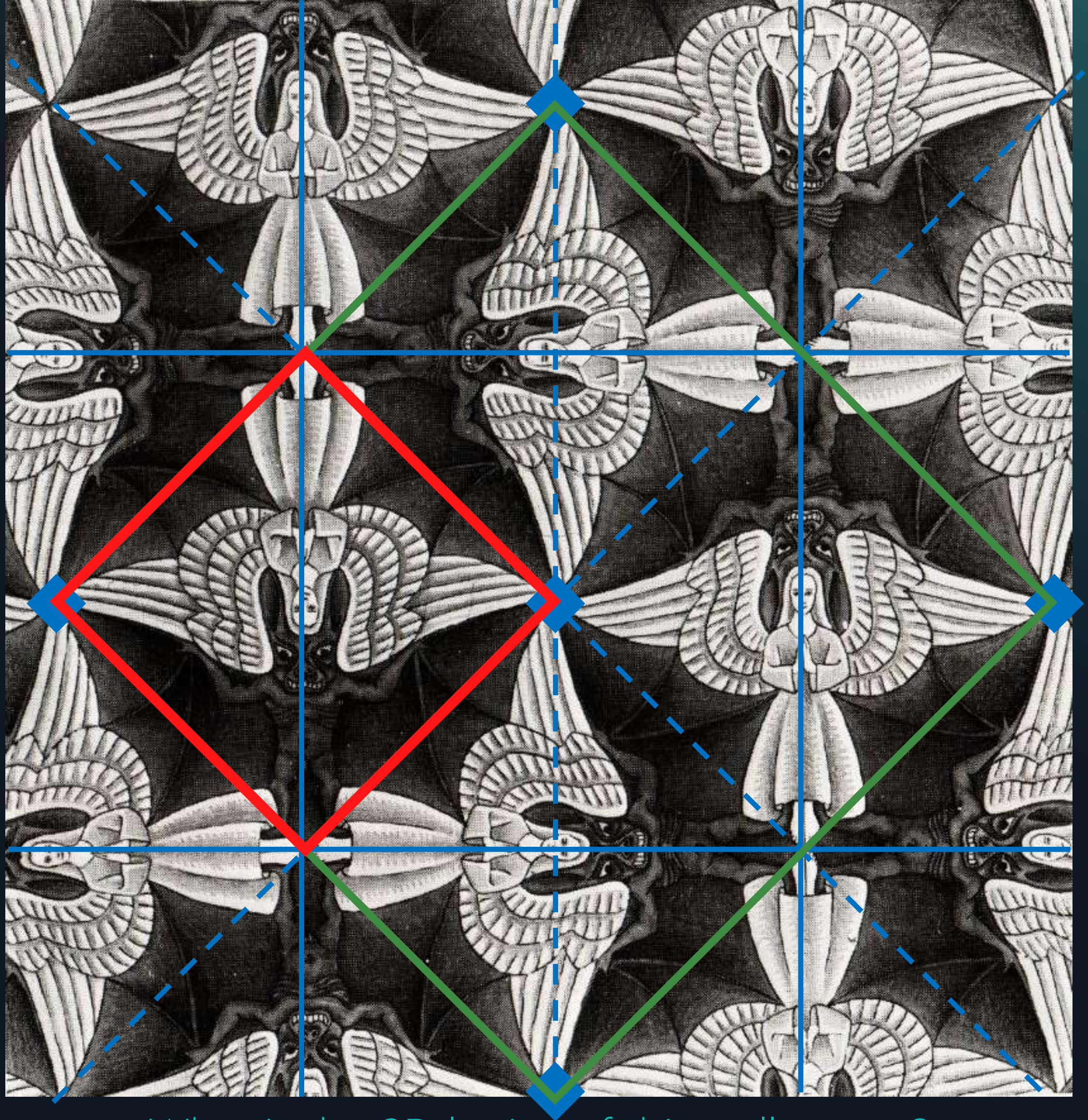


What is the 2D lattice of this wall-paper?
What symmetry elements do you see?

Symmetry & translation

In a two-dimensional design, such as that of a wall-paper, a unit of pattern is repeated at regular intervals. Let us chose some representative point in the unit of pattern, and mark the position of similar points in all the other units. If these points be considered alone, the pattern being for the moment disregarded, it will be seen that they form a regular network. By drawing lines through them, the area can be divided into a series of cells each of which contains a unit of the pattern. It is immaterial which point of the design is chosen as representative, for a similar network of points will always be obtained

Bragg, Sir Lawrence, et al. The Crystalline State, Volumes I-IV. Ithaca, NY: Cornell University Press, 1965



What is the 2D lattice of this wall-paper?
What symmetry elements do you see?

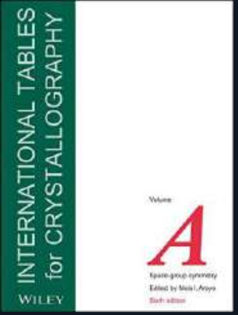
Asymmetric unit & unit cell

Asymmetric unit

The asymmetric unit of a space group is that part of the crystallographic unit cell which can be used to generate the complete unit cell by the symmetry of the space group.

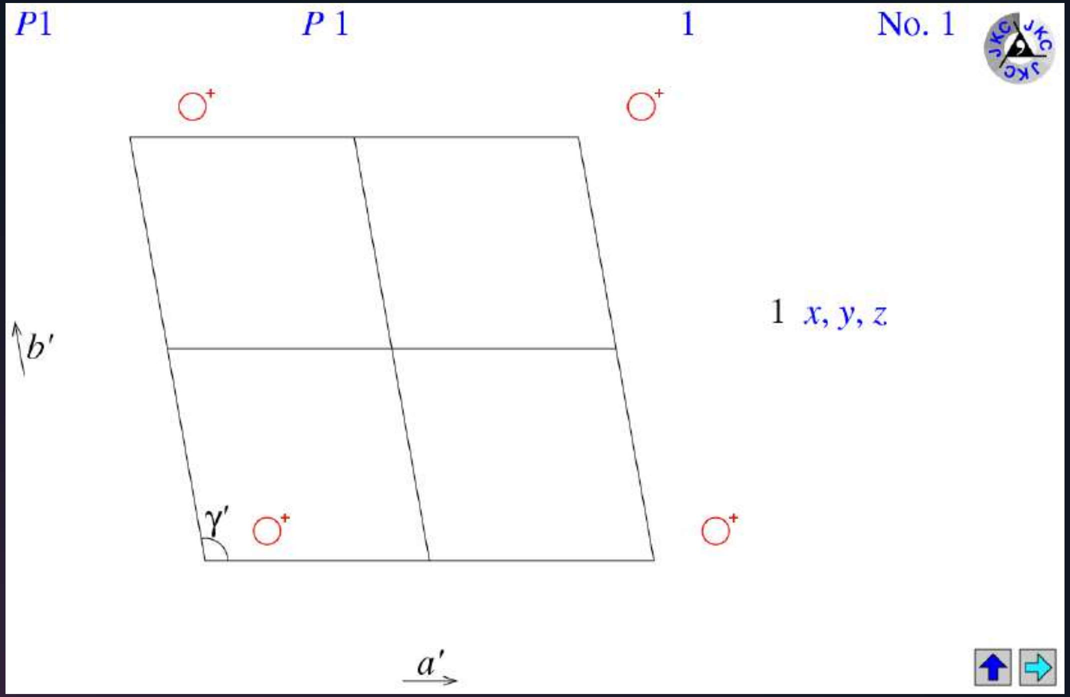
Unit cell

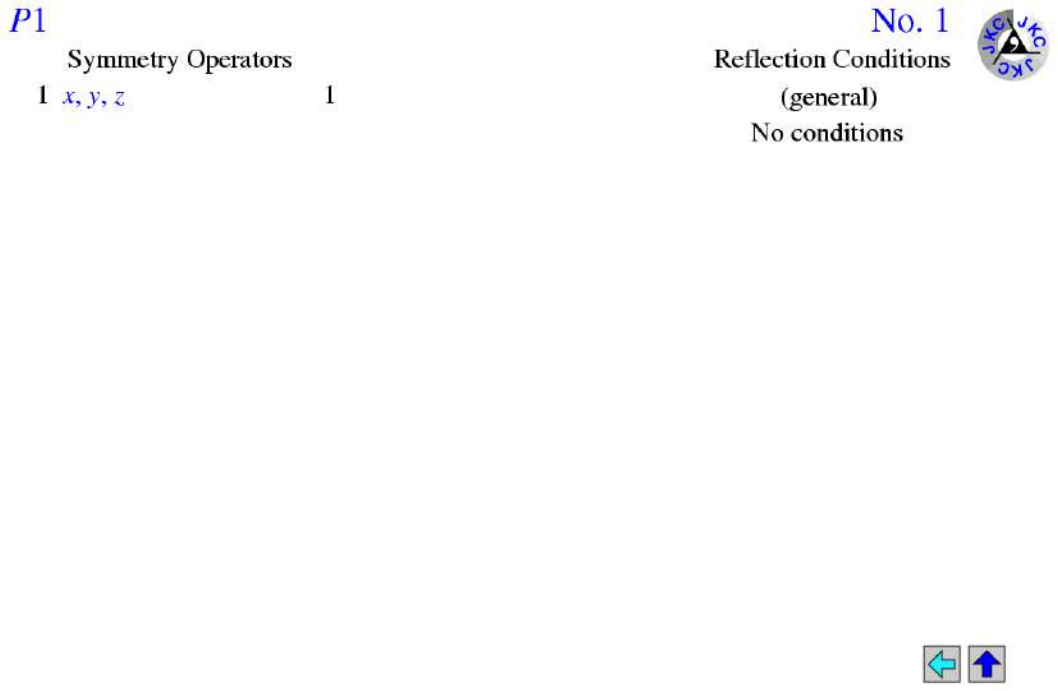
The unit cell is the minimum portion of space that can generate the complete crystal structure only by translation operations.



Space group diagrams and tables

Source: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm





*P*1 No. 1

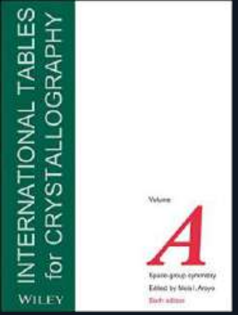
Symmetry Operators

1 *x*, *y*, *z* 1

Reflection Conditions

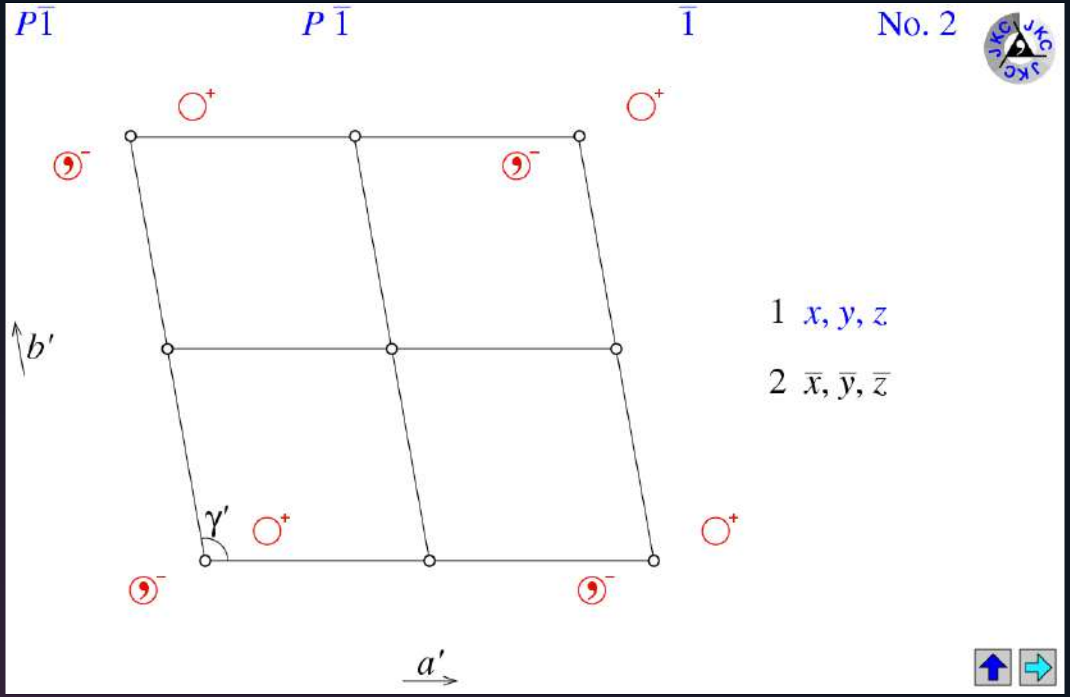
(general)

No conditions



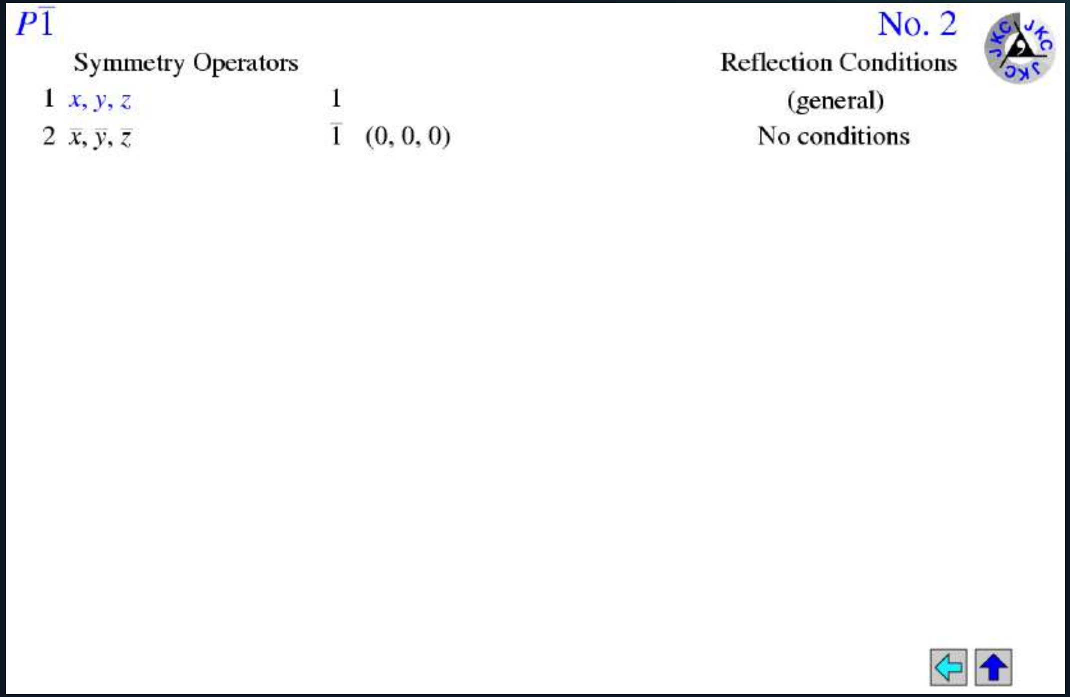
Space group diagrams and tables

Source: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm



1 x, y, z

2 $\bar{x}, \bar{y}, \bar{z}$



$P\bar{1}$ No. 2

Symmetry Operators

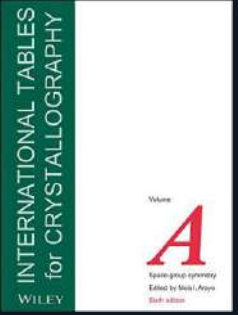
1 x, y, z 1

2 $\bar{x}, \bar{y}, \bar{z}$ $\bar{1}$ (0, 0, 0)

Reflection Conditions

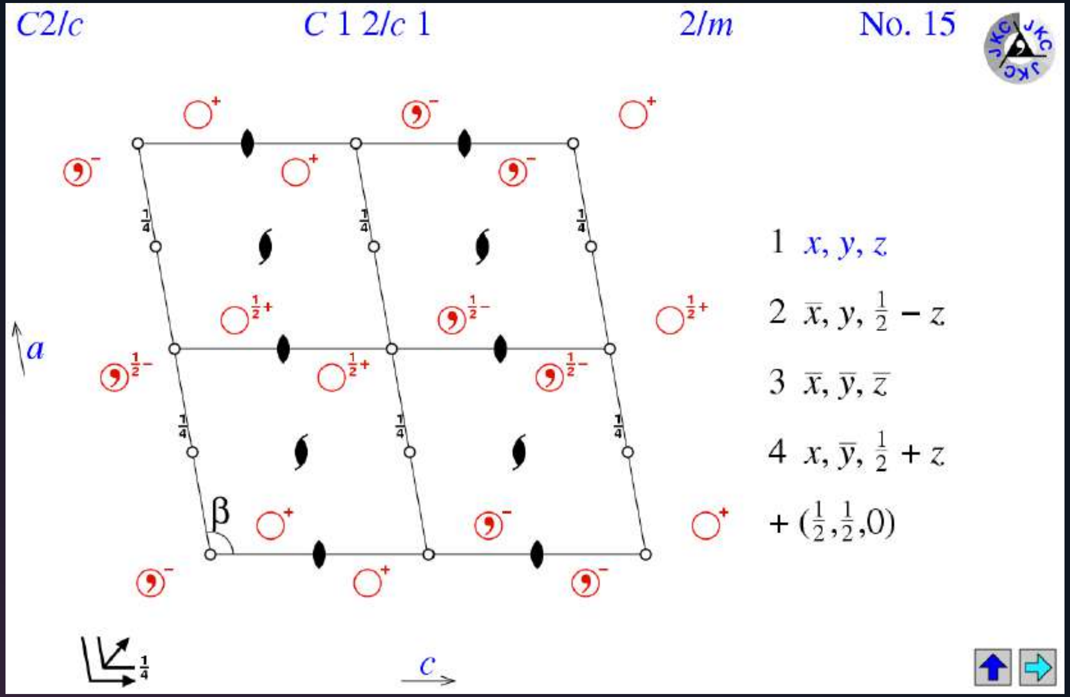
(general)

No conditions



Space group diagrams and tables

Source: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm



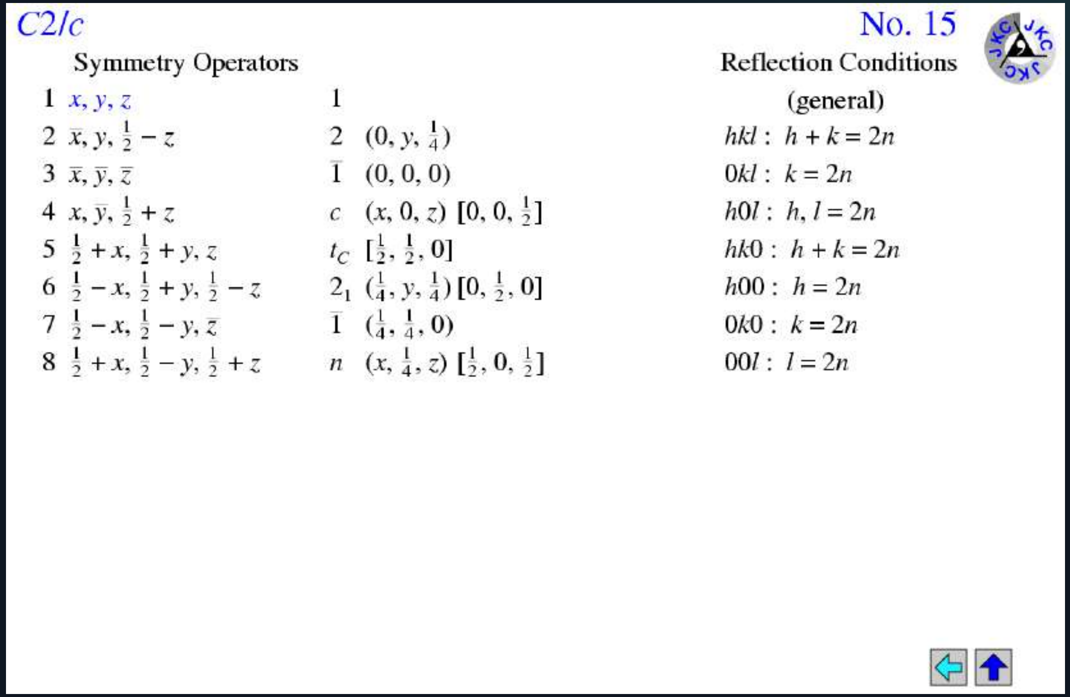
1 x, y, z

2 $\bar{x}, y, \frac{1}{2} - z$

3 $\bar{x}, \bar{y}, \bar{z}$

4 $x, \bar{y}, \frac{1}{2} + z$

$+ (\frac{1}{2}, \frac{1}{2}, 0)$


C2/c — No. 15

Symmetry Operators		
1	x, y, z	1
2	$\bar{x}, y, \frac{1}{2} - z$	$2\ (0, y, \frac{1}{4})$
3	$\bar{x}, \bar{y}, \bar{z}$	$\bar{1}\ (0, 0, 0)$
4	$x, \bar{y}, \frac{1}{2} + z$	$c\ (x, 0, z)\ [0, 0, \frac{1}{2}]$
5	$\frac{1}{2} + x, \frac{1}{2} + y, z$	$t_C\ [\frac{1}{2}, \frac{1}{2}, 0]$
6	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	$2_1\ (\frac{1}{4}, y, \frac{1}{4})\ [0, \frac{1}{2}, 0]$
7	$\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$	$\bar{1}\ (\frac{1}{4}, \frac{1}{4}, 0)$
8	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	$n\ (x, \frac{1}{4}, z)\ [\frac{1}{2}, 0, \frac{1}{2}]$

Reflection Conditions
(general)

$hkl:\ h + k = 2n$

$0kl:\ k = 2n$

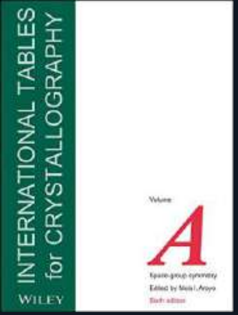
$h0l:\ h, l = 2n$

$hk0:\ h + k = 2n$

$h00:\ h = 2n$

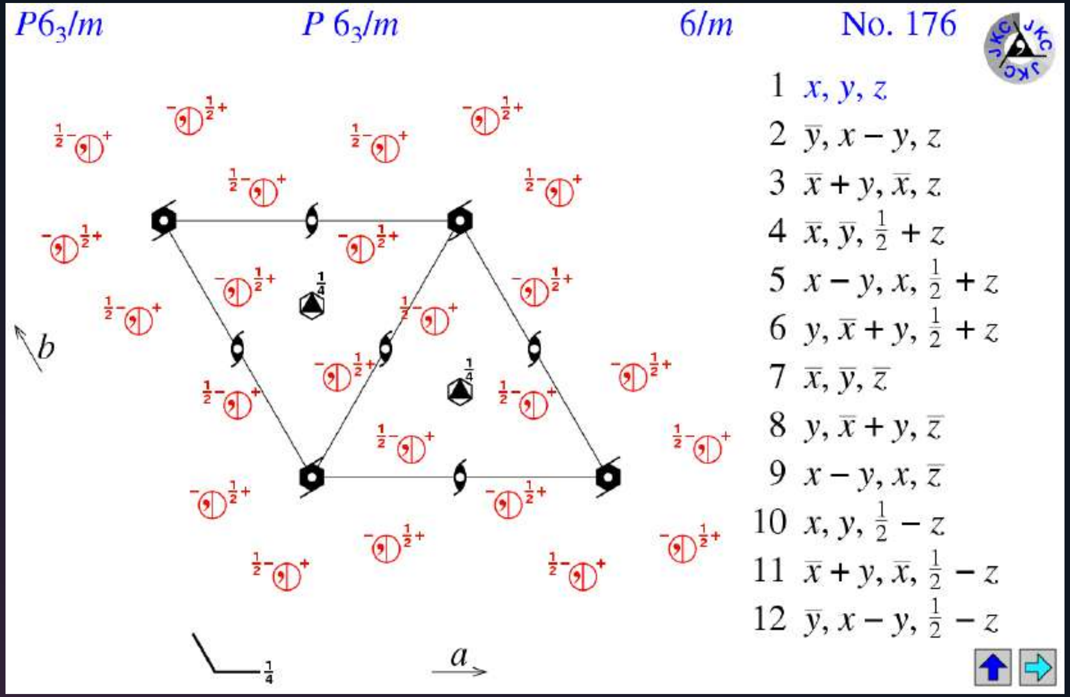
$0k0:\ k = 2n$

$00l:\ l = 2n$

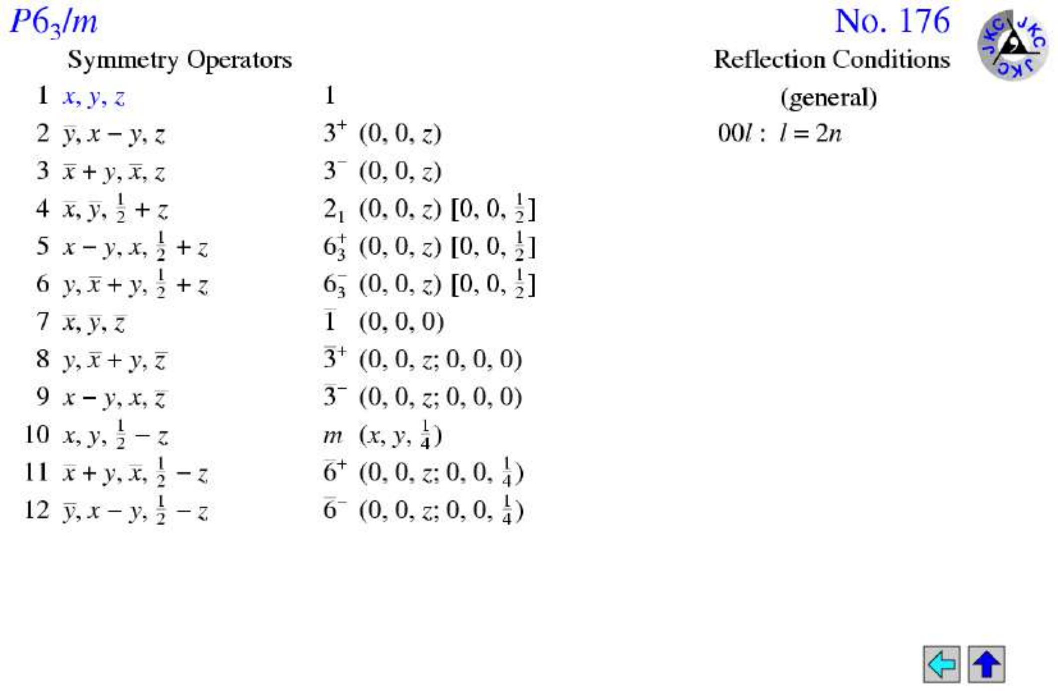


Space group diagrams and tables

Source: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm



1 x, y, z
2 $\bar{y}, x-y, z$
3 $\bar{x}+y, \bar{x}, z$
4 $\bar{x}, \bar{y}, \frac{1}{2}+z$
5 $x-y, x, \frac{1}{2}+z$
6 $y, \bar{x}+y, \frac{1}{2}+z$
7 $\bar{x}, \bar{y}, \bar{z}$
8 $y, \bar{x}+y, \bar{z}$
9 $x-y, x, \bar{z}$
10 $x, y, \frac{1}{2}-z$
11 $\bar{x}+y, \bar{x}, \frac{1}{2}-z$
12 $\bar{y}, x-y, \frac{1}{2}-z$



$P6_3/m$ No. 176

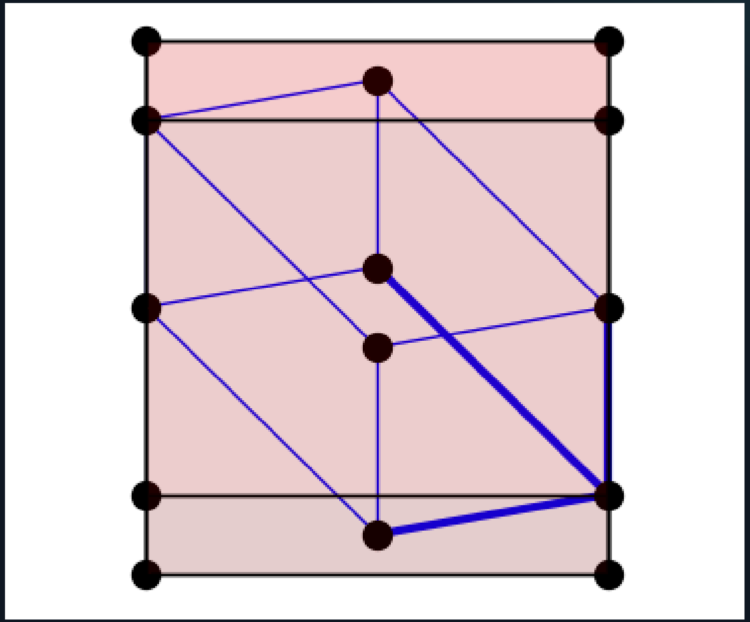
	Symmetry Operators	
1	x, y, z	1
2	$\bar{y}, x-y, z$	3^+ $(0, 0, z)$
3	$\bar{x}+y, \bar{x}, z$	3^- $(0, 0, z)$
4	$\bar{x}, \bar{y}, \frac{1}{2}+z$	2_1 $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
5	$x-y, x, \frac{1}{2}+z$	6_3^+ $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
6	$y, \bar{x}+y, \frac{1}{2}+z$	6_3^- $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
7	$\bar{x}, \bar{y}, \bar{z}$	$\bar{1}$ $(0, 0, 0)$
8	$y, \bar{x}+y, \bar{z}$	$\bar{3}^+$ $(0, 0, z; 0, 0, 0)$
9	$x-y, x, \bar{z}$	$\bar{3}^-$ $(0, 0, z; 0, 0, 0)$
10	$x, y, \frac{1}{2}-z$	m $(x, y, \frac{1}{4})$
11	$\bar{x}+y, \bar{x}, \frac{1}{2}-z$	$\bar{6}^+$ $(0, 0, z; 0, 0, \frac{1}{4})$
12	$\bar{y}, x-y, \frac{1}{2}-z$	$\bar{6}^-$ $(0, 0, z; 0, 0, \frac{1}{4})$

Reflection Conditions
(general)
$00l$: $l = 2n$

Cubic lattices

Characteristics

	Simple	BCC	FCC
Volume, conventional (crystallographic) cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	${}^{1}/_{2}\, a^3$	${}^{1}/_{4}\, a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbours	6	8	12
Nearest-neighbour distance	a	$3^{1/2}\, a/2$	$a/2^{1/2}$
Number of second neighbours	12	6	6
Second neighbour distance	$2^{1/2}/a$	a	a
Packing fraction	$\frac{1}{6}\pi$	$\frac{1}{8}\pi\sqrt{3}$	$\frac{1}{6}\pi\sqrt{2}$

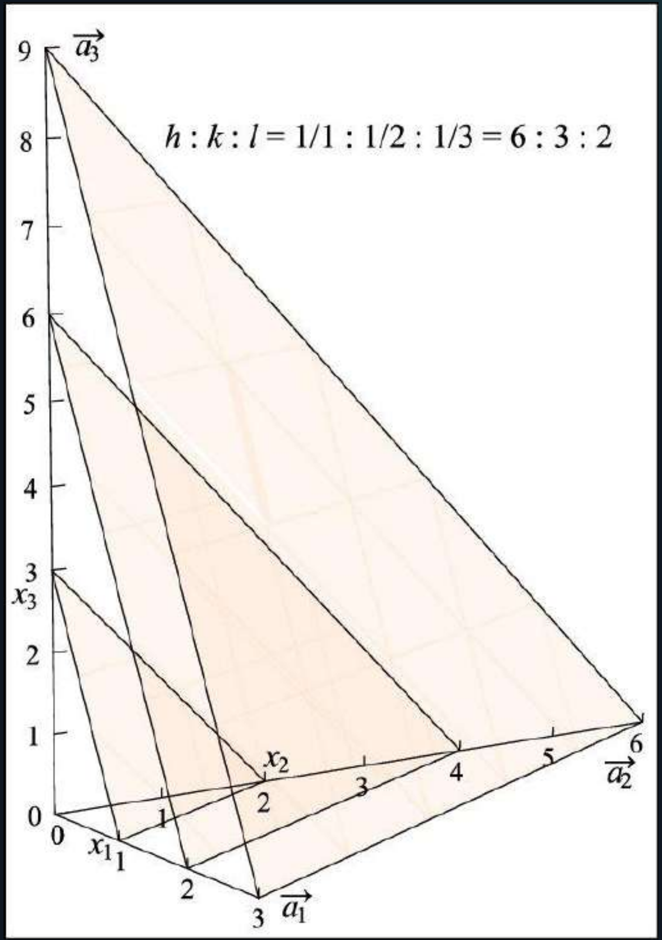


Example of an FCC lattice

Crystal planes

How to describe them

- Crystal planes are determined by three non-collinear points.
- The three points are used to determine three indices that define the crystal plane in this way:
    1. Find the intercepts of the three points on the axes $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$. In the example, $x_1 = (1,0,0)$, $x_2 = (0,2,0)$ and $x_3 = (0,0,3)$, thus the numbers are 1, 2 and 3;
    2. Take the reciprocal of these numbers, hence $1/1$, $1/2$ and $1/3$;
    3. Reduce to three integers having the same ratio, thus $\frac{1}{1} : \frac{1}{2} : \frac{1}{3} \rightarrow \frac{6}{6} : \frac{3}{6} : \frac{2}{6} \rightarrow 6 : 3 : 2$
    4. Encolse these three integers in parentheses $(hkl) = (632)$ – Miller Indices
- If the intercept is at infinity (plane parallel to the axis), the corresponding index is zero.
- If the plane cuts an axis on the negative side of the origin, the corresponding index is negative and labeled as a number with the minus sign above the index [e.g., $(0\bar{1}1)$]

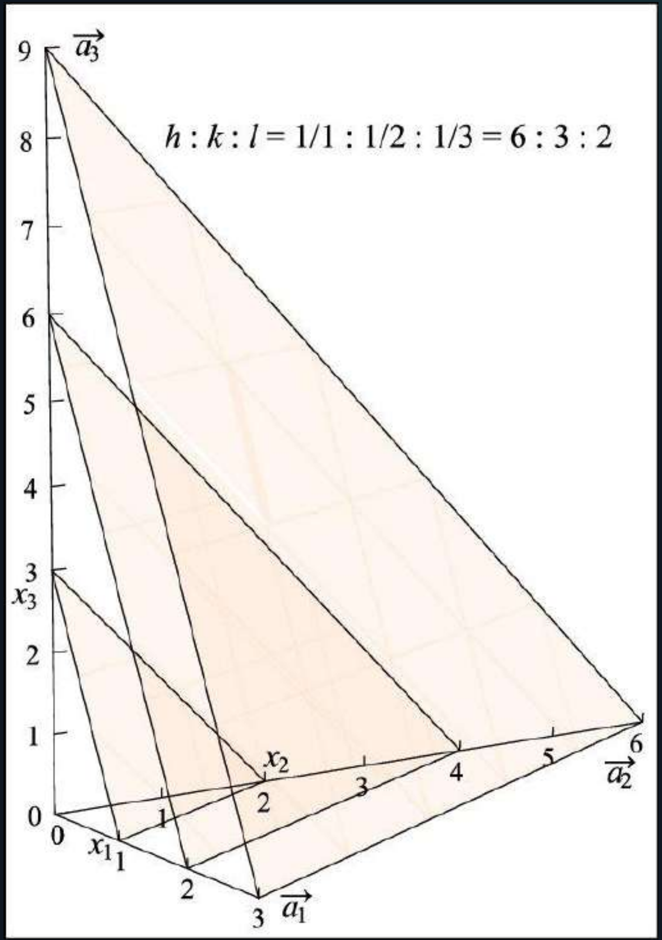


Crystal planes

How to describe them

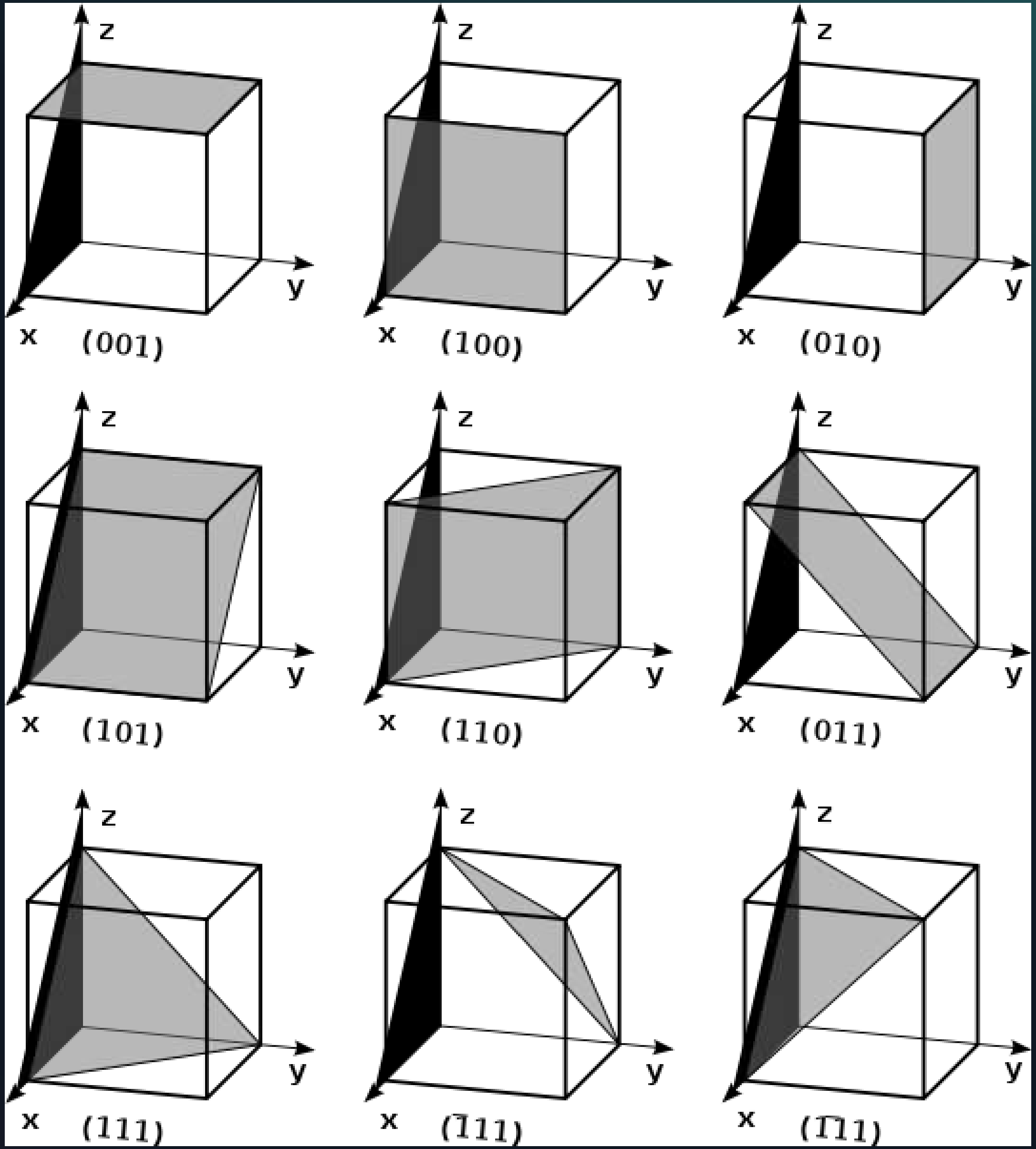
Some notes:

- Planes that are equivalent by symmetry are denoted by curly brakets, e.g., the set of cube faces are $\{100\}$ and in the example on the right all the planes are parallel to the (632), hence they form the $\{632\}$ family.
- The (200) plane is parallel to the (100) one, but cuts the a axis on $a/2$.



Important crystal planes in cubic crystals

- Note the symmetry equivalency



Crystal directions

How to describe them

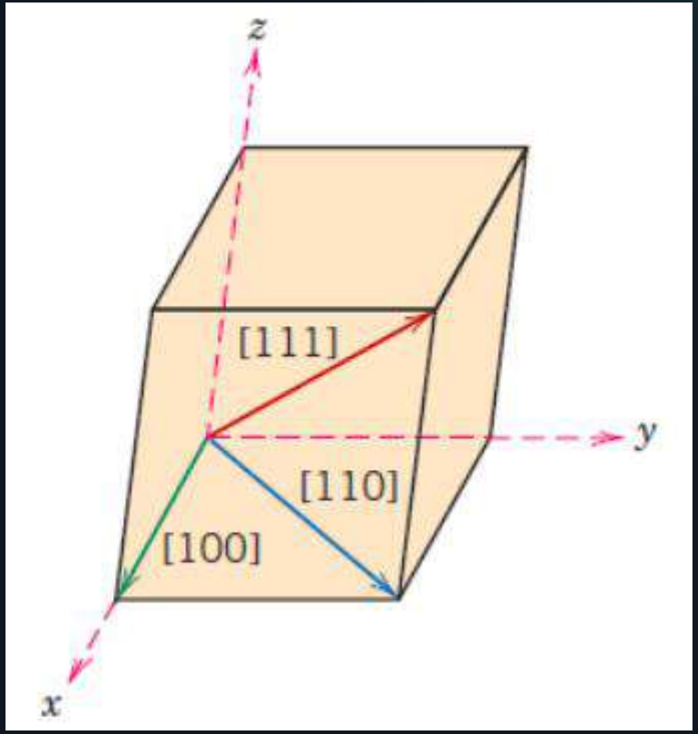
The Miller-Bravais indices:

$$[u, v, w]$$

They describe a vector $u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ that originates from the origin of the cell, $(0,0,0)$.

Notes:

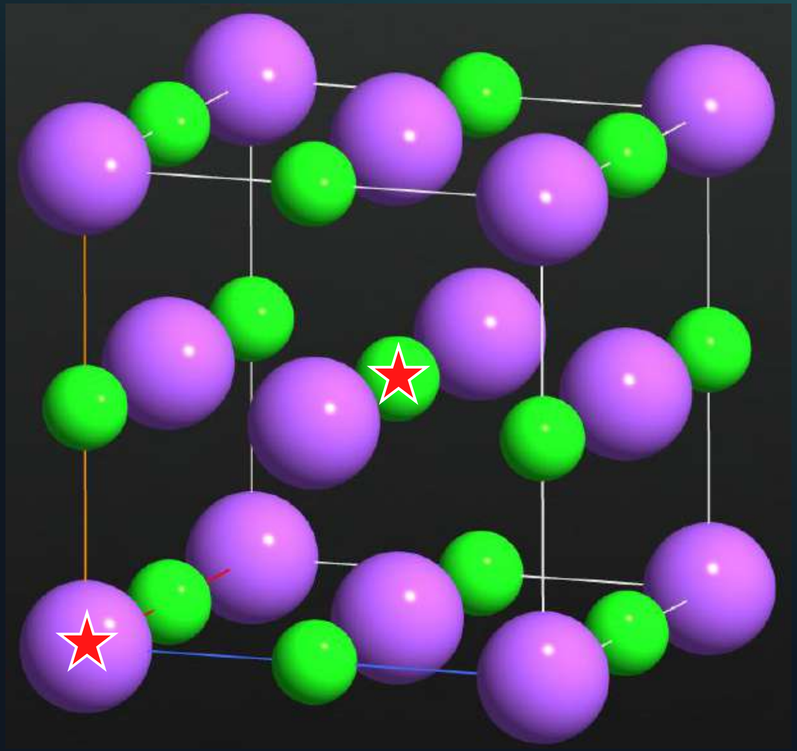
- Directions that are equivalent by symmetry are denoted by brakets, e.g., all the directions parallel to the $[1,1,1]$ are labeled as the $\langle 1,1,1 \rangle$ family.
- In cubic crystals, the direction $[u, v, w] = [h, k, l]$ is perpendicular to the plane (h, k, l), but this is not generally true in other crystal systems.



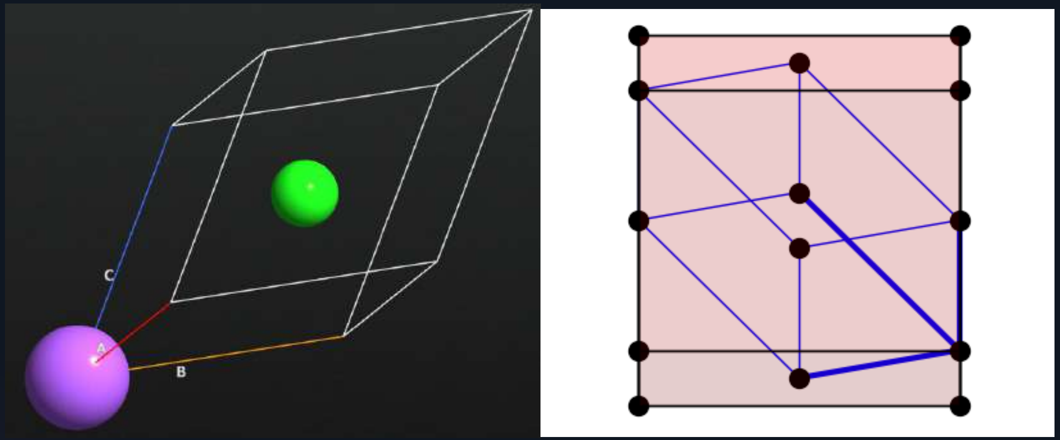
Simple crystal structures
NaCl

- Bravais lattice: FCC
- Basis: one Na atom at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ and one Cl atom at $(0,0,0)$
- Other isostructural crystals:

Crystal	*a* (Å)		Crystal	*a* (Å)
LiH	4.08		AgBr	5.77
NaCl	5.63		MgO	4.20
KCl	6.29		MnO	4.43
PbS	5.92		KBr	6.59



Crystallographic cell

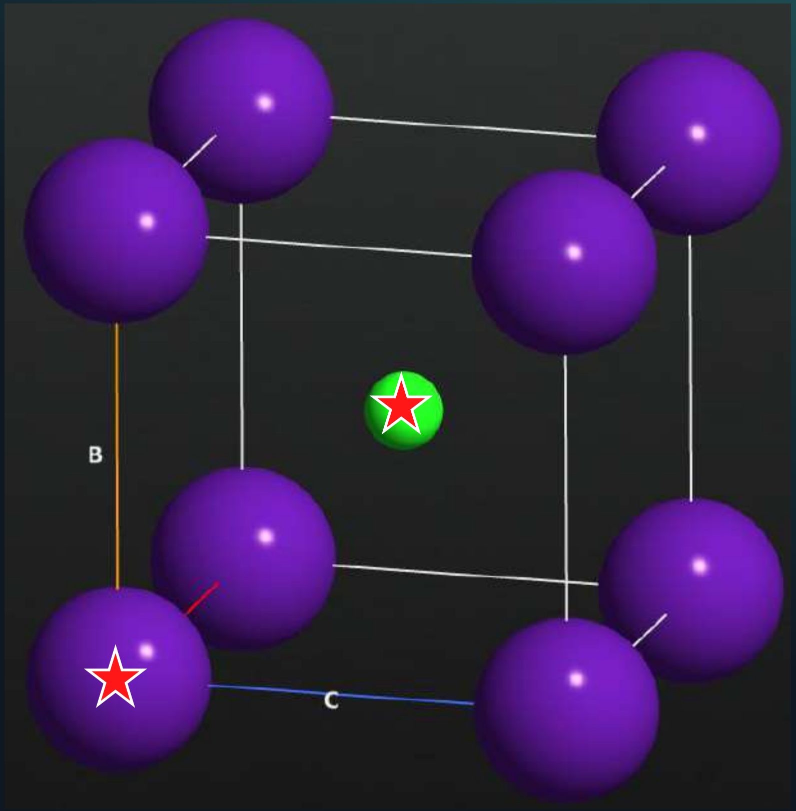


Primitive cell

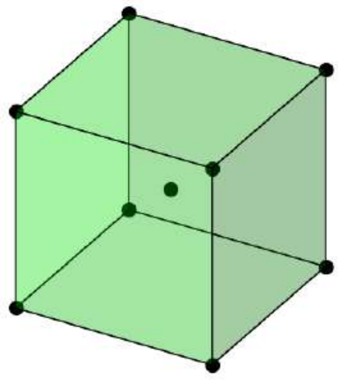
Simple crystal structures
CsCl

- Bravais lattice: BCC
- Basis: one Cl atom at $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ and one Cs atom at $(0, 0, 0)$
- Other isostructural crystals:

Crystal	*a* (Å)		Crystal	*a* (Å)
CsCl	4.11		CuZn	2.94
TlBr	3.97		AgMg	3.28
NH_4Cl	3.87		LiHg	3.29

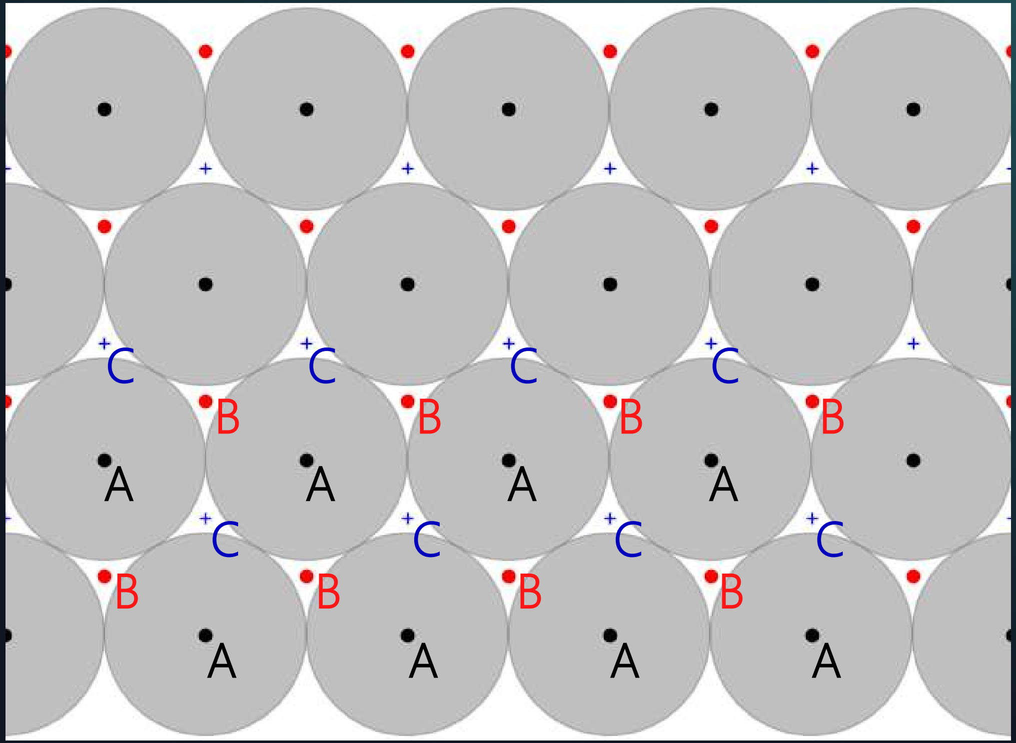


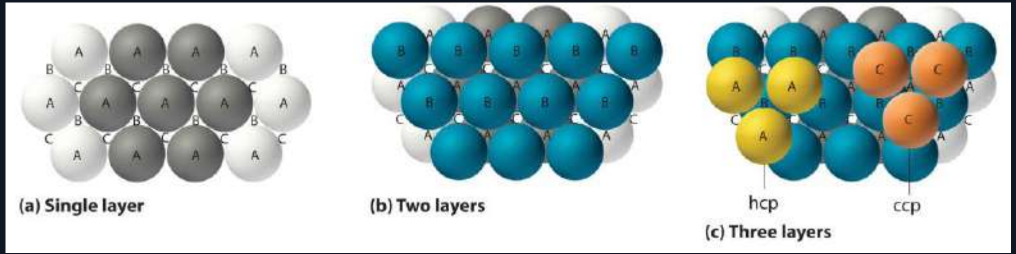
Crystallographic cell



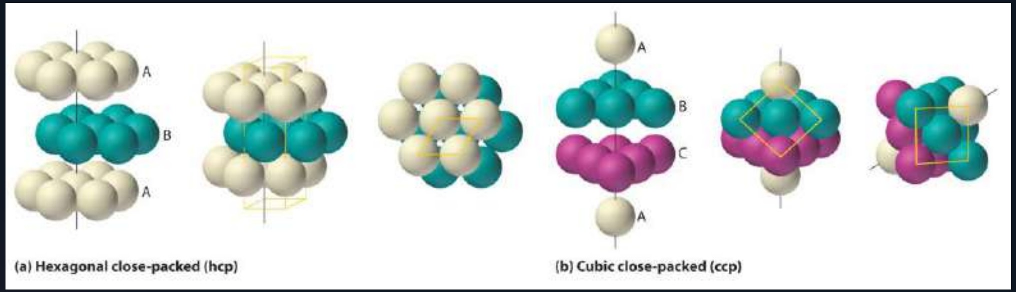
Hexagonal close-packed structure (hcp)

- Different ways to arrange spheres in the 3D space to minimize the interstitial volume.
- In the first layer, A, each sphere is surrounded by six other spheres. The second layer (equivalent to A) is placed on the B holes, where each sphere is in contact with three spheres from the A layer.
- The third layer can be added in two ways:
  1. over the holes C in the first layer, not occupied by the second layer → ABCABC packing → FCC structure
  2. directly over the spheres of the A layer → ABABAB packing → hexagonal structure
- In each case, the filled volume is 74% of the total volume.





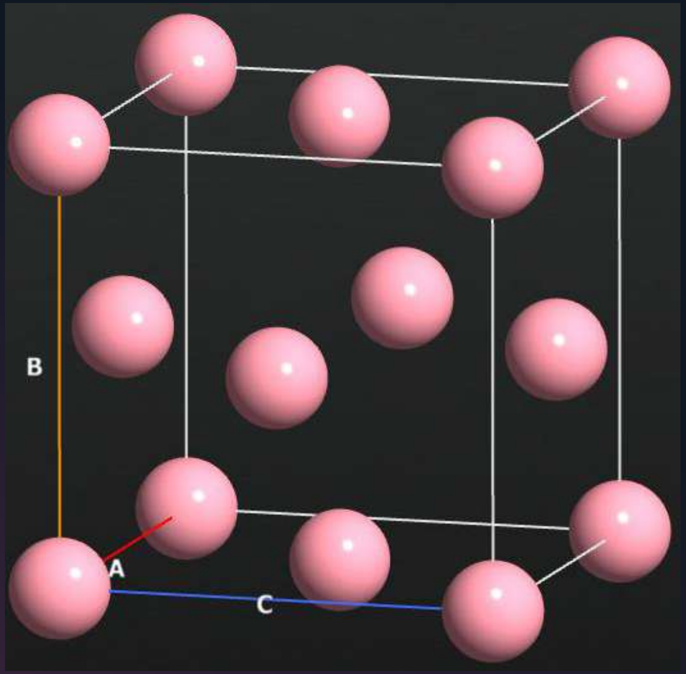
(a) Single layer
(b) Two layers
(c) Three layers



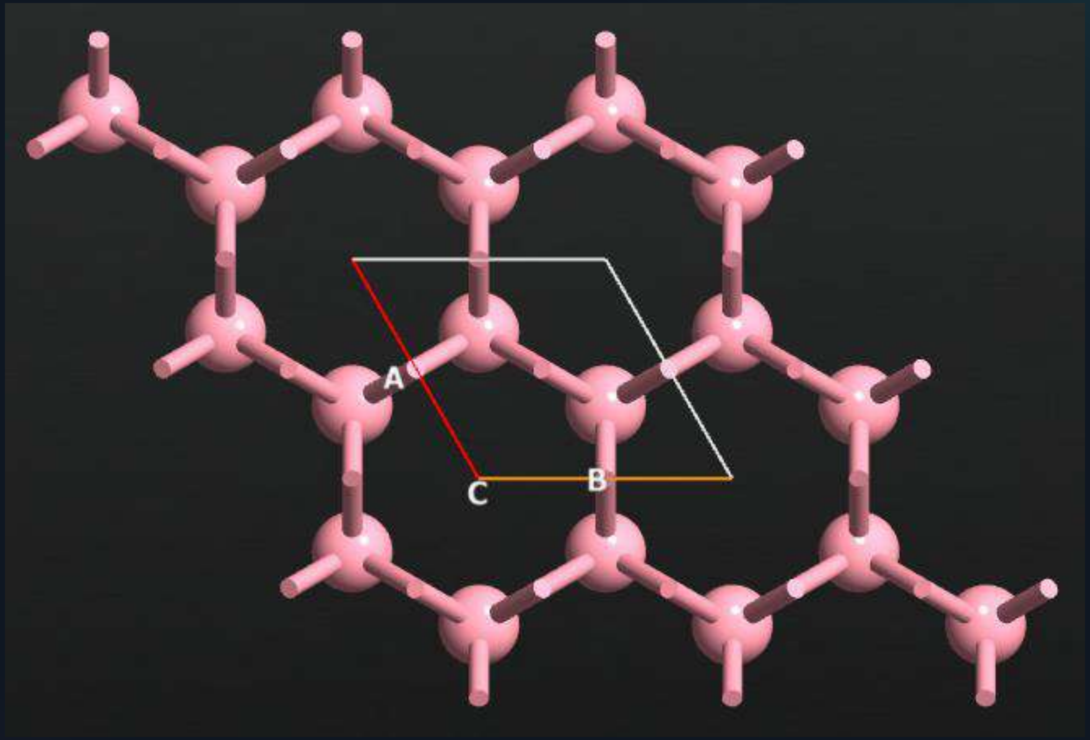
(a) Hexagonal close-packed (hcp)
(b) Cubic close-packed (ccp)

Hexagonal close-packed structure (hcp)

α-Cobalt



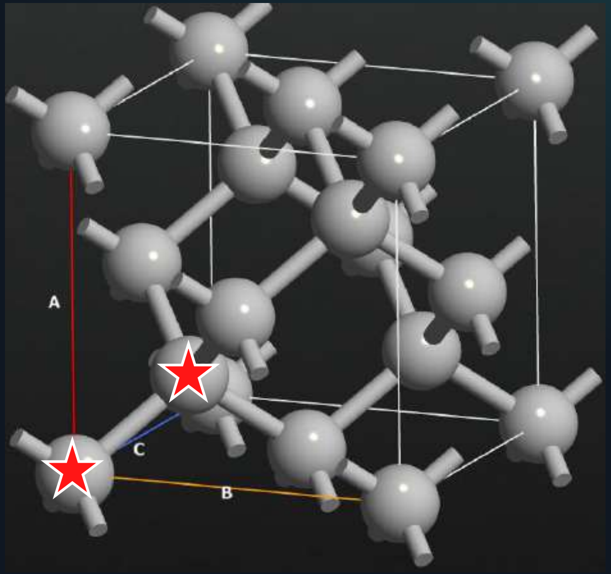
ε-Cobalt



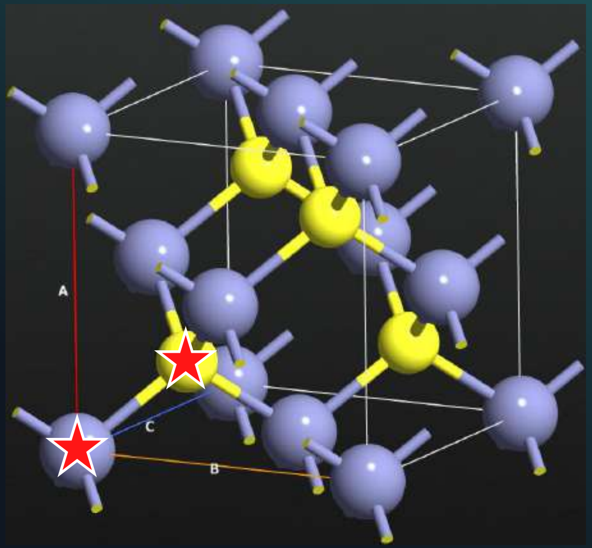
Simple crystal structures
Diamond and cubic ZnS

- Bravais lattice: FCC
- Basis: two atoms at $(0,0,0)$ and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$
- It is a consequence of the directional covalent bonding
- Other isostructural crystals:

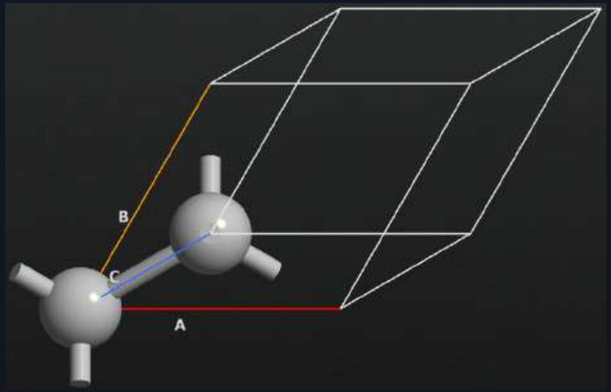
Crystal	*a* (Å)		Crystal	*a* (Å)
C	3.56		ZnS	5.41
Si	5.43		CuF	4.26
Ge	5.65		SiC	4.35
Sn	6.46		AgI	6.47



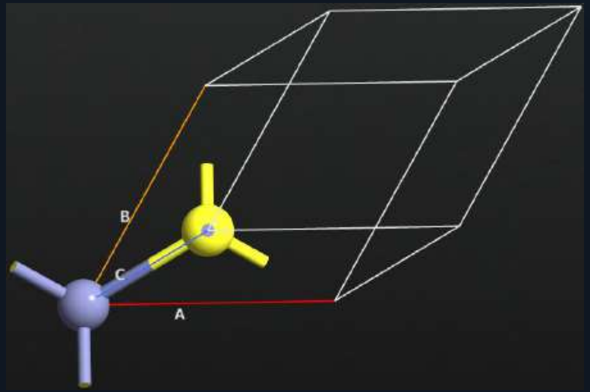
Diamond crystallographic cell



ZnS crystallographic cell



Diamond primitive cell

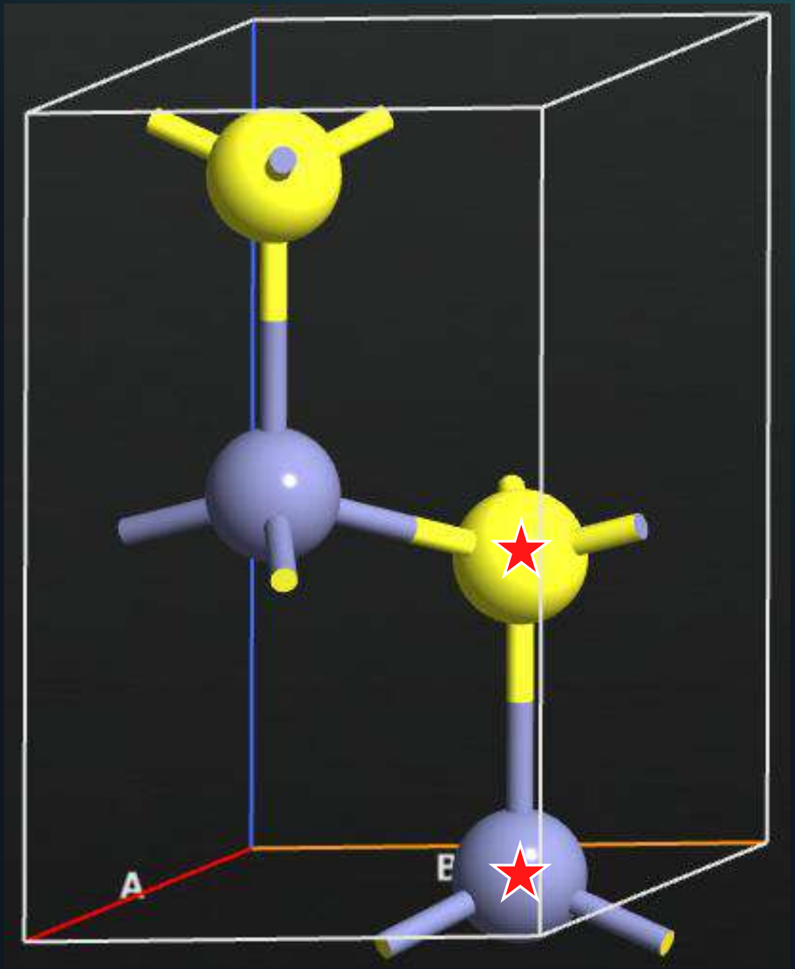


ZnS primitive cell

Simple crystal structures
Hexagonal ZnS

- Bravais lattice: Hexagonal
- Basis: one Zn atom at $\left(\frac{1}{3}, \frac{2}{3}, 0\right)$and $\left(\frac{1}{3}, \frac{2}{3}, \frac{3}{8}\right)$
- Other isostructural crystals:

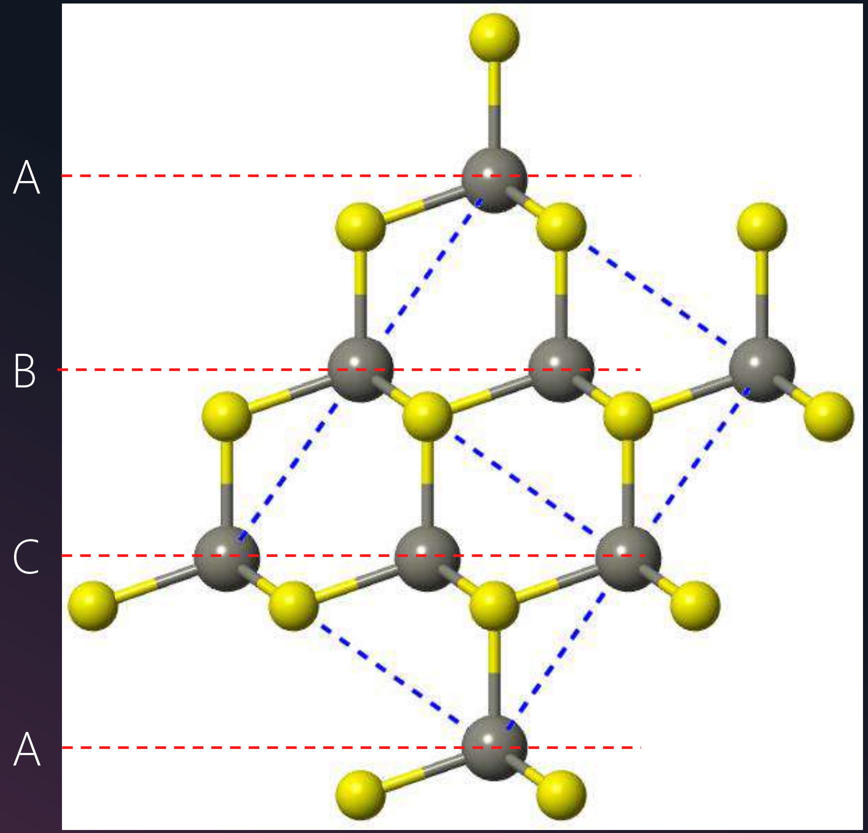
Crystal	*a* (Å)	*c* (Å)		Crystal	*a* (Å)	*c* (Å)
ZnS	3.81	6.23		SiC	3.25	5.21
ZnO	3.25	5.12		Hex. Diamond	2.52	4.12



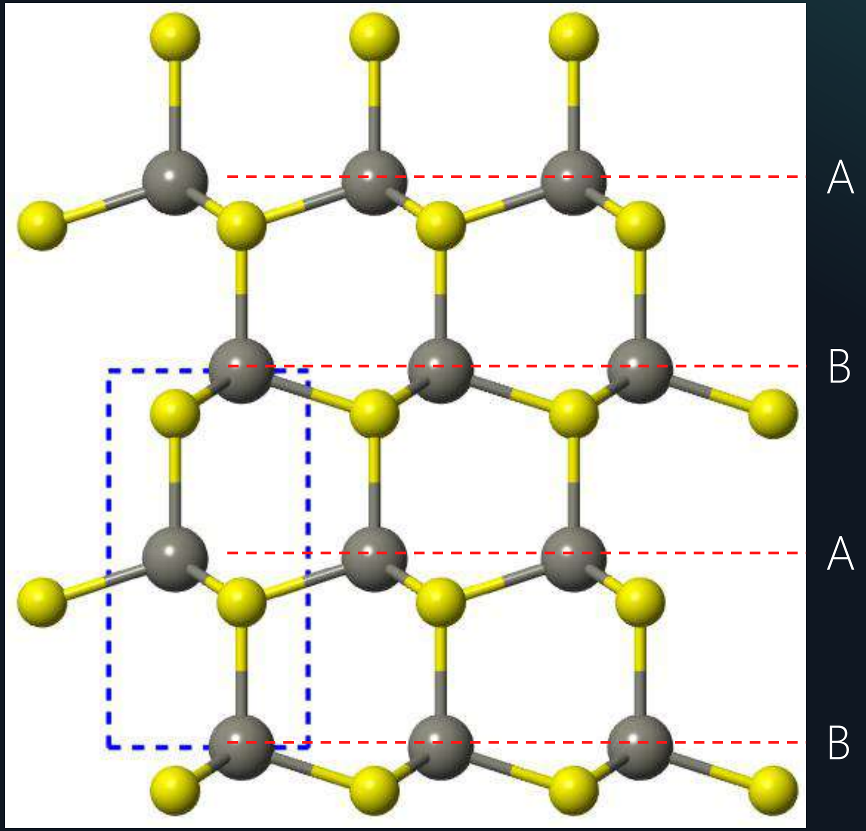
Hexagonal ZnS (wurtzite)

Cubic *vs* Hexagonal ZnS

Cubic ZnS

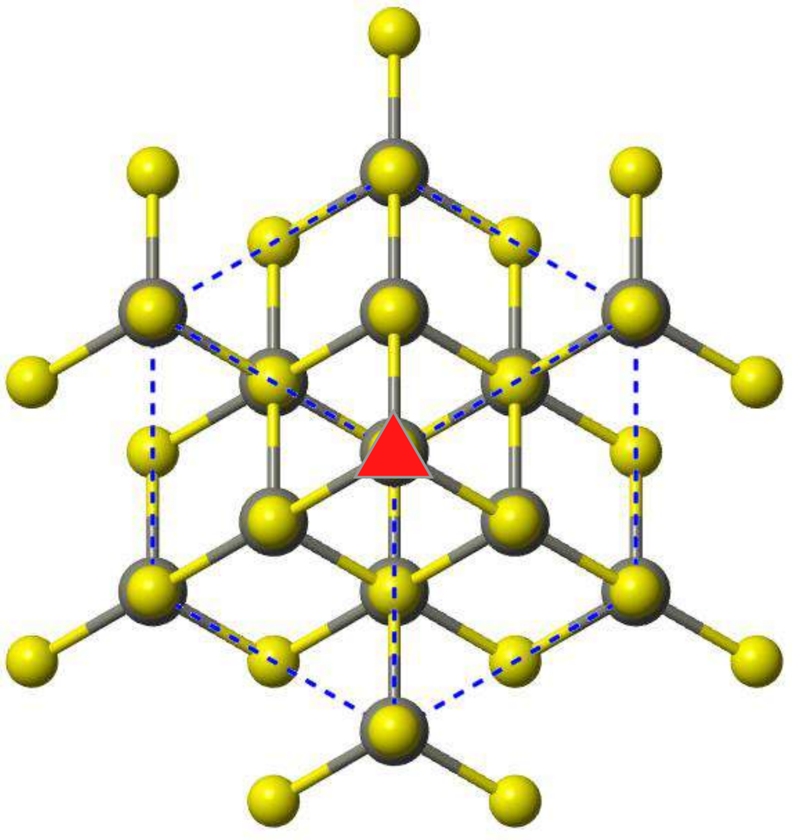


Hexagonal ZnS

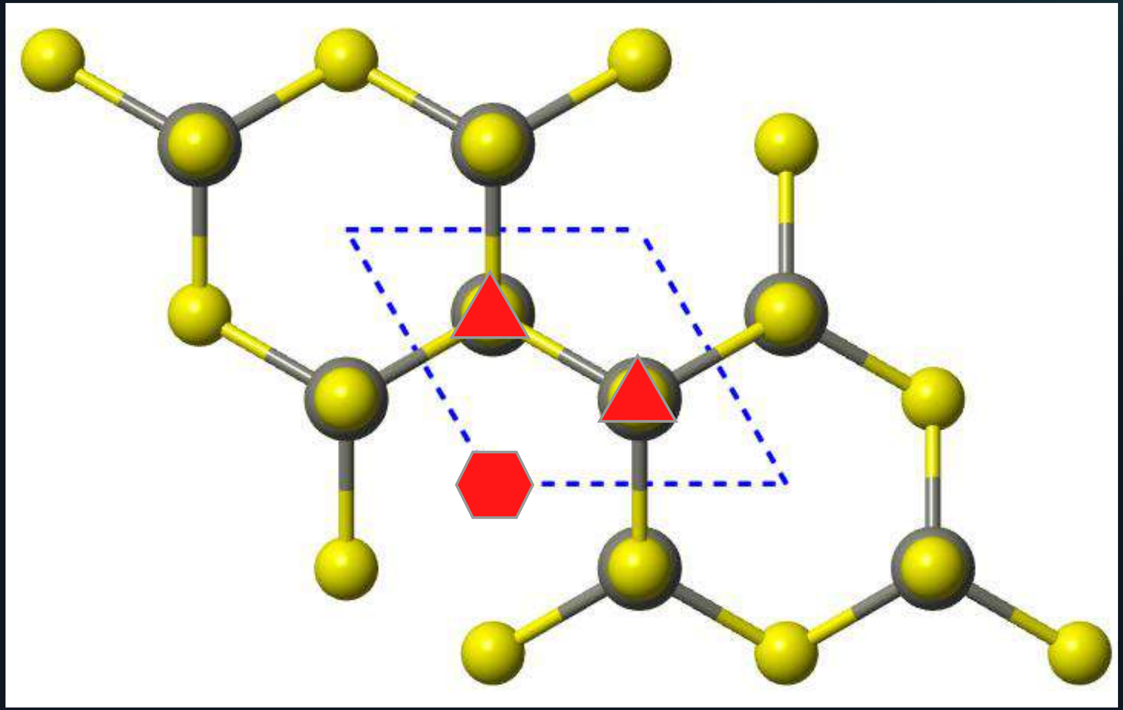


Cubic *vs* Hexagonal ZnS

Cubic ZnS



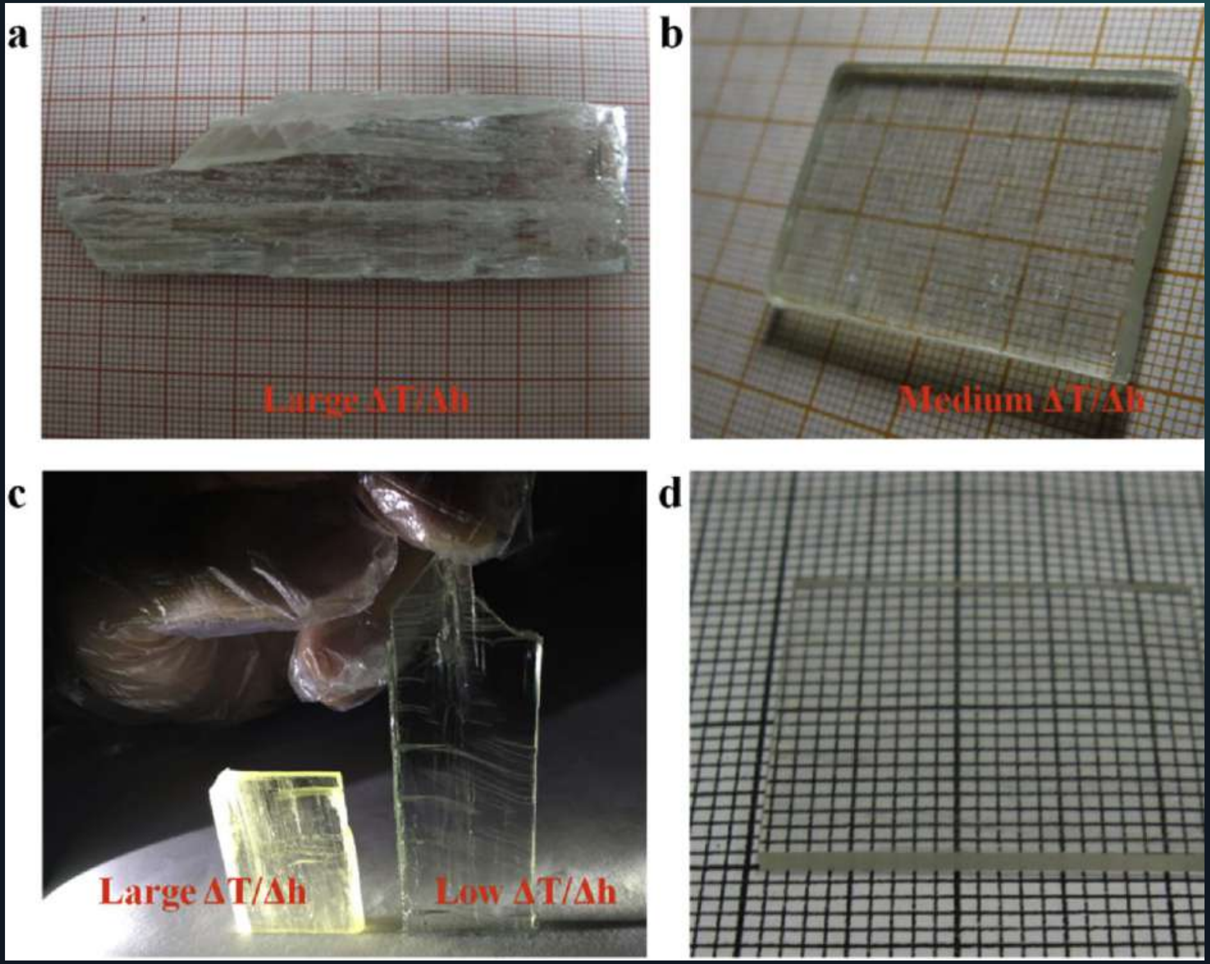
Hexagonal ZnS



Anisotropy

It was observed that several physical properties are anisotropic, i.e., they vary or assume different values according to the direction on which they are measured. These properties are related to the crystal-chemical features of the material. For example:

- Crystal growth velocity;



Mu, W., Jia, Z., Yin, Y., Hu, Q., Li, Y., Wu, B., Zhang, J. & Tao, X. (2017). *J Alloy Compd* **714**, 453-458.

Anisotropy

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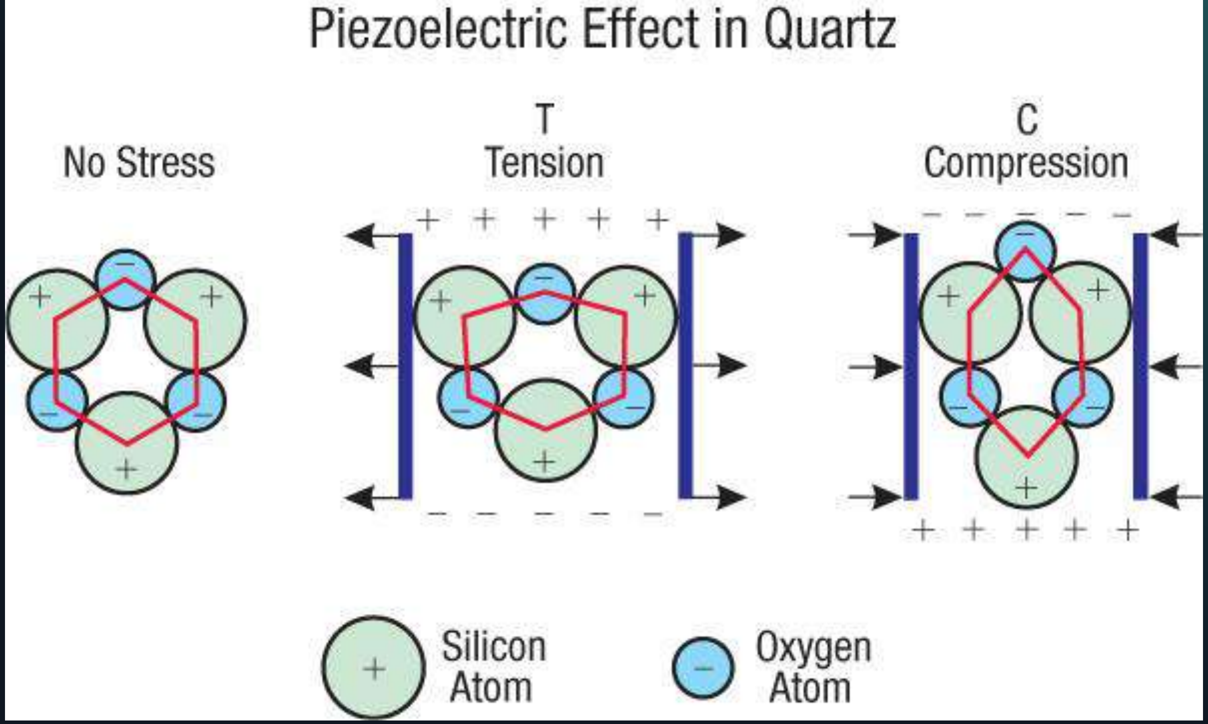
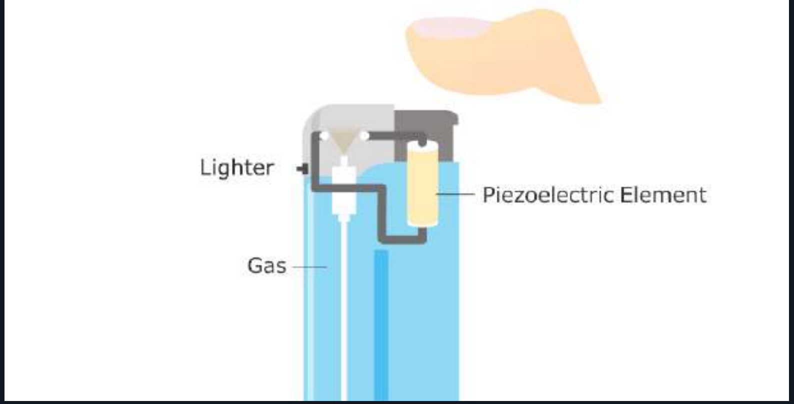
- Crystal growth velocity;
- Piezoelectricity;



Source: https://www.autodesk.com/



Source: https://global.kyocera.com/fcworld/charact/elect/piezo.html

Anisotropy

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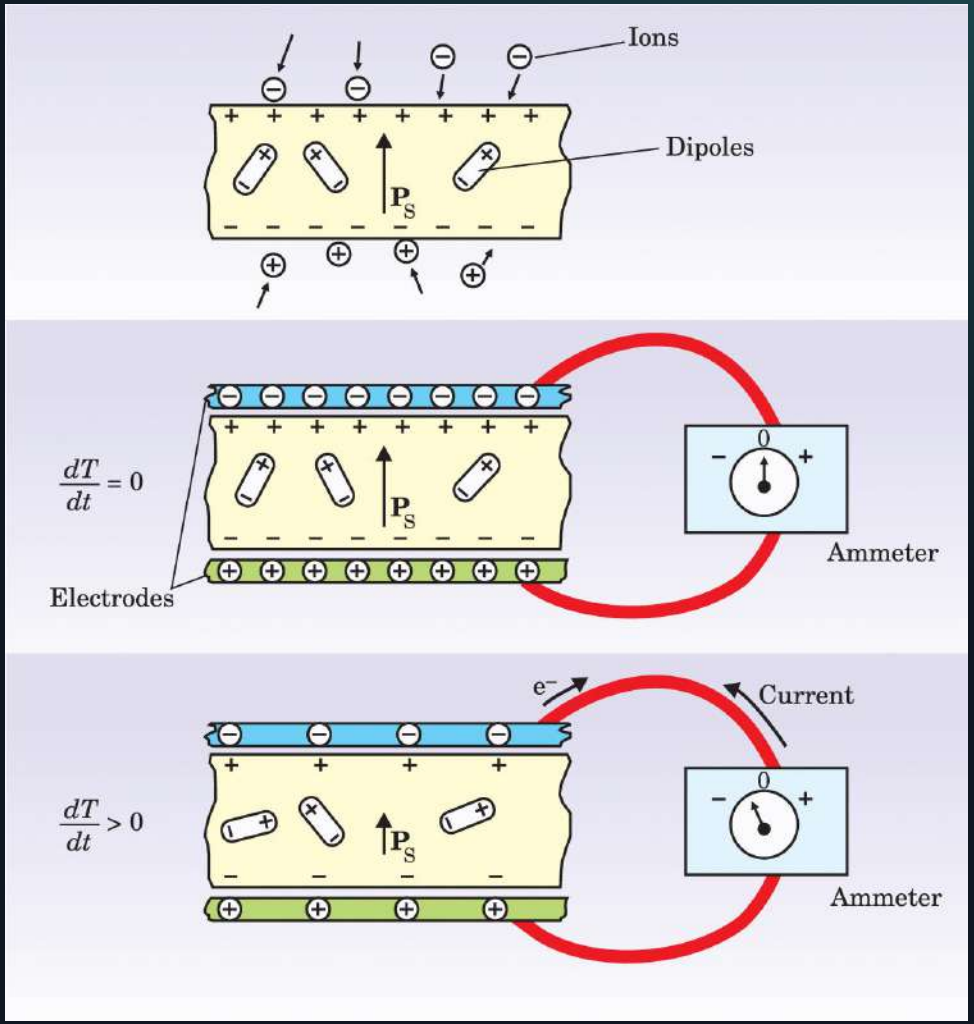
- Crystal growth velocity;
- Piezoelectricity;
- Pyroelectricity;

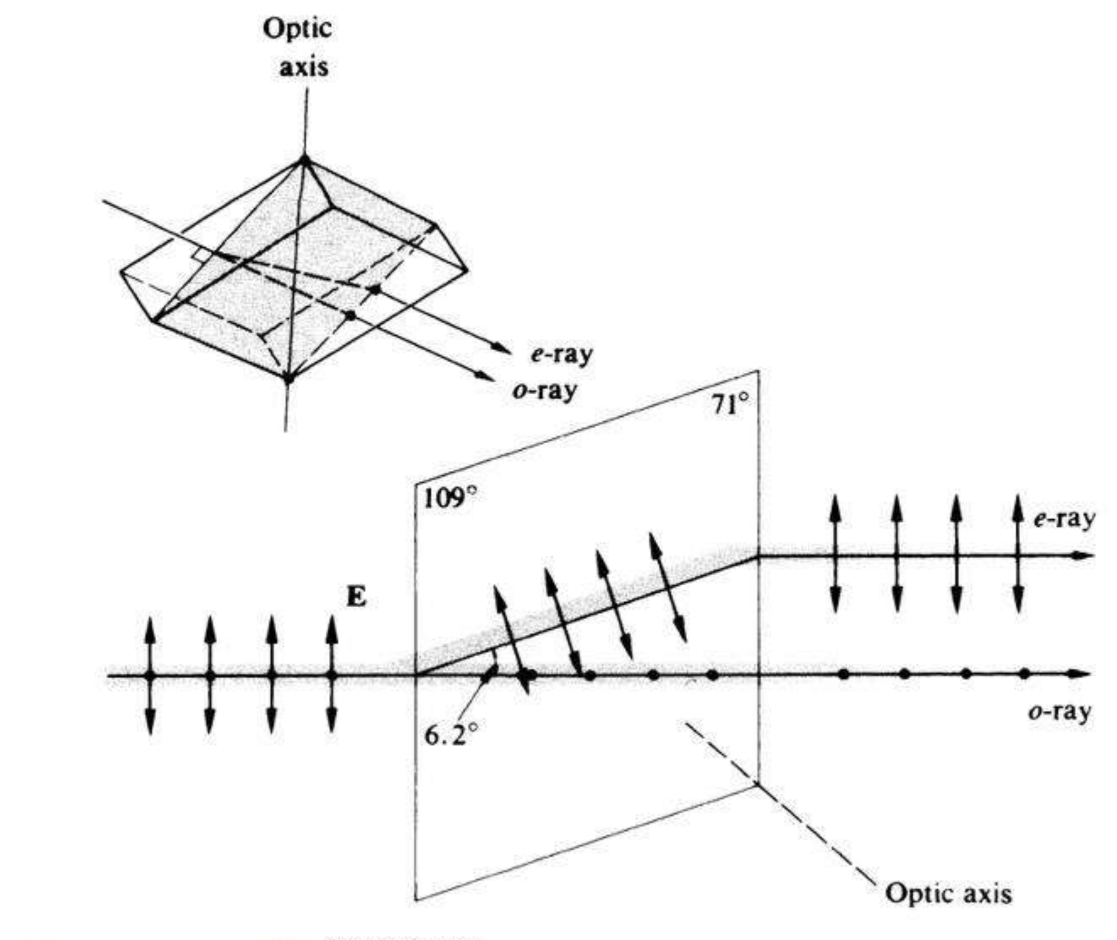


Source: S. Lang (2005) «Pyroelectricity: From Ancient Curiosity to Modern Imaging Tool», Physics Today, 58(8), 31.

Anisotropy

It was observed that several physical properties are anisotropic, i.e., they vary or assume different values according to the direction on which they are measured. These properties are related to the crystal-chemical features of the material. For example:

- Crystal growth velocity;
- Piezoelectricity;
- Pyroelectricity;
- Birefringence;



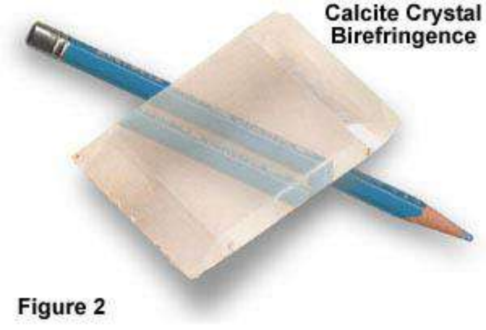


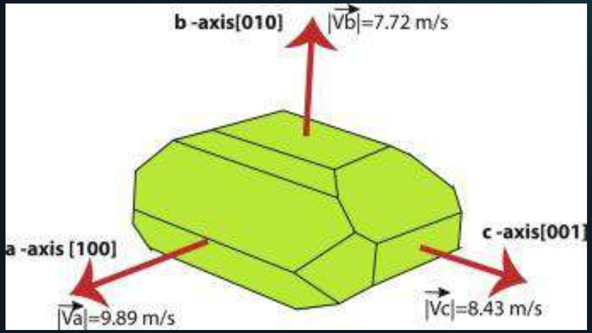
Figure 2

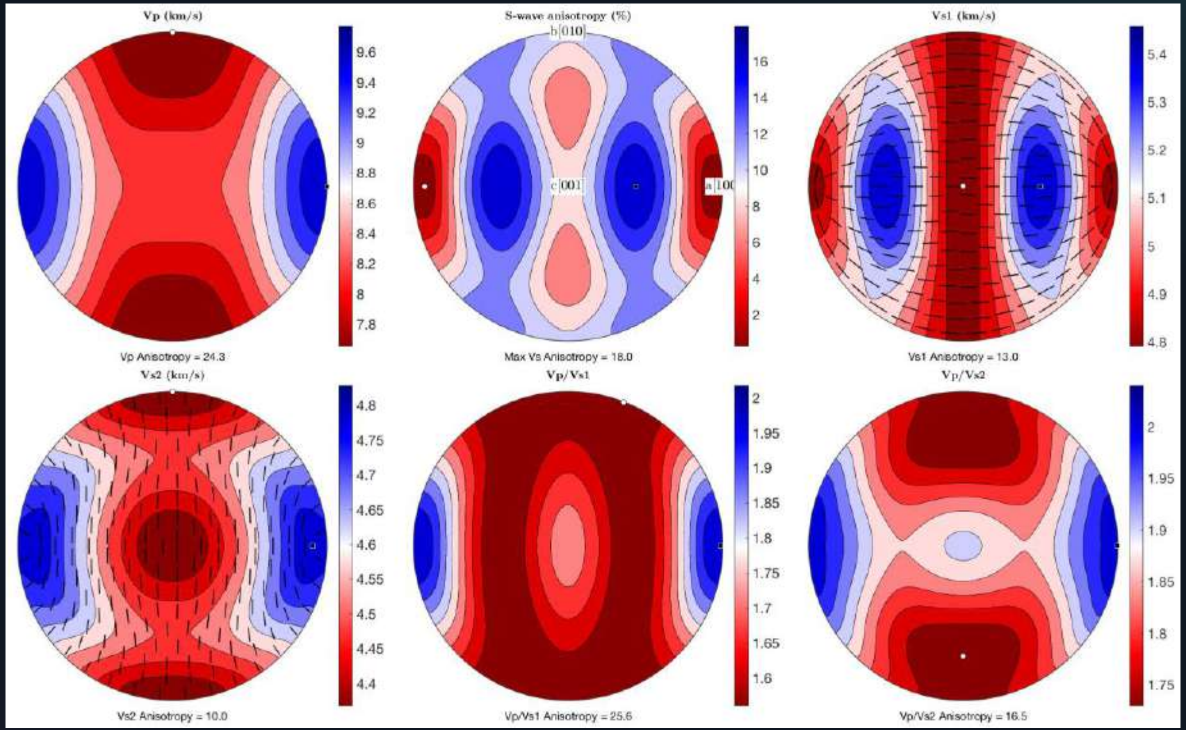
Source: https://www.olympus-lifescience.com/

Anisotropy

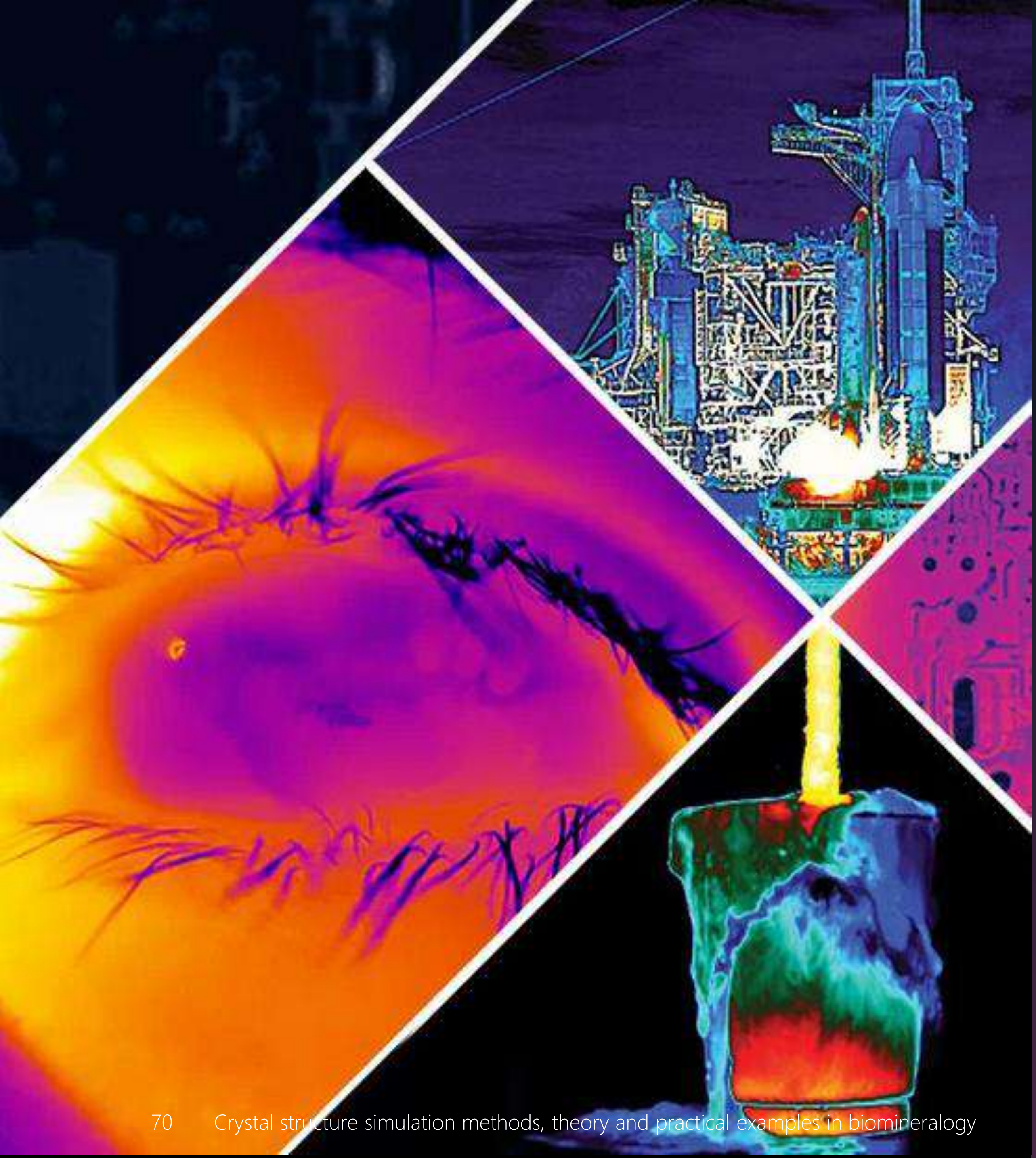
It was observed that several physical properties are anisotropic, i.e., they vary or assume different values according to the direction on which they are measured. These properties are related to the crystal-chemical features of the material. For example:

- Crystal growth velocity;
- Piezoelectricity;
- Pyroelectricity;
- Birefringence;
- Elasticity and derived properties (e.g., seismic wave velocities);
- ...and many more!





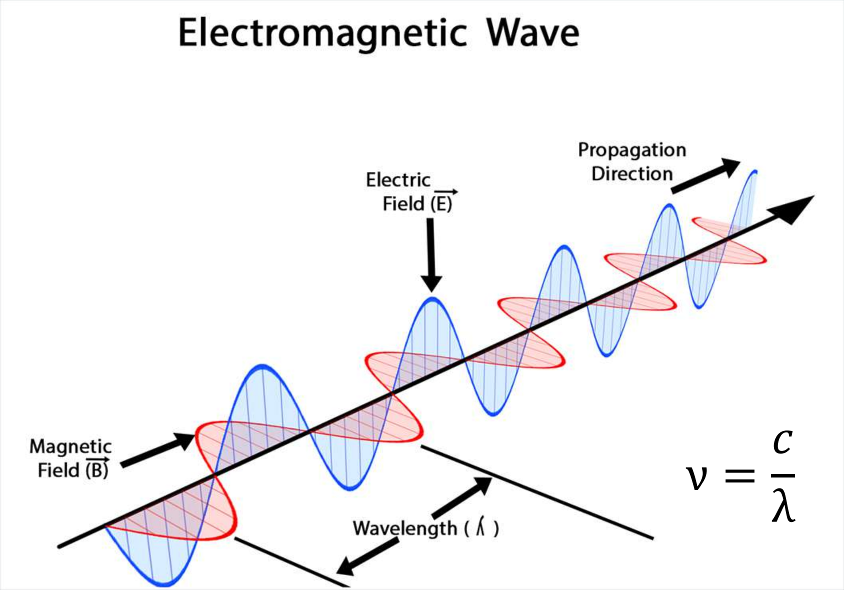
Source: http://www.gm.univ-montp2.fr/PERSO/mainprice



Infrared & Raman spectroscopies

Basics and applications

Electromagnetic spectrum



$$\nu = \frac{c}{\lambda}$$

The energy per photon *E* can be calculated with the Planck-Einstein relation:

$$E = \frac{hc}{\lambda} = h\nu = hc\bar{\nu}$$

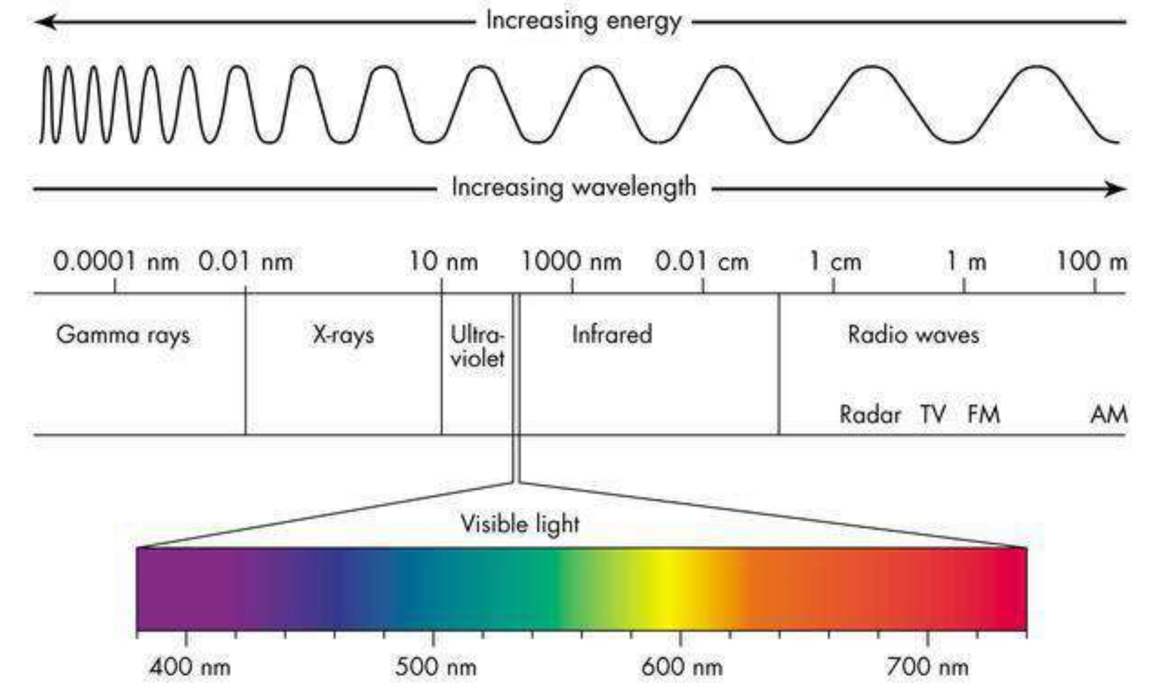
c = speed of light in vacuum = $3 \cdot 10^{10}\ cm\ s^{-1}$

h = Planck's constant = $6.620607 \cdot 10^{-34}\ m^2 kg\ s^{-1}$

λ = wavelength (nm)

ν = frequency (Hz)

$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \text{wavenumber (cm}^{-1}\text{)}$



Spectroscopies

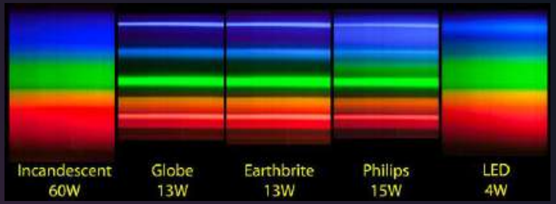
Three main types

1

Emission

Materials may emit light when excited by other means than EM waves (current, temperature)

- Cathodoluminescence
- Thermal emission



2

Absorption

Materials may adsorb part of the EM radiation that hits them

- in trasmission
- in reflection

3

Scattering

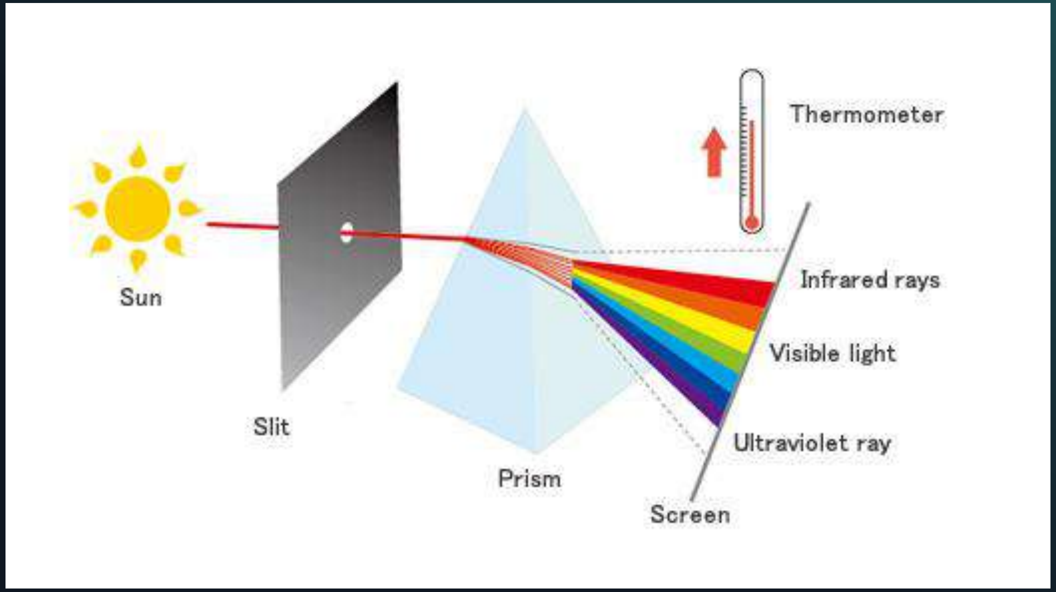
Materials may produce small perturbations of the radiation that collides onto them (elastic and/or inelastic scattering)

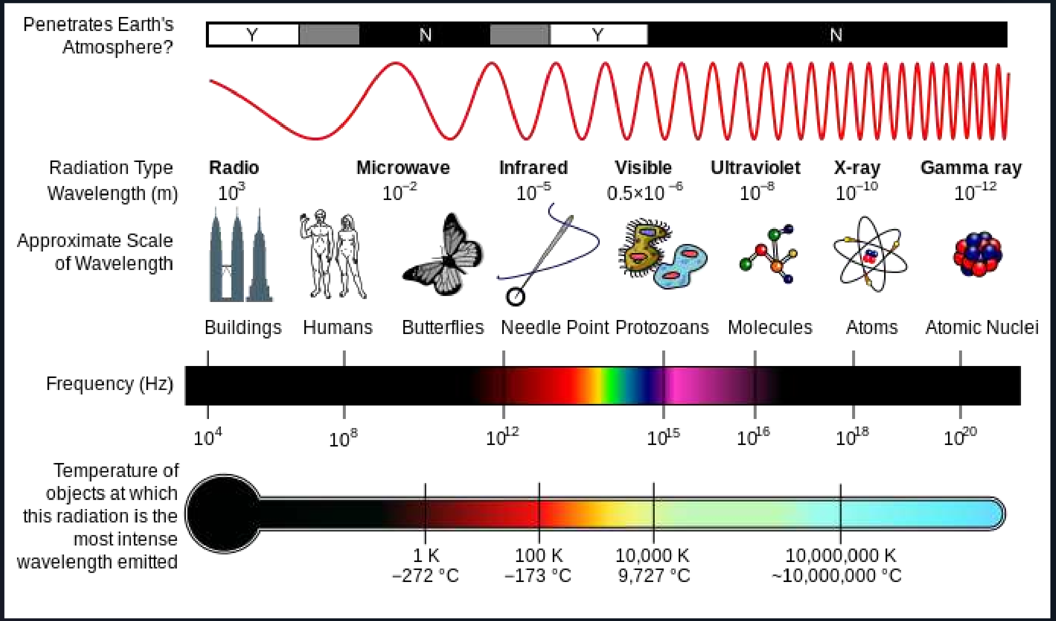
- in transmission
- in reflection

Infrared light

Frederick William Herschel discovered infrared (IR) radiation and the IR adsorption phenomenon. He imagined other components of the sun light that were invisible to the human eye and developed several experiments to found them.

In a very simple experiment, he put a thermometer below the visible red light (from refraction) and observed that the temperature rose up to the room temperature. Furthermore, he found that, by placing a test tube filled with water in the infrared light path before the thermometer, the recorded temperature was lower. This means that the water sample adsorbed the infrared light.



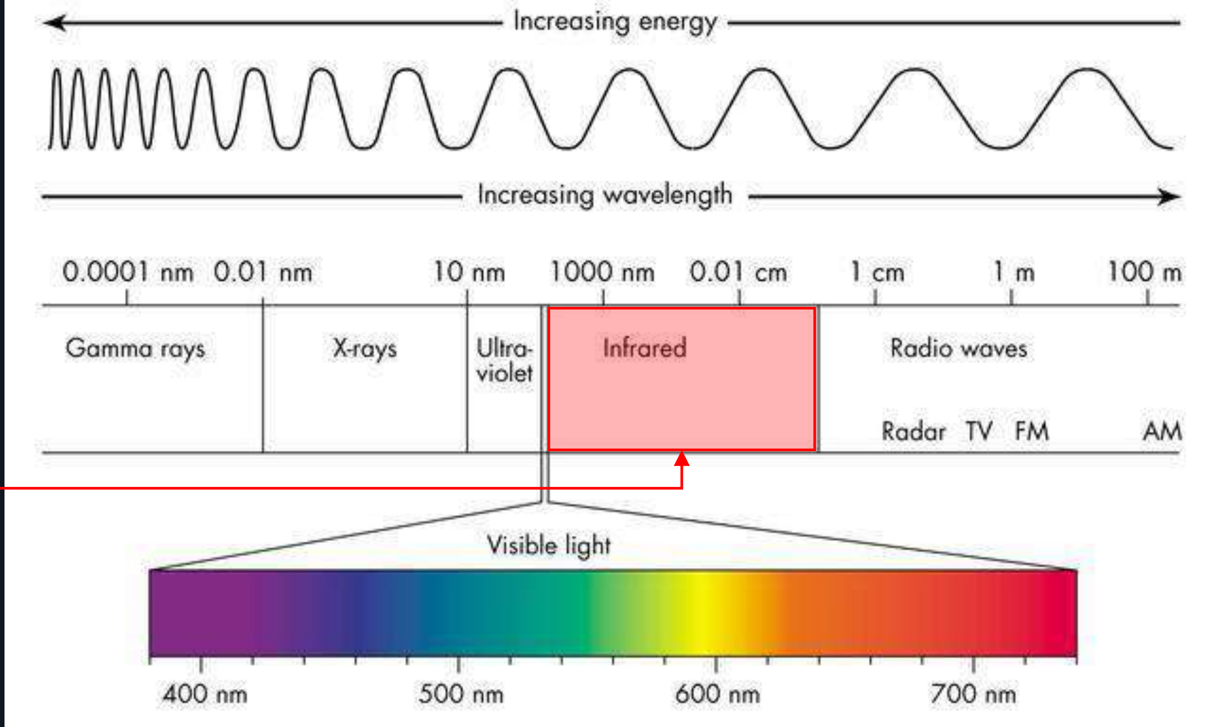


Infrared light

$$4000\ cm^{-1} < \bar{\nu} < 400\ cm^{-1}$$

$$2500\ nm < \lambda < 25000\ nm$$

Vibrational frequencies
of molecules and solids



Atomic bonds and harmonic potential

First approximation (harmonic approximation):

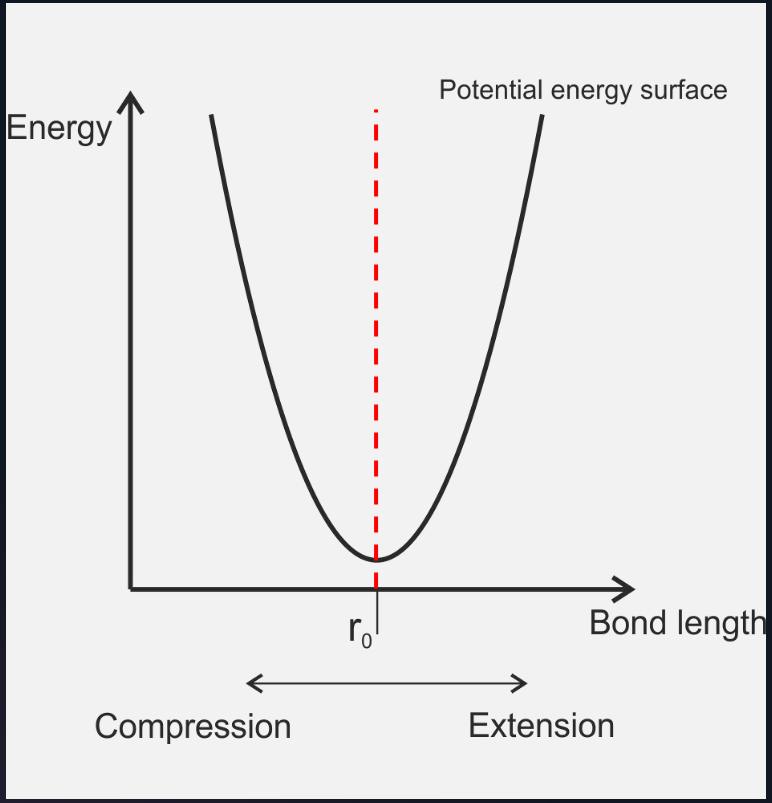
atomic bonds = springs

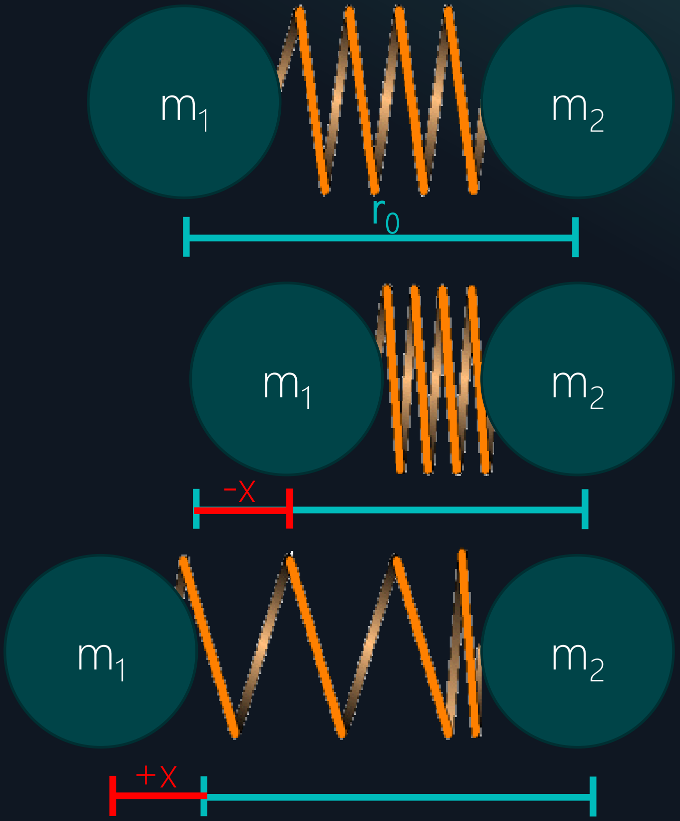
Within the harmonic approximation, we can describe their motion according to Hooke's law.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

$$E = \frac{1}{2}kx_{\max}^2$$

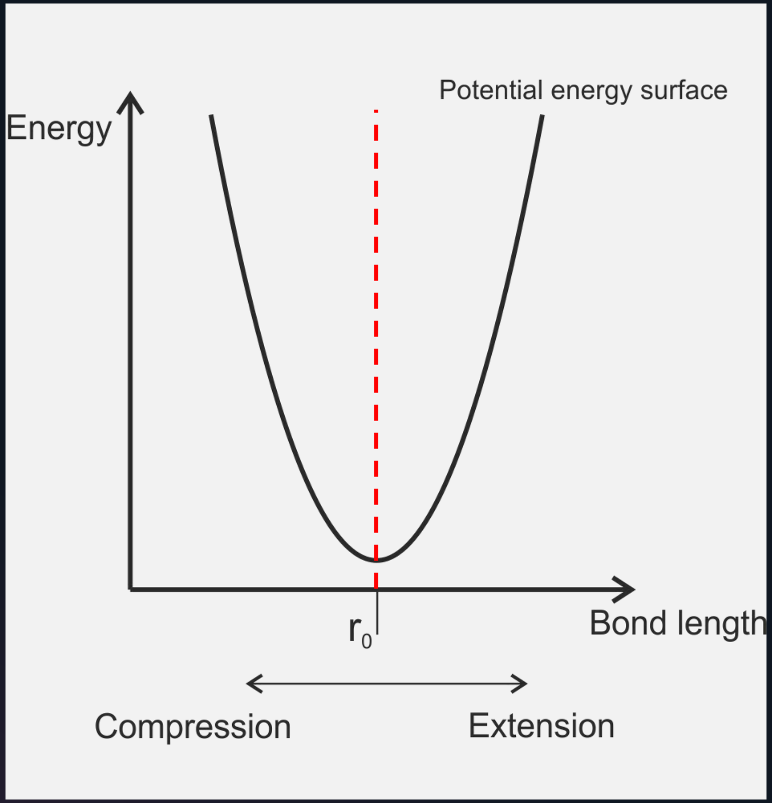


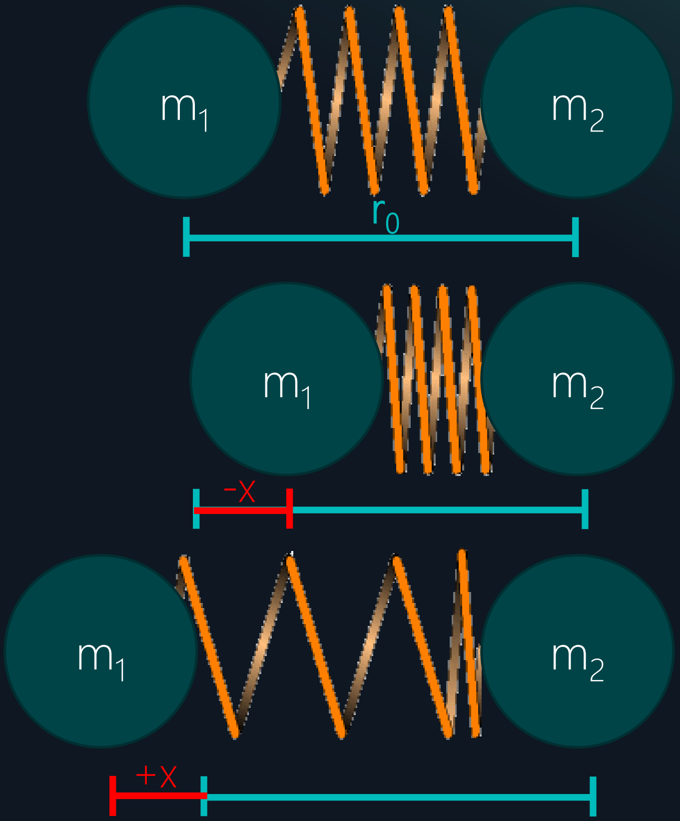


Atomic bonds and harmonic potential

The vibrational (oscillating) frequency ν depends on:

1. the spring constant k
   - high k = high ν
   - low k = low ν
2. the mass of the atoms connected by the spring
   - high μ = low ν

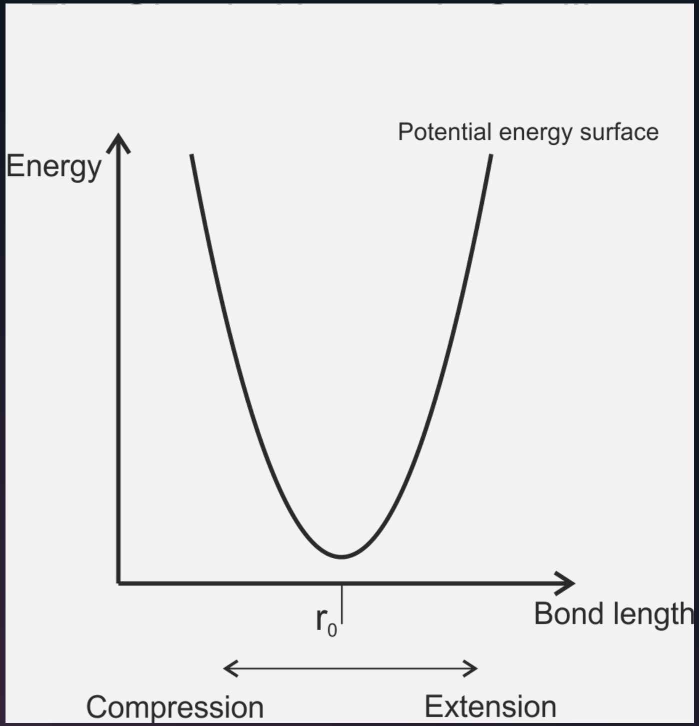




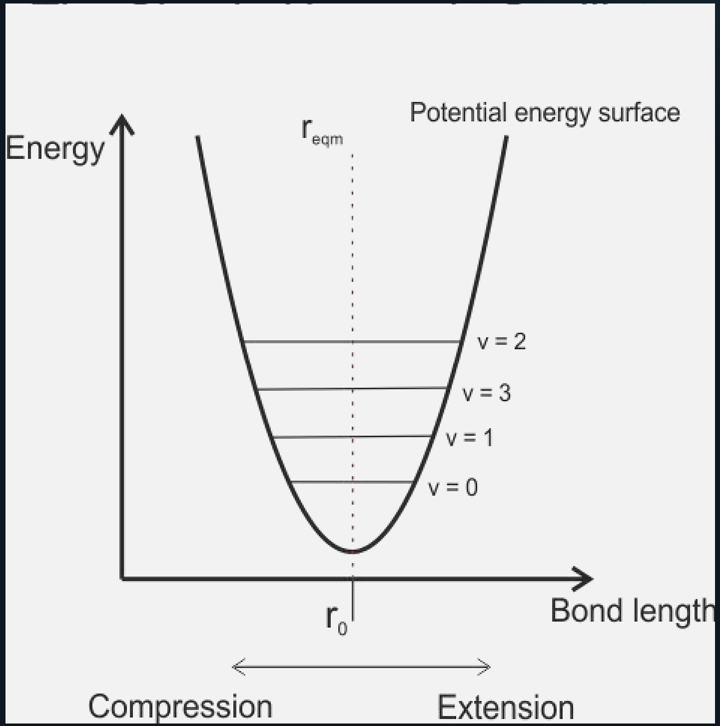
Quantum harmonic potential

However, the Hooke's law is not adequate to describe the (vibrational) motion of atoms because of their extremely small masses. When dealing with such small objects, we need to introduce quantum effects.

Harmonic potential



Quantum harmonic potential



Quantum harmonic potential

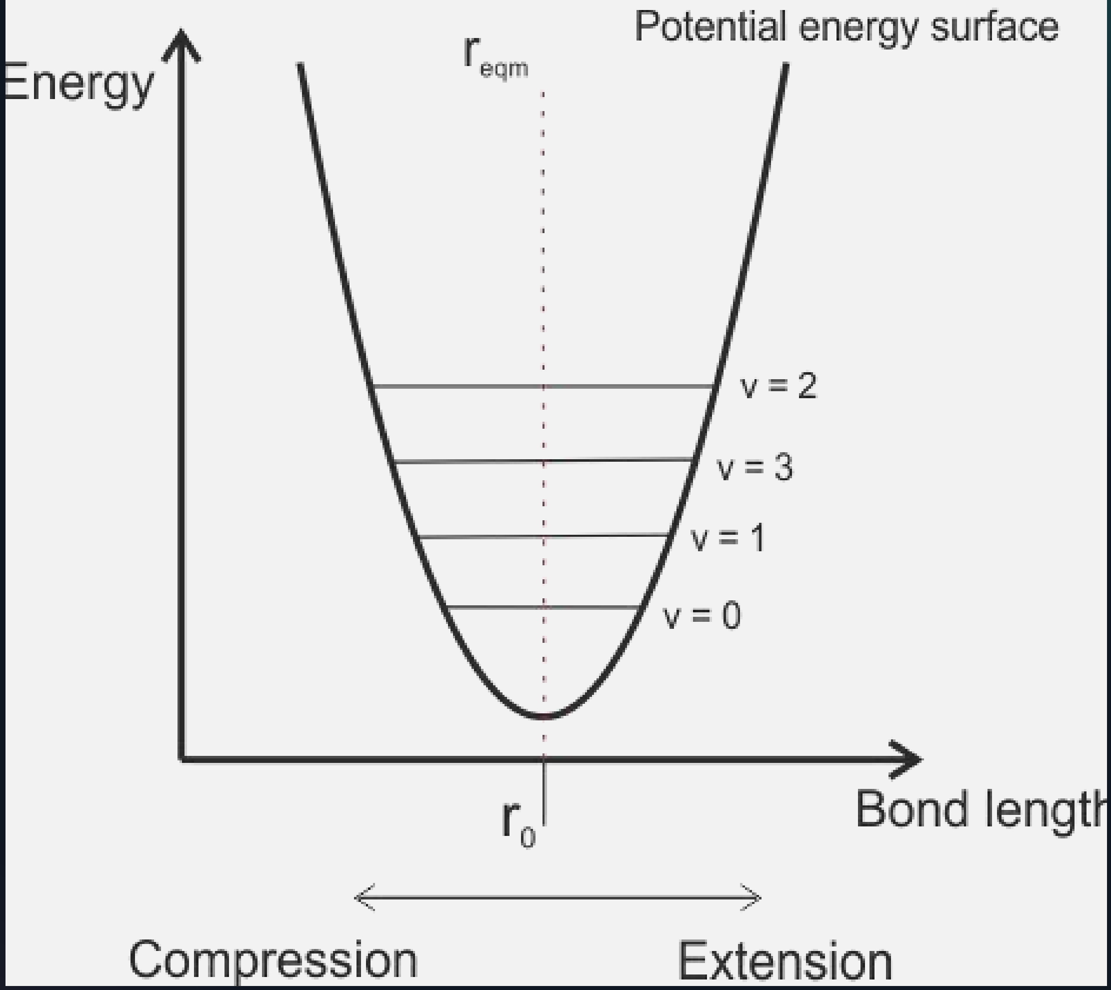
While at macroscopic level, the two masses may have all intermediate potential energy values, at atomic level this is not possible.

In quantum regime, the energies allowed by the atoms are those related to the following expression:

$$E_n = \left(n + \frac{1}{2}\right) h\nu \quad n = 0,1,2\ldots$$

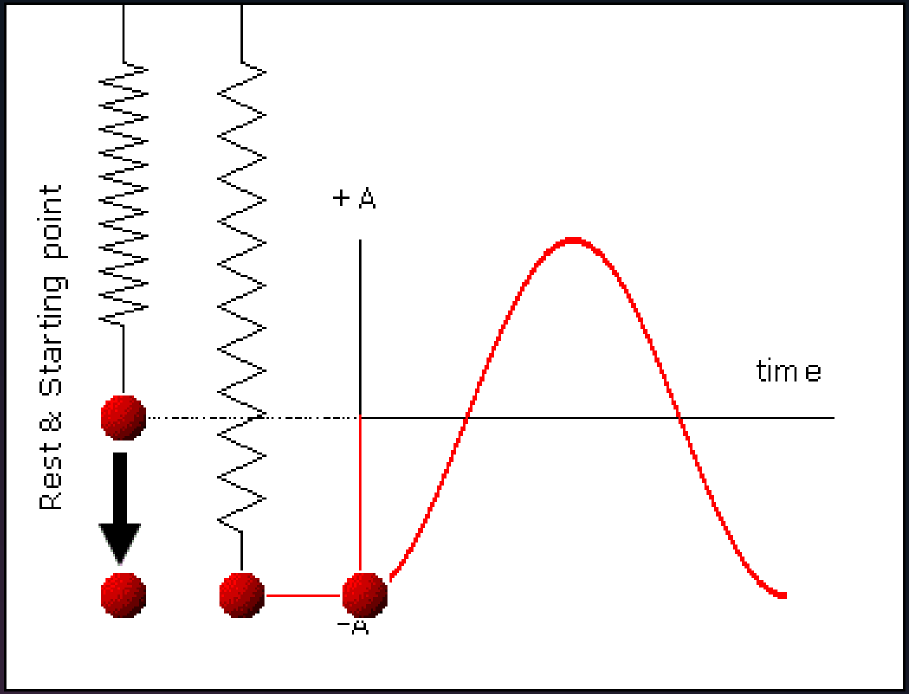
with E_n the vibrational energy and n the vibrational level.

Quantum harmonic potential

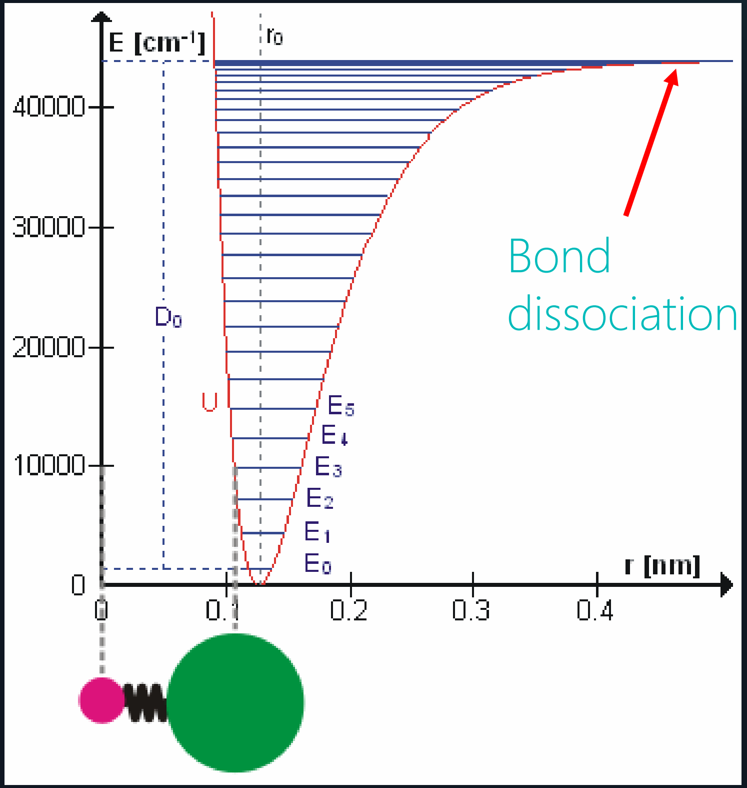


Quantum harmonic potential

Harmonic potential



Quantum (an)harmonic potential



Vibrational energy levels

Bonded atoms vibrate with an energy equal to the potential energy at the maximum (allowed) compression/expansion of the bond:

$$E = \frac{1}{2} k x_{\mathrm{max}}^2 = \left(n + \frac{1}{2}\right) h\nu \quad n = 0,1,2\ldots$$

As previously mentioned, these energies fall in the infrared region of the EM spectrum

$$0.5\ \mathrm{eV} < E < 0.05\ \mathrm{eV}$$

$$\Downarrow$$

$$4000\ cm^{-1} < \bar{\mathrm{v}} < 400\ cm^{-1}$$

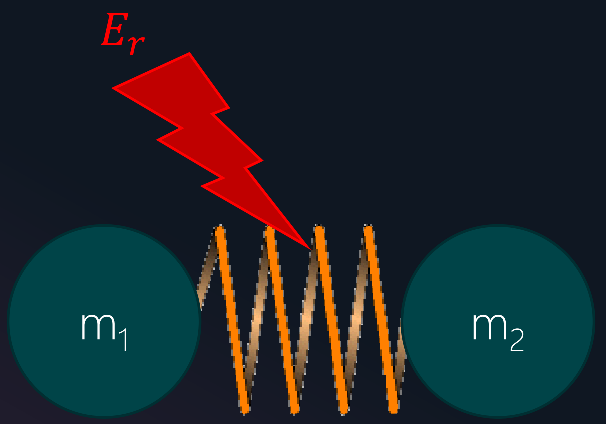
Vibrational energy levels

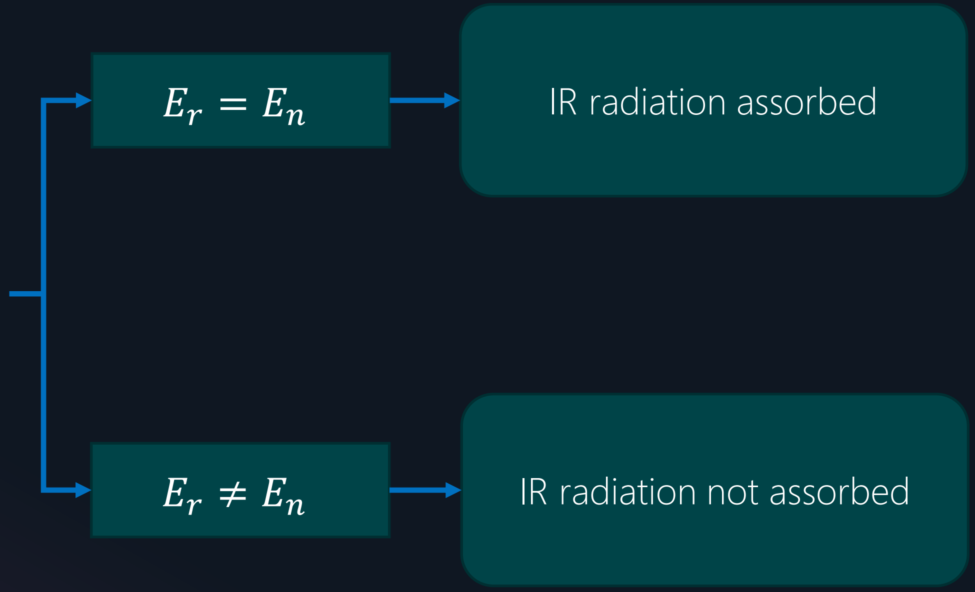
When an infrared radiation, with energy $E_r = hc\bar{\nu}$, hit a molecule/solid/liquid, it will **augment the vibrational energy (level)** of the system if, and only if, the IR radiation has **the same energy** of the "spring":

$$E_r = hc\bar{\nu} = \left(n + \frac{1}{2}\right)h\nu = E_n$$

In this case, the IR radiation is **absorbed** by the system → **selective absorption** → IR spectroscopy

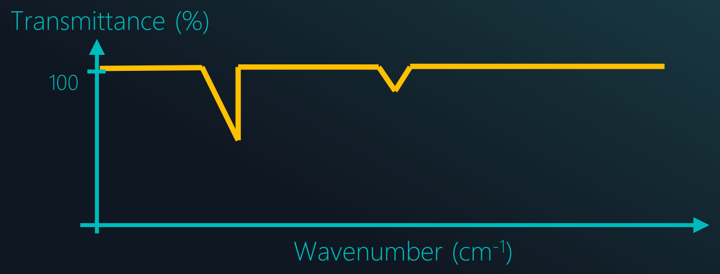
IR Spectroscopy

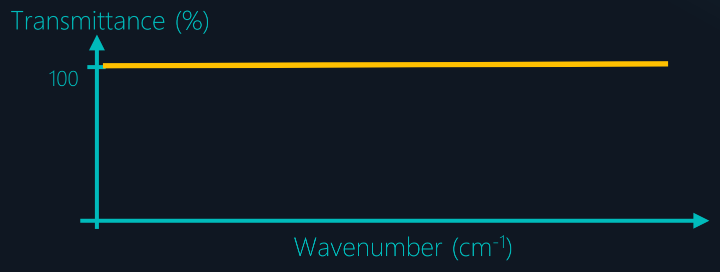




$E_r = E_n$ → IR radiation assorbed

$E_r \neq E_n$ → IR radiation not assorbed





Absorption intensity: $I(\lambda) = I_0(\lambda) \cdot e^{-\alpha x}$ with α the absorption coefficient.

Generally, the spectrum is expressed in terms of transmittance $\%T(\lambda) = 100\,\frac{I(\lambda)}{I_0(\lambda)}$

or absorbance $A(\lambda) = \log\frac{I_0(\lambda)}{I(\lambda)}$

Vibrational modes

How many vibrational modes has …

…a molecule?

A single, isolated molecule has $3N$ degrees of freedom, with N the number of atoms, subdivided as follows:

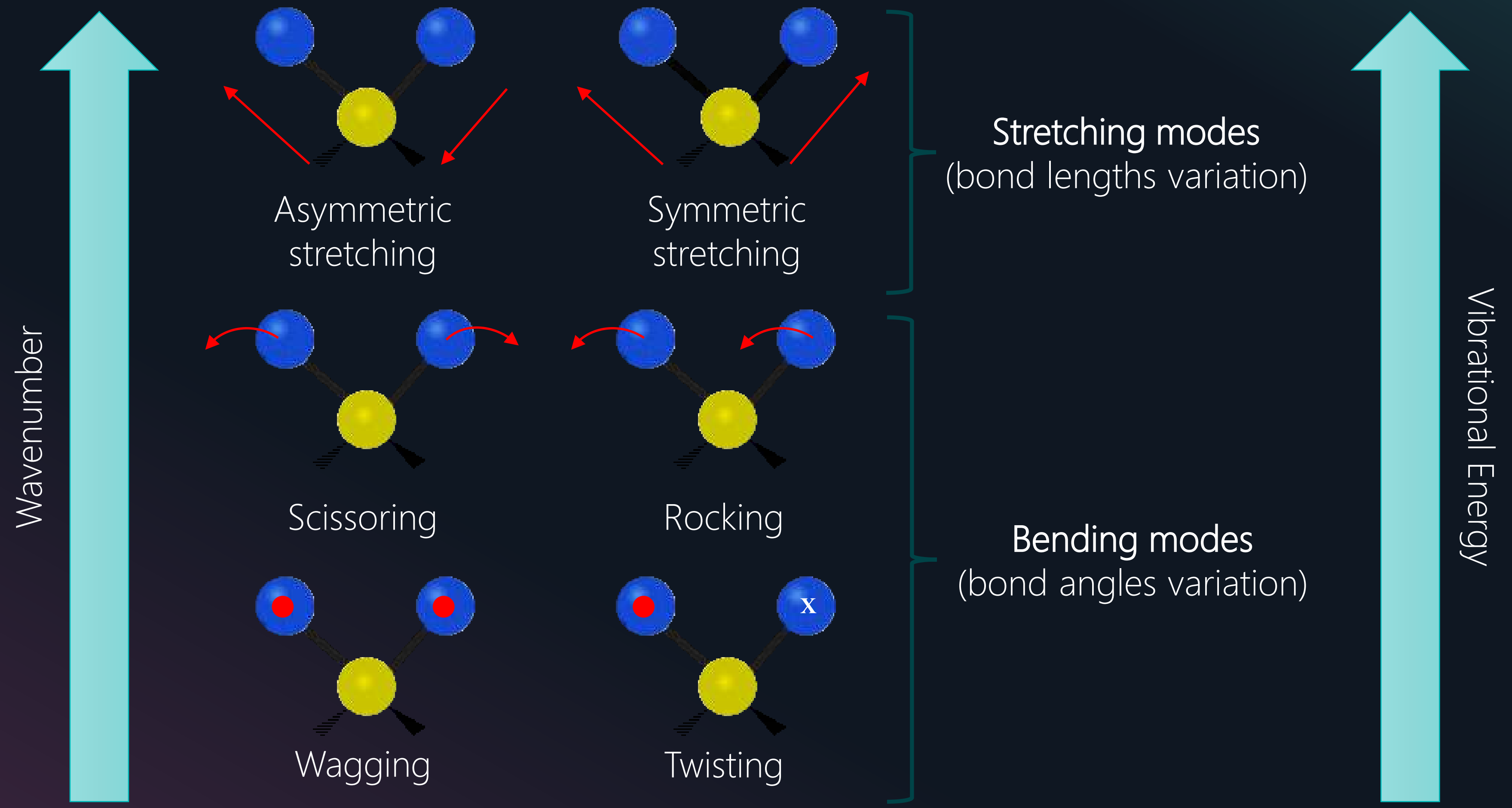
- 3 translations in the space;
- 3 rotations in the space (only 2 if the molecule is linear) ;
- $3N-6$ vibrational modes ($3N-5$ for linear molecules);

…a solid?

In solids, the rotational degrees of freedom are absent, hence there are:

- 3 acoustic modes (not visible in standard IR spectroscopy);
- $3N-3$ vibrational modes.

Vibrational modes



Wavenumber

Asymmetric stretching

Symmetric stretching

Scissoring

Rocking

Wagging

Twisting

Stretching modes
(bond lengths variation)

Bending modes
(bond angles variation)

Vibrational Energy

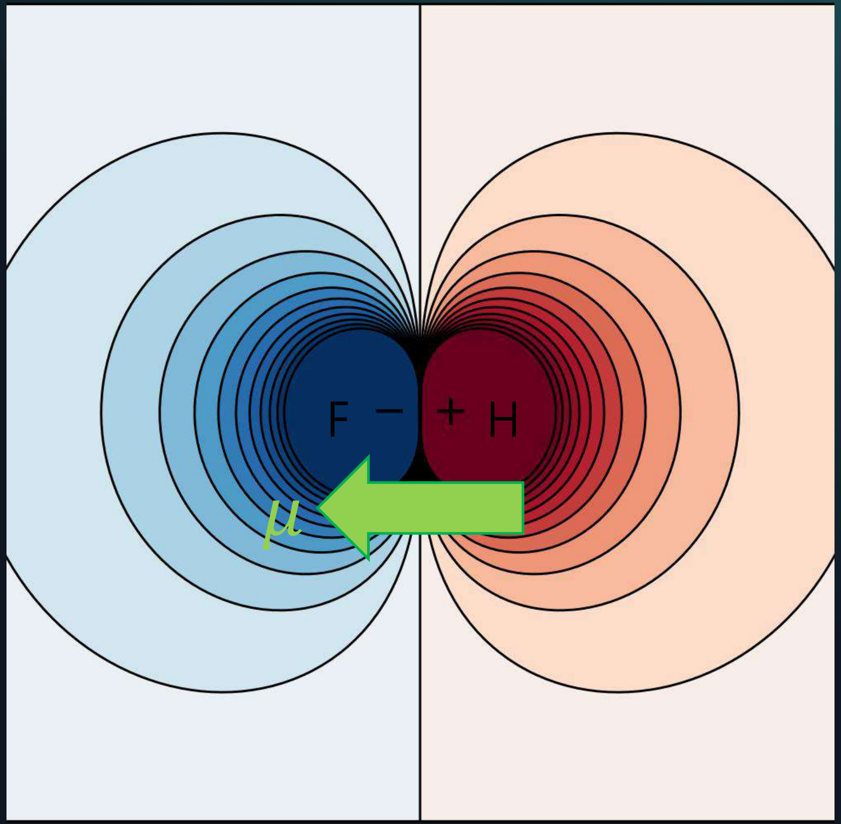
Infrared selection rules

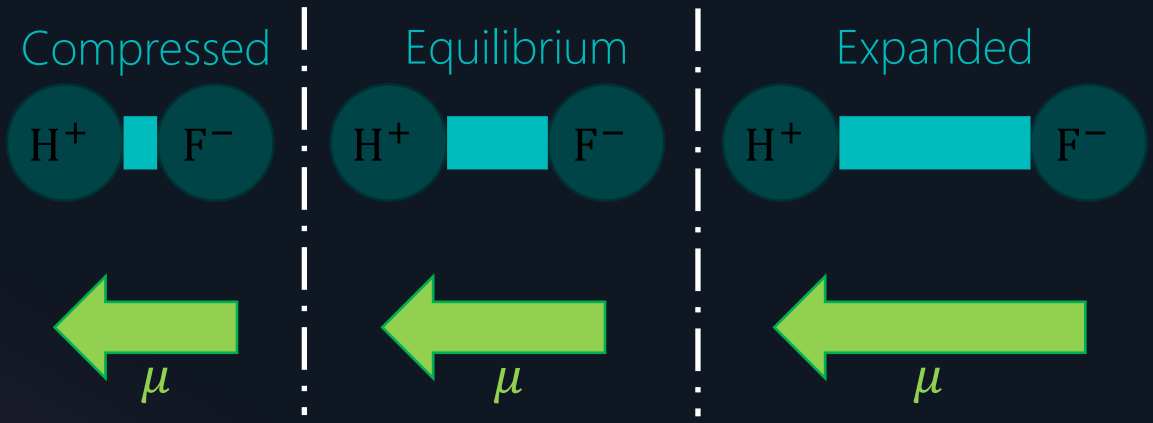
1. $E_r = hc\bar{\nu} = \left(n + \frac{1}{2}\right) h\nu = E_n$
2. During the vibration, the displacements of the atoms must change the dipole moment μ of the system.
3. The only allowed transitions in vibrational energy are those for which $\Delta n = \pm 1$

If all these rules are satisfied, we can see a signal in the IR spectrum related to the specific vibrational mode

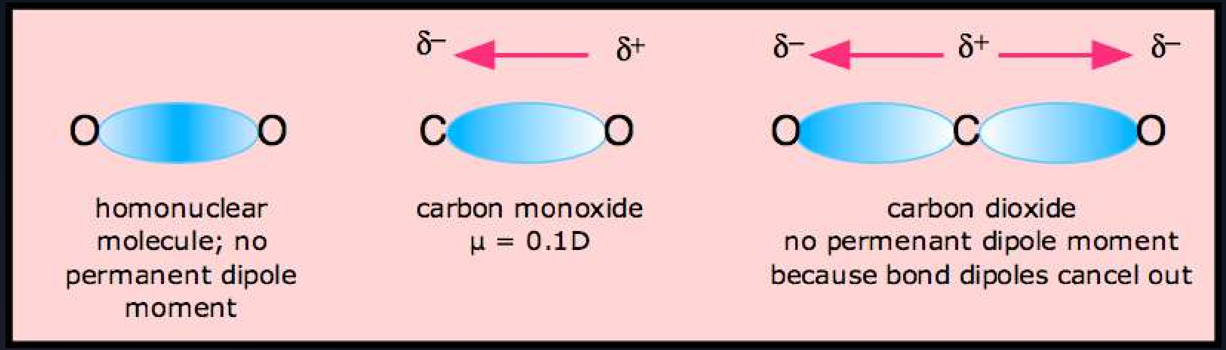
Dipole moment

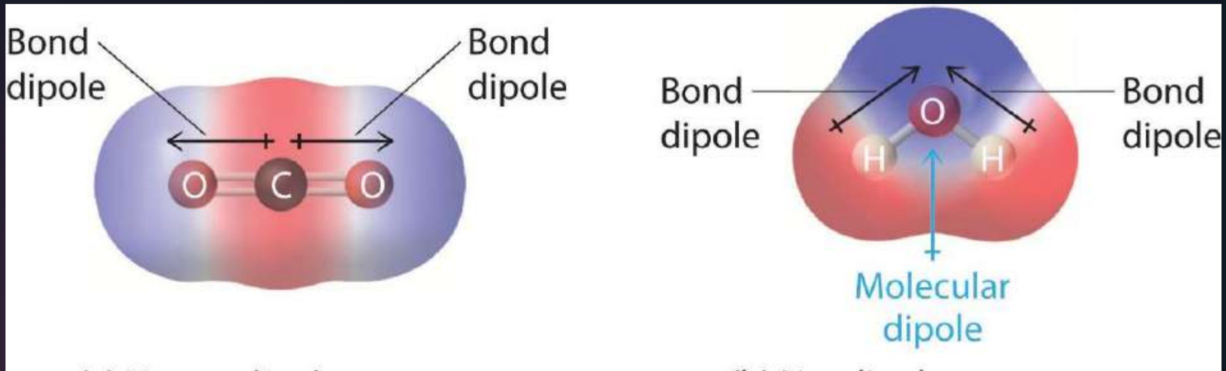
- It is a vector quantity related to the electric dipole in a system. In molecules and solids, it is due to the non-uniform distribution of both positive and negative charges in the bonds.
- For example, in the molecule HF, the electron density is not equivalently shared between the two atoms. In this case, we have a *permanent dipole*, with its vector parallel to the H – F bond and directed toward the fluoride anion.
- For hydrogen fluoride, the vibration along the bond direction causes a variation of the dipole moment.





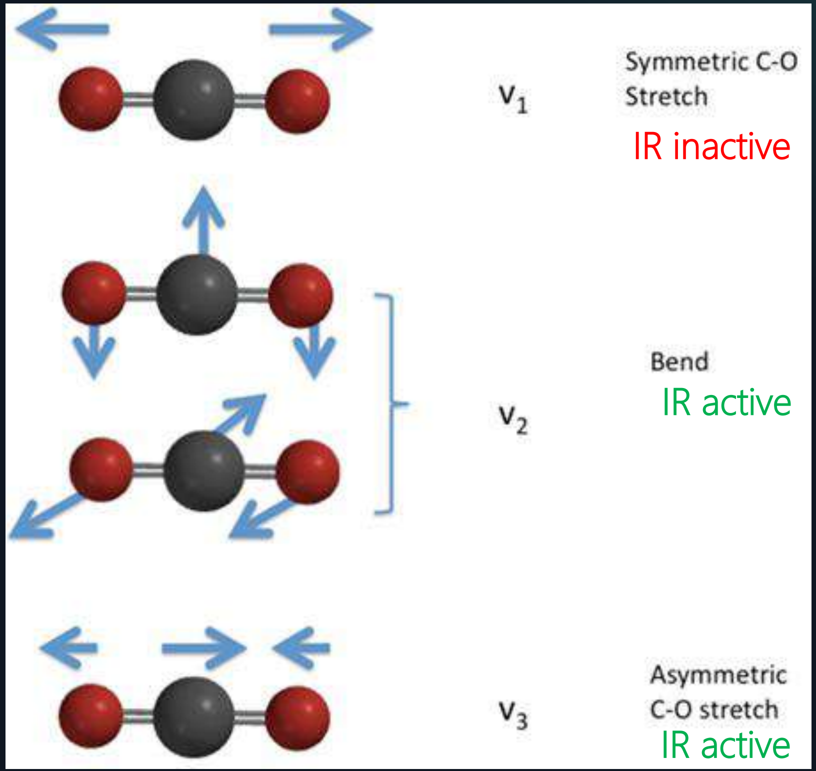
Dipole moment





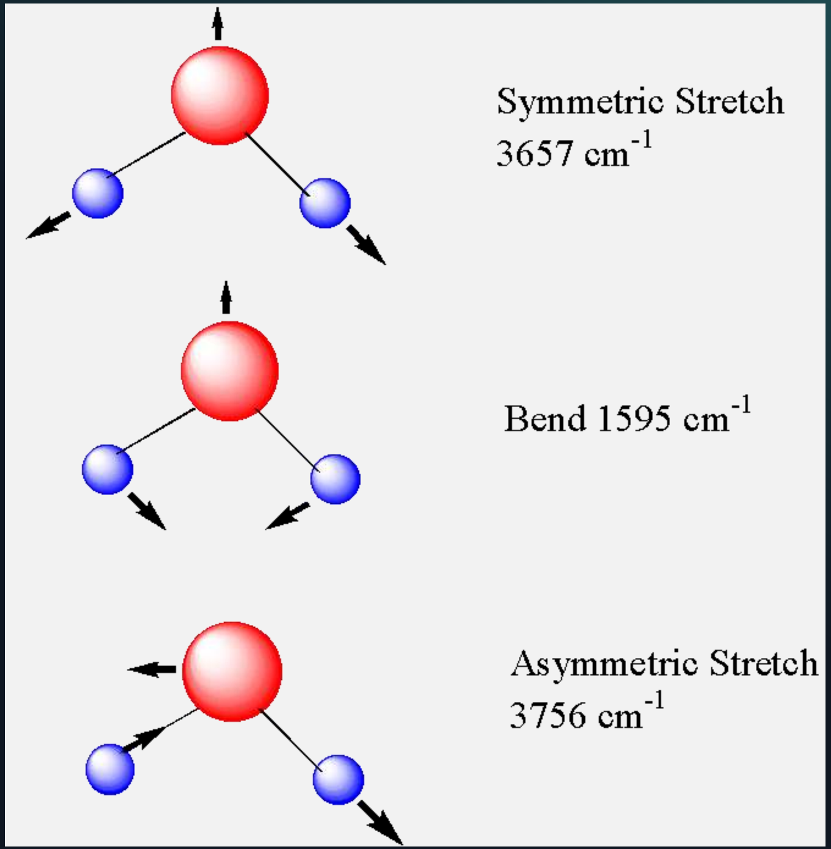
(a) No net dipole moment

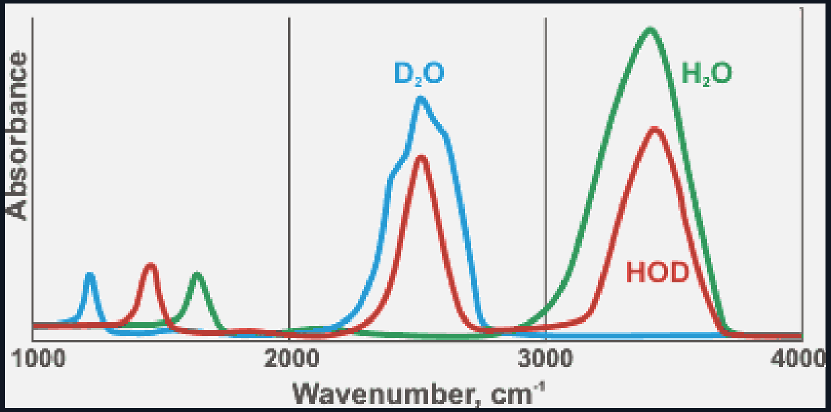
(b) Net dipole moment



Example: water molecule

- As the spring case, the energy (and associated wavenumber) of a vibrational mode changes if the atomic masses are different, as in the case of deuterated water (HOD and D_2O) and other isotopic substitutions.
- In addition, the chemical environment surrounding the molecule affects the position of the IR signals.

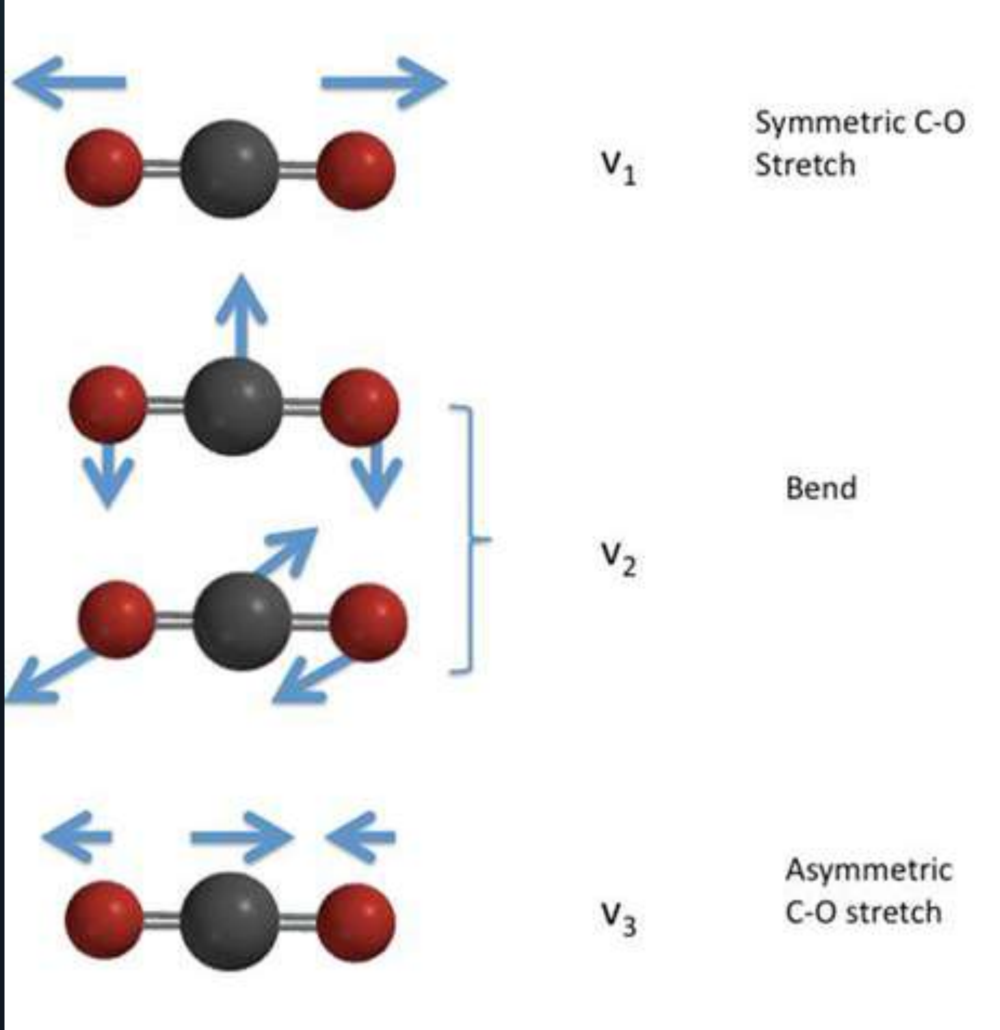




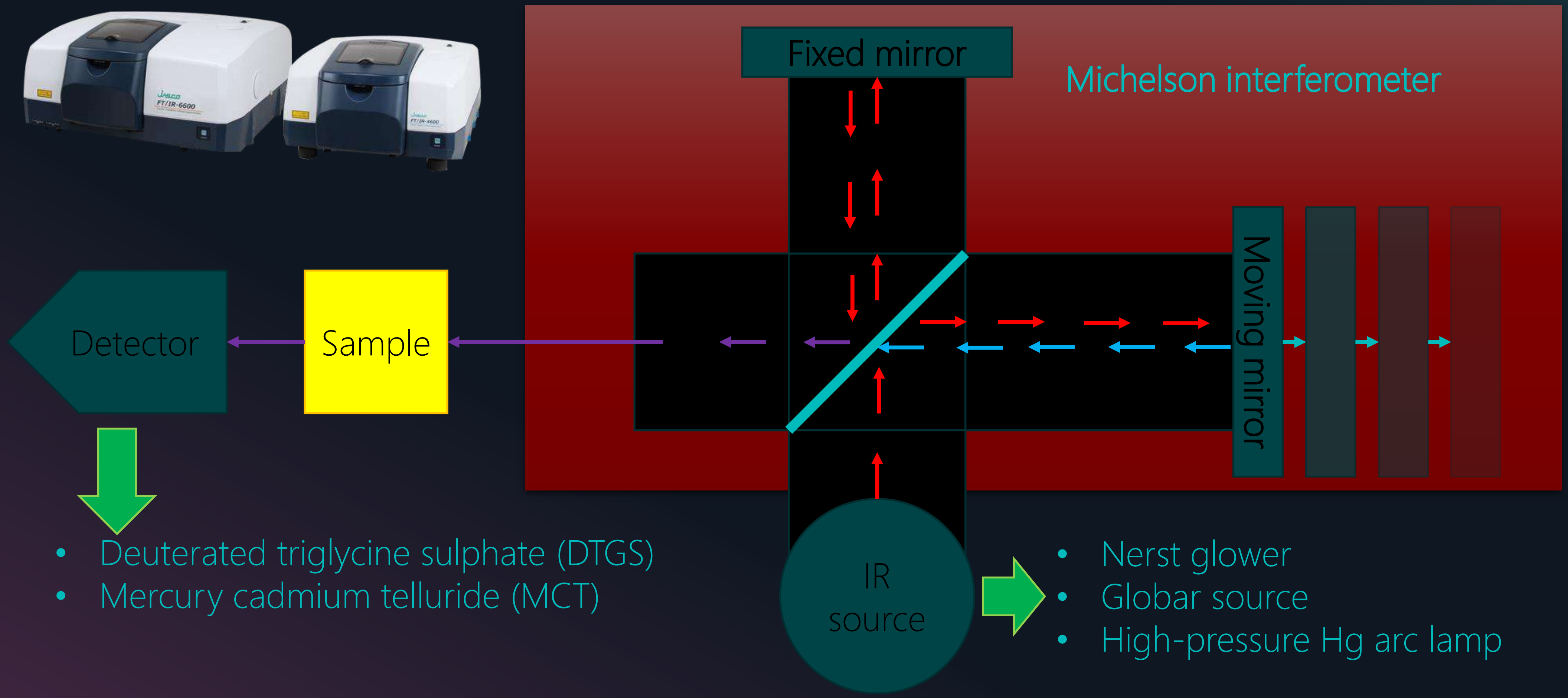
Degenerate modes

If the sample molecule/solid has high punctual/spatial symmetry, some vibrational modes may be (doubly or triply) degenerate: this means that they have the same energy and hence are excited by the same IR radiation. As a consequence, we will see only one signal related to these modes in the spectrum.

For example, there are two bending modes (ν_2) in carbon dioxide that have the same energy bending.



Fourier-Transform InfraRed (FTIR) spectrometer



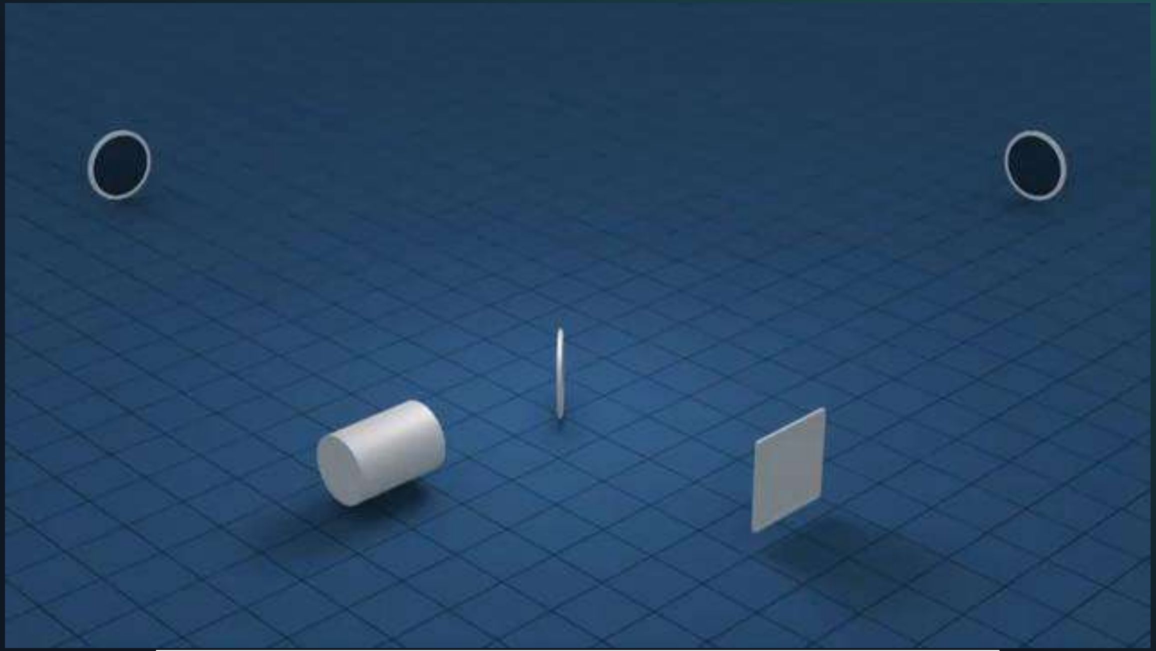
- Deuterated triglycine sulphate (DTGS)
- Mercury cadmium telluride (MCT)

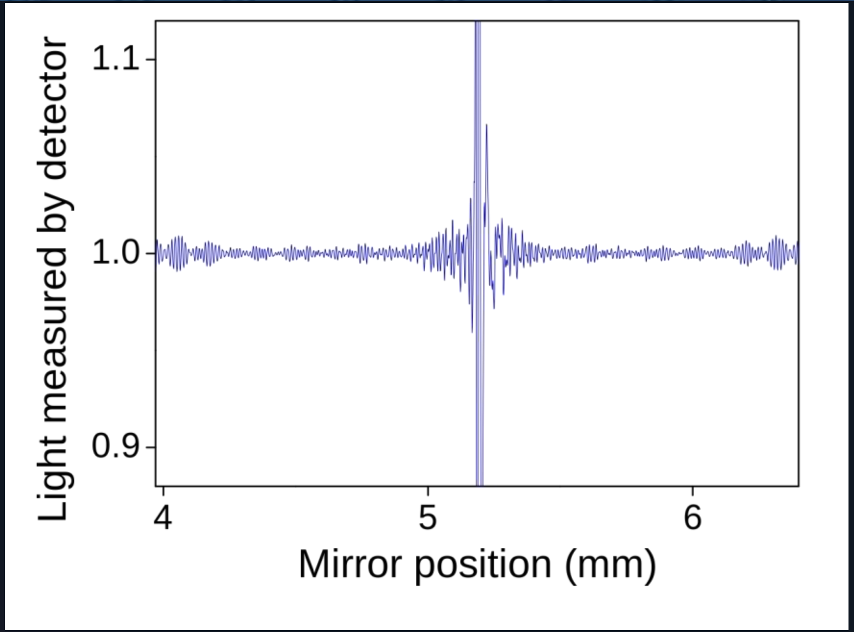
- Nerst glower
- Globar source
- High-pressure Hg arc lamp

Fourier-Transform InfraRed (FTIR) spectrometer

- During a single scan, the moving mirror moves forward and backward with respect to the beam splitter
- Depending on the difference in the optical path of the two rays, there is either constructive or destructive interference
- An interferogram is obtained, i.e., a plot of the intensity as a function of the optical path, which is constituted by all the IR radiations sent to the detector.
- The interferogram is converted in a signal as a function of frequency by means of Fourier transform

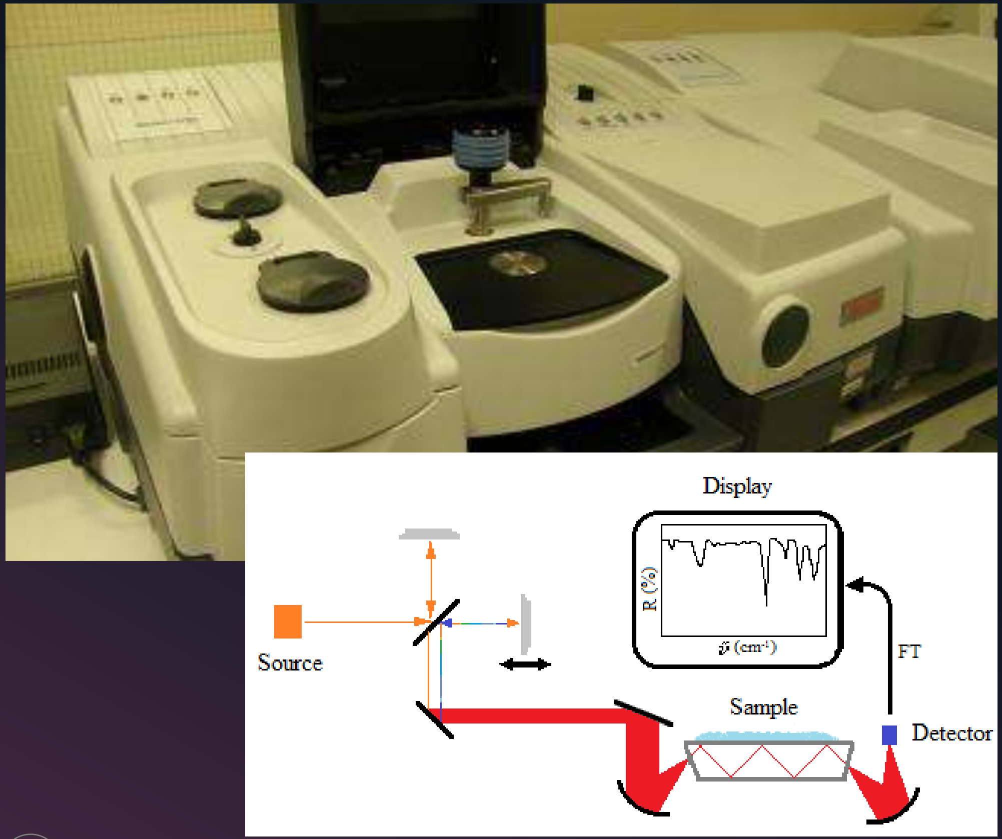
Michelson interferometer





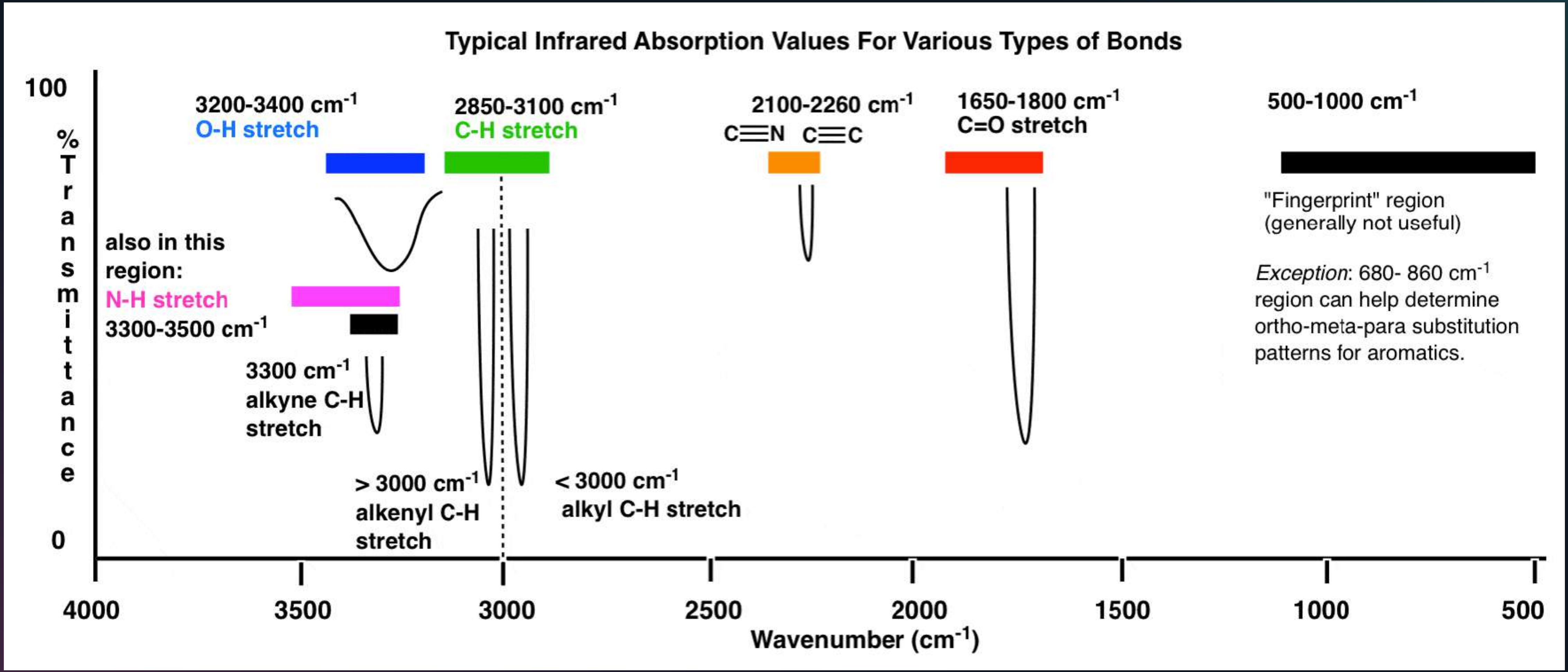
Other FTIR setups

Attenuated Total Reflectance (ATR) FTIR

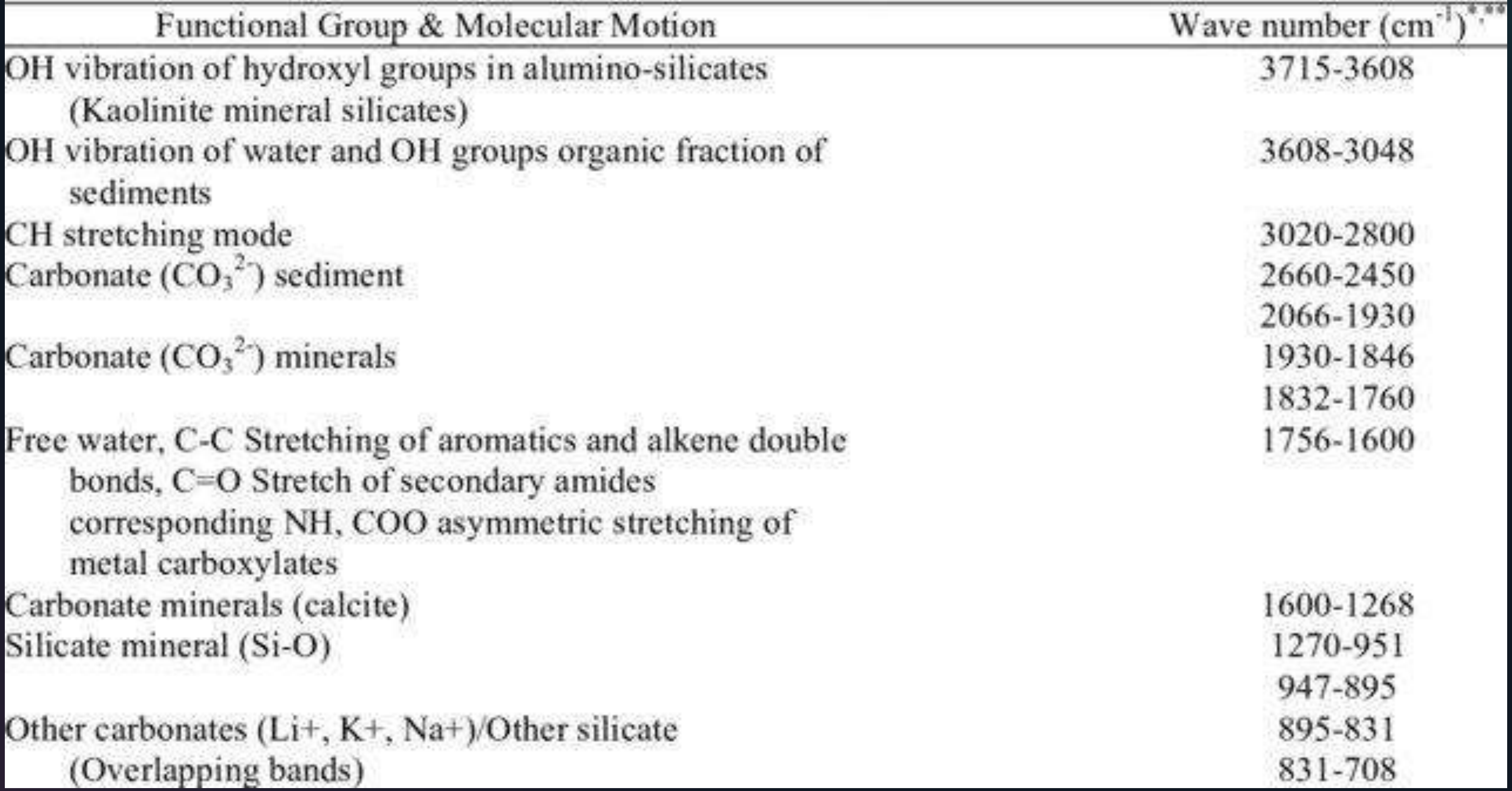


Portable FTIR

IR spectra – organic molecules

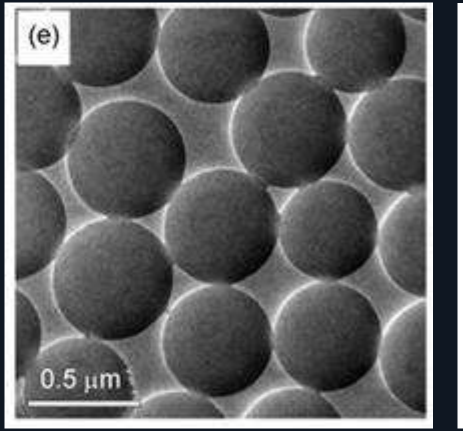


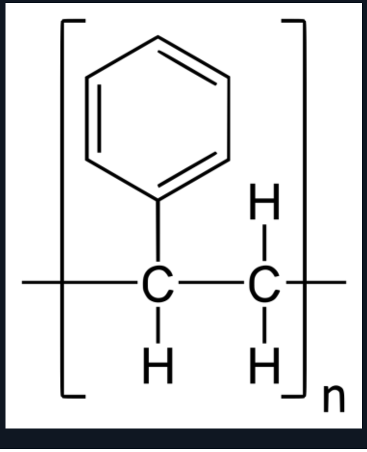
IR spectra – ionic groups in minerals

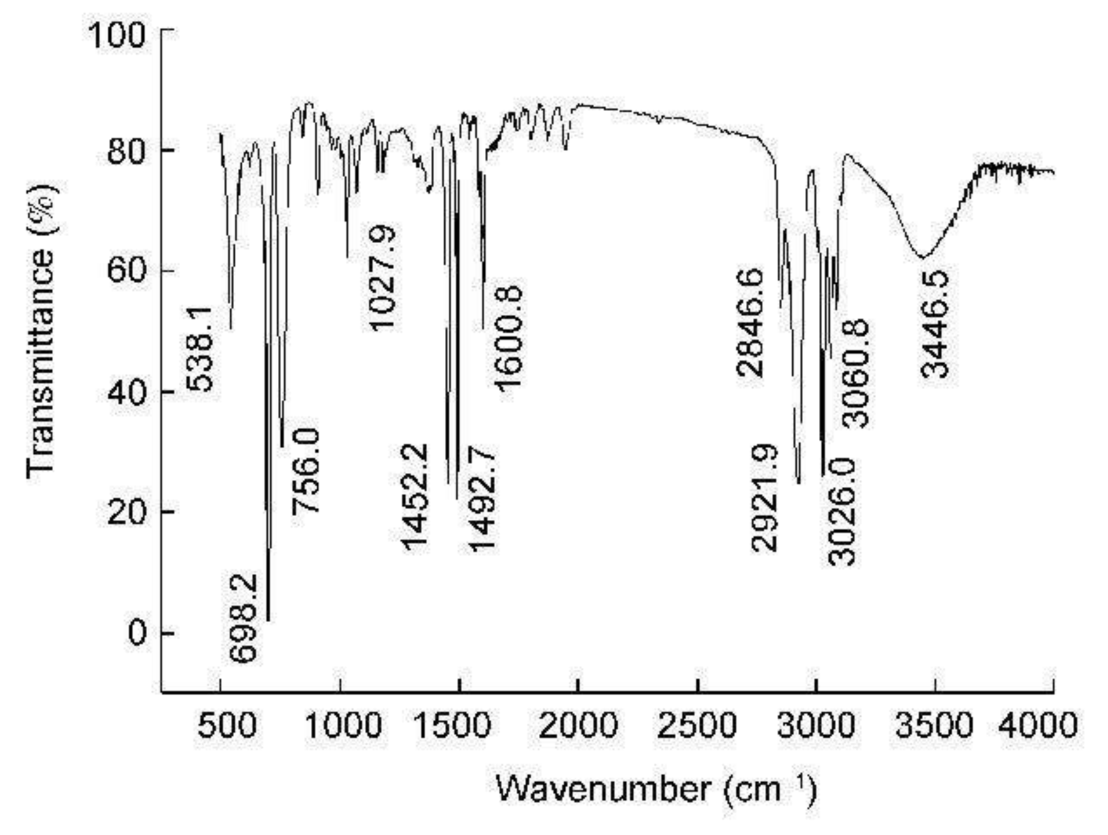


Functional Group & Molecular Motion	Wave number $(cm^{-1})^{*,**}$
OH vibration of hydroxyl groups in alumino-silicates (Kaolinite mineral silicates)	3715-3608
OH vibration of water and OH groups organic fraction of sediments	3608-3048
CH stretching mode	3020-2800
Carbonate (CO_3^{2-}) sediment	2660-2450
Carbonate (CO_3^{2-}) minerals	2066-1930 1930-1846 1832-1760
Free water, C-C Stretching of aromatics and alkene double bonds, C=O Stretch of secondary amides corresponding NH, COO asymmetric stretching of metal carboxylates	1756-1600
Carbonate minerals (calcite)	1600-1268
Silicate mineral (Si-O)	1270-951 947-895
Other carbonates (Li+, K+, Na+)/Other silicate (Overlapping bands)	895-831 831-708

Ranges – not fixed numbers – because of different chemical environment!







IR spectra

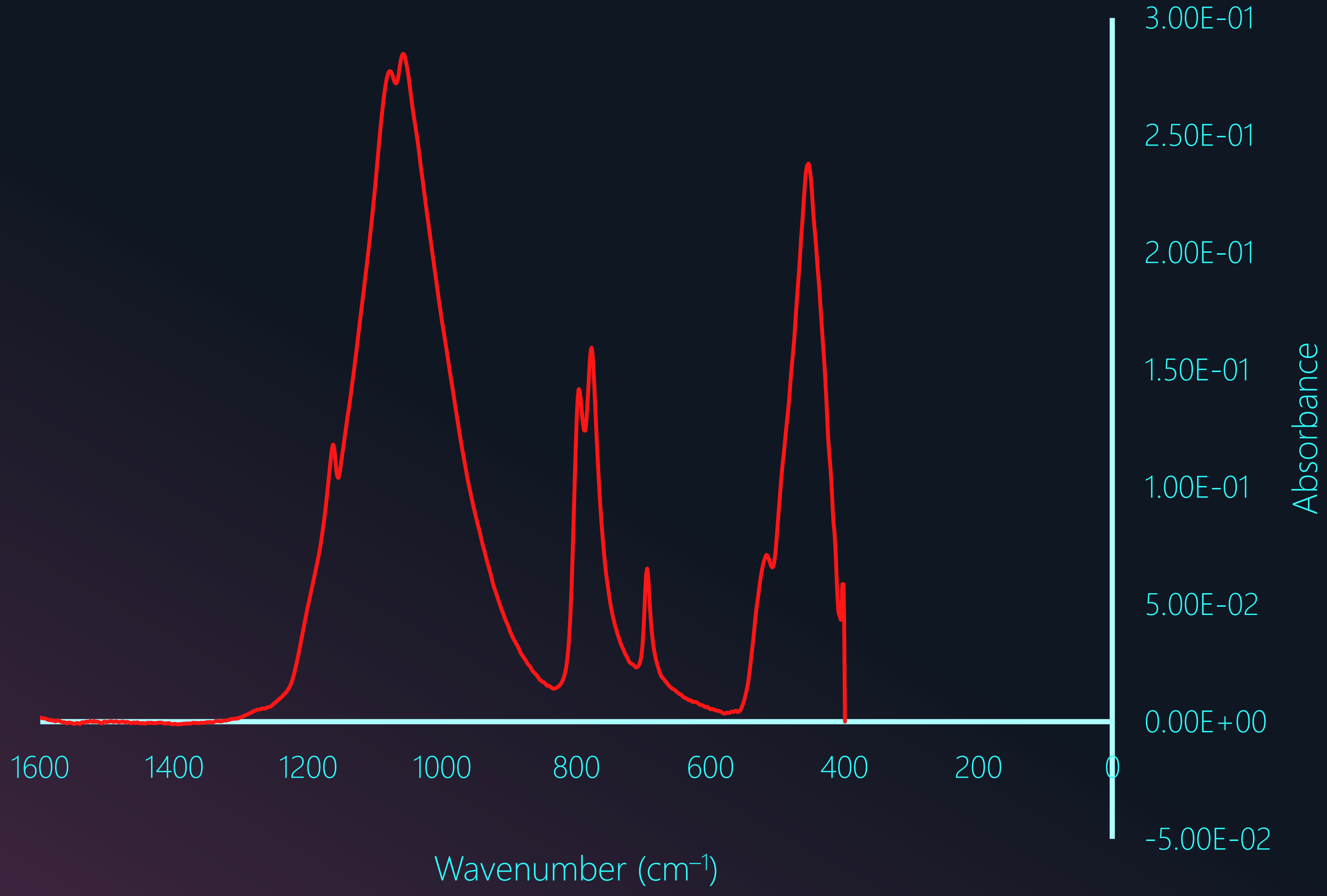
Polystyrene spheres

Main signals:

- Aromatic C – H stretching → 3026 cm^{-1} and 3061 cm^{-1};
- CH_2 stretching → 2847 cm^{-1} and 2922 cm^{-1};
- Deformation of CH_2 bonds and aromatic C=C 1452 cm^{-1}.

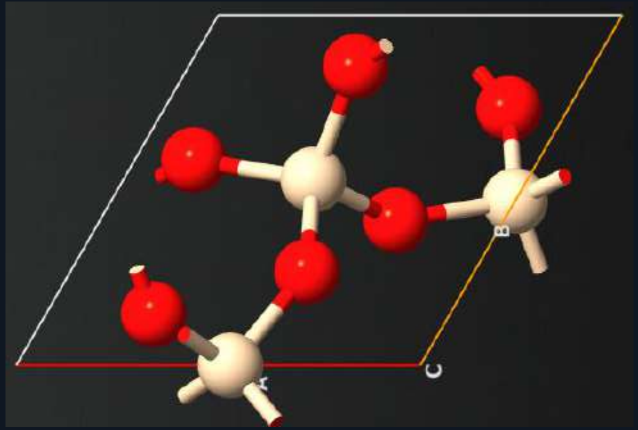
IR spectra

Quartz SiO_2

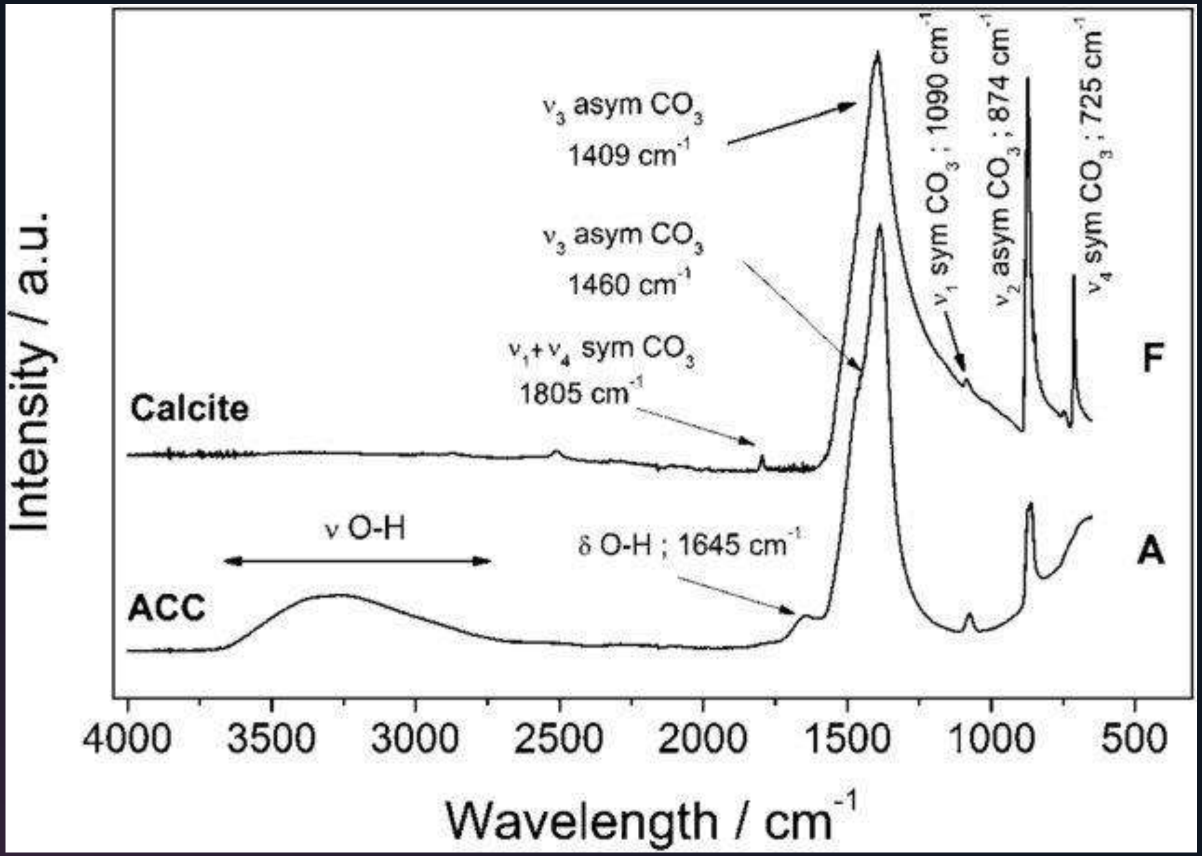


Main signals

- asymmetric stretching vibration of the Si–O groups, 1200 – 900 cm^{-1};
- symmetric stretch at 800 and 780 cm^{-1}
- symmetric and asymmetric Si–O bending mode at 695 cm^{-1}, 520 cm^{-1} and 450 cm^{-1}



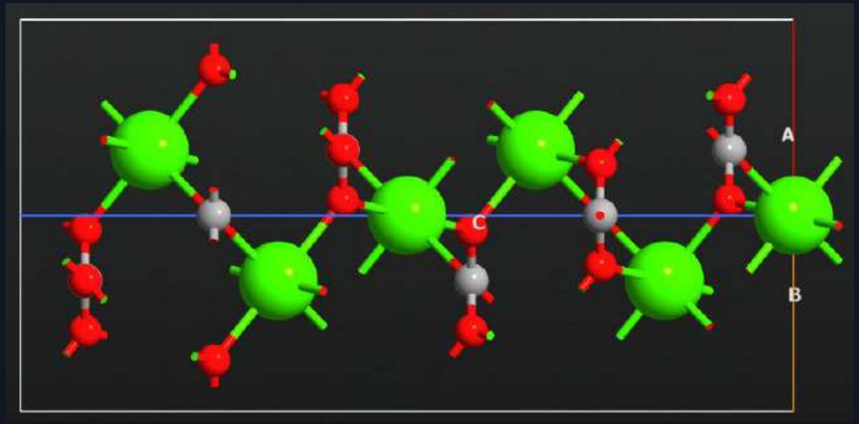
IR spectra



Calcite $CaCO_3$

Main signals:

- asymmetric CO_3 stretching (ν_3) → 1409 cm^{-1};
- symmetric CO_3 stretching (ν_1) → 1090 cm^{-1};
- asymmetric CO_3 bending (ν_2) → 874 cm^{-1};
- symmetric CO_3 bending (ν_4) → 725 cm^{-1}.



Raman effect

It was discovered by the Nobel Prize C. V. Raman in 1928.

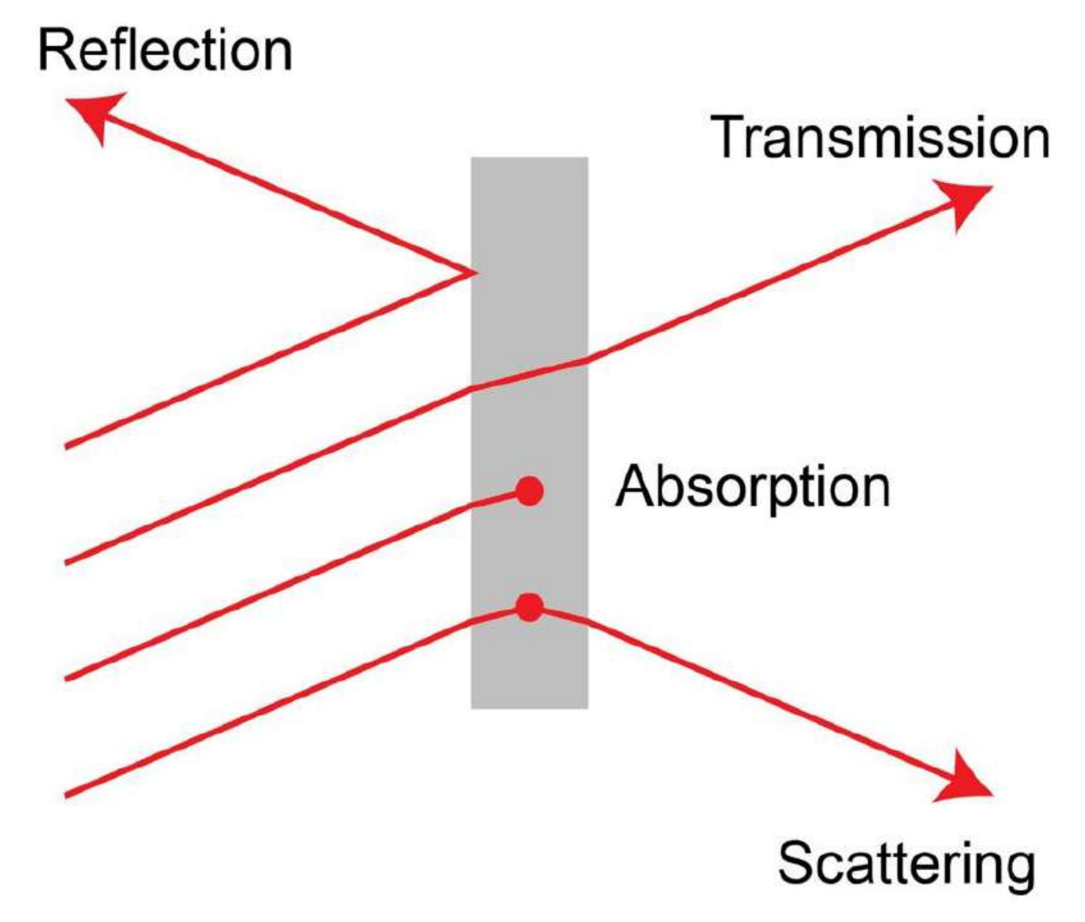
The Raman effect is the result of the **inelastic scattering of photons** from the sample irradiated by monochromatic light.

A monochromatic light source has a single wavelength, λ *(e.g.* laser source).

Raman effect

When a monochromatic radiation collides with the sample, it could be:

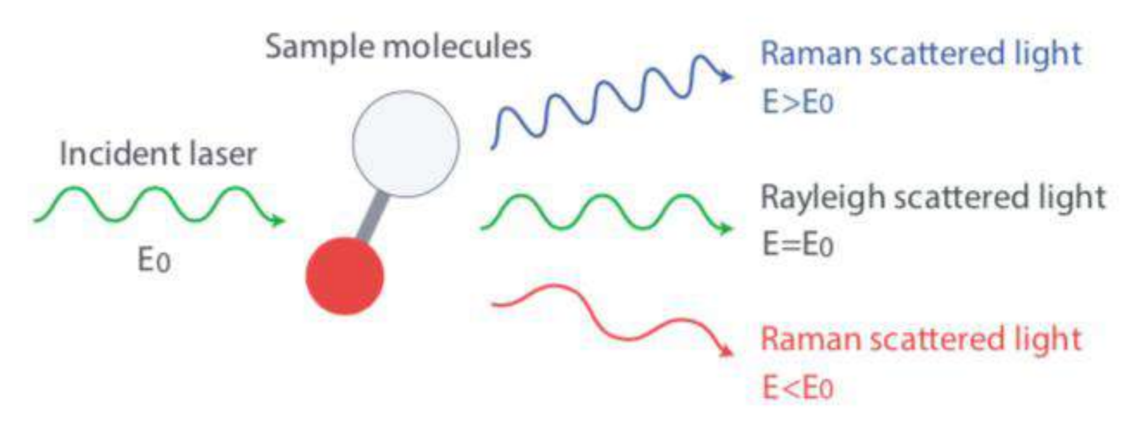
- adsorbed, if the energy of the wave is equal to the energy of a vibrational level transition (IR case);
- transmitted, if it does not interact with matter;
- reflected;
- scattered.



Raman effect

The Raman effect is related to photons scattered from the sample. The scattering process could be:

- Elastic → the energy (and hence the wavelength) of the scattered radiation is equal to that of the light source (Rayleigh scattering);
- Inelastic → the scattered photon has a different energy from that of the light source (Raman scattering).



Note: the Raman scattering is a minute fraction of all the scattered photons (10^{-6})!

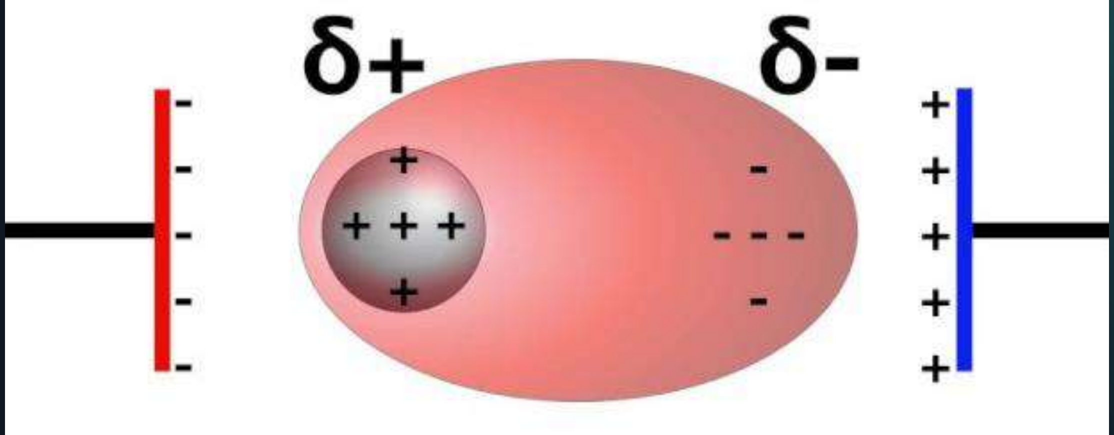
Raman selection rules

In order to observe the Raman effect (and hence a signal), during the molecular vibration(s) **the polarizability of the molecule/crystal must vary**.

When a molecule/crystal is immersed in an electric field E, an *induced dipole moment*, μ_{ind}, is generated according to:

$$\mu_{ind} = \Delta\mu = \alpha E$$

where α is the *polarizability* of the system.



The polarizability is a tensor quantity that describes the tendency of a molecule/crystal to be polarized by an applied electric field.

A single, isolated atom is isotropically polarizable, whereas even a biatomic molecule (such as $\mathrm{H_2}$, $\mathrm{O_2}$,…) has an anisotropic polarizability.

For example, in the $\mathrm{H_2}$ molecule the electron density distribution in more easily distorted by an applied electric field parallel to the H – H bond than perpendicularly to it.

Polarizability

$$\Delta\mu_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$
$$\Delta\mu_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$
$$\Delta\mu_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

↓

$$\begin{bmatrix} \Delta\mu_x \\ \Delta\mu_y \\ \Delta\mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Classical derivation of Raman effect

To explain the Raman effect, let's consider a single molecule in the gas phase subjected to an external electric field. In the classical theory of electromagnetism, the electric field can be described as:

$$E = E_0 \cos(2\pi\bar{\nu}_e t)$$

In this situation, the variation of the dipolar moment is:

$$\Delta\mu = \alpha E_0 \cos(2\pi\bar{\nu}_e t)$$

Now, let's take any vibrational mode m of the molecule. The variation of its vibrational coordinate Q (example, the variation of a bond length) can be described by a sinusoidal law (harmonic oscillator):

$$Q = Q_0 \cos(2\pi\bar{\nu}_m t)$$

It is to be expected that the polarizability will be a function of the nuclear coordinates (we do not consider free rotations of the molecule).

The variation of components in polarizability tensor with vibrational coordinates is expressed in a Taylor series.

$$\alpha_{ij} = \left(\alpha_{ij}\right)_0 + \frac{\partial\alpha_{ij}}{\partial Q} Q + \ldots = \left(\alpha_{ij}\right)_0 + \frac{\partial\alpha_{ij}}{\partial Q} Q_0 \cos(2\pi\bar{\nu}_m t) + \ldots$$

We can obtain the polarizability tensor for the mode m (truncated at the second term):

$$\alpha_m = \alpha_0 + \frac{\partial\alpha_m}{\partial Q} Q_0 \cos(2\pi\bar{\nu}_m t)$$

Classical derivation of Raman effect

By substituting the previous expression in the one related to the dipole moment variation we obtain:

$$\Delta\mu = \alpha_0 E_0 \cos(2\pi\bar{\nu}_e t) + \frac{\partial \alpha_m}{\partial Q} Q_0 E_0 \cos(2\pi\bar{\nu}_e t)\cos(2\pi\bar{\nu}_m t)$$

We now apply the Werner's formula :

$$\cos\theta\cos\varphi = \frac{1}{2}[\cos(\theta-\varphi)+\cos(\theta+\varphi)]$$

in the second term of the expression. We obtain:

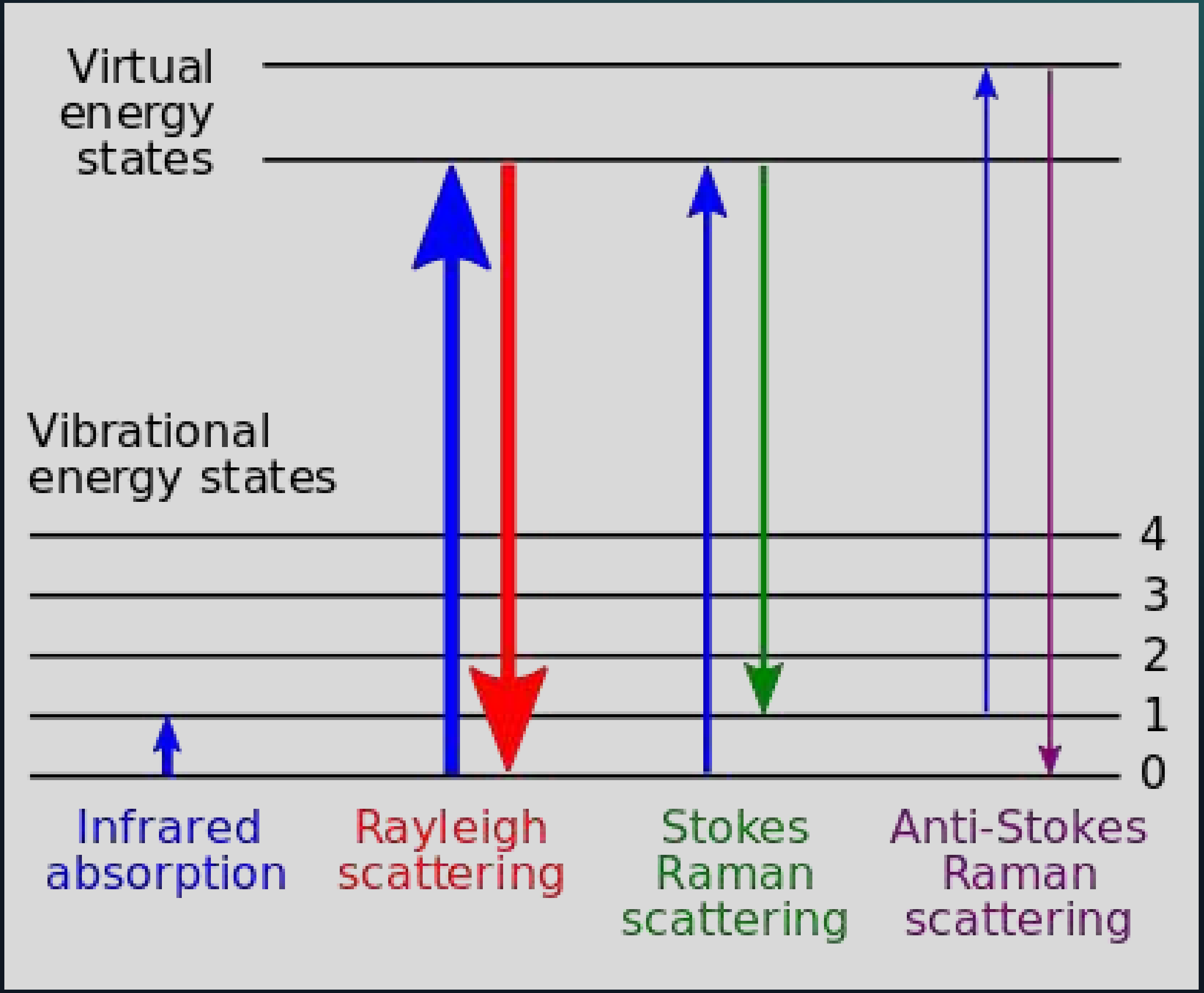
$$\Delta\mu = \underbrace{\boxed{\alpha_0 E_0 \cos(2\pi\bar{\nu}_e t)}}_{\text{Reyleigh scattering}} + \frac{1}{2}\frac{\partial \alpha_m}{\partial Q} Q_0 E_0 \{ \underbrace{\boxed{\cos[2\pi(\bar{\nu}_e - \bar{\nu}_m)t]}}_{\text{Raman scattering (Stokes)}} + \underbrace{\boxed{\cos[2\pi(\bar{\nu}_e + \bar{\nu}_m)t]}}_{\text{Raman scattering (anti-Stokes)}} \}$$

Quantum derivation of Raman effect

From the quantum mechanics point of view, the Raman effect can be explained by considering the vibrational energy levels of the system (molecule/crystal).

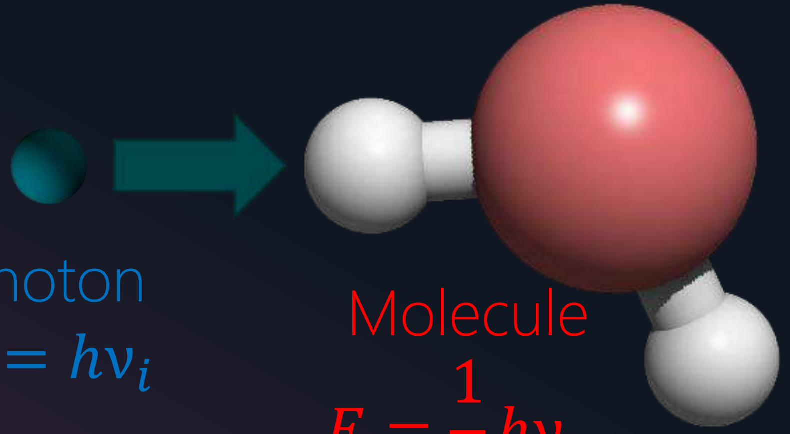
When a photon collides with the system, the latter goes through a "virtual" excited energy level, from where it spontaneously decades to the ground level.

Elastic and inelastic scattering are explained by the principle of energy conservation.



Quantum derivation of Raman effect

Before impact



Photon

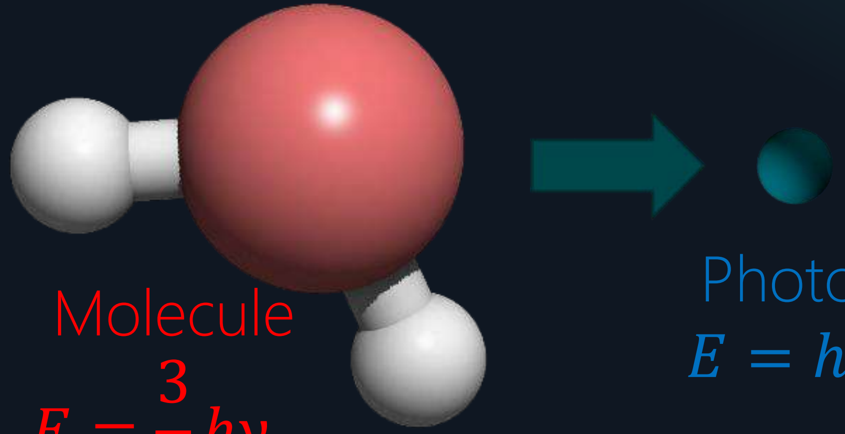
$E = h\nu_i$

Molecule

$E = \frac{1}{2}h\nu_m$

$$E_i = h\nu_i + \frac{1}{2}h\nu_m$$

After impact



Molecule

$E = \frac{3}{2}h\nu_m$

Photon

$E = h\nu_f$

$$E_f = h\nu_f + \frac{3}{2}h\nu_m$$

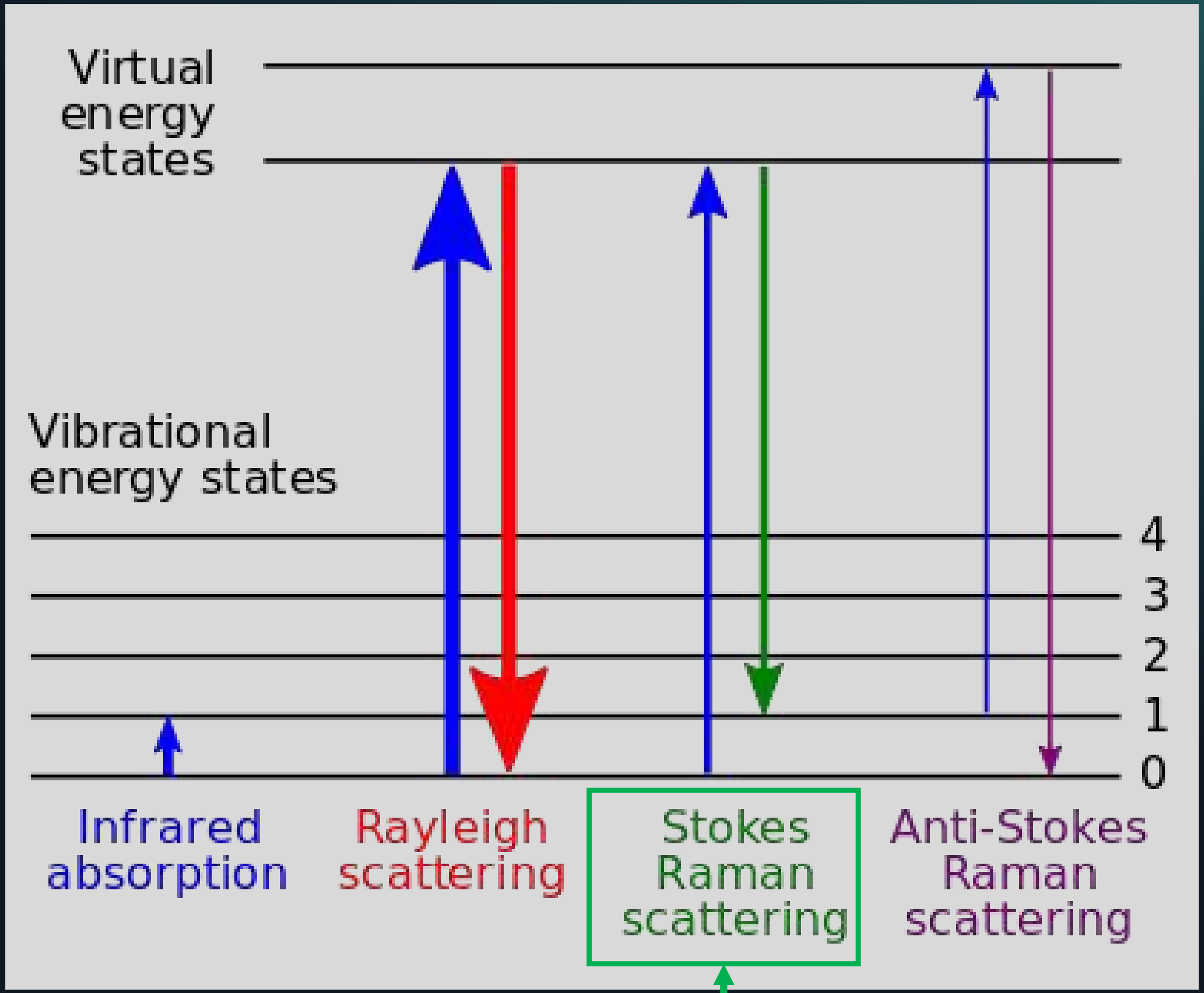
Quantum derivation of Raman effect

According to the principle of conservation of energy, it must be:

$$E_i = E_f$$

$$E_i = h\nu_i + \frac{1}{2}h\nu_m = h\nu_f + \frac{3}{2}h\nu_m = E_f$$

$$\boxed{h\nu_f = h\nu_i - h\nu_m}$$



Raman intensity

The intensity of the Raman scatttering intensity is given by:

$$I = I_0 \cdot \frac{\sin^2\varphi}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4 \cdot \alpha^2$$

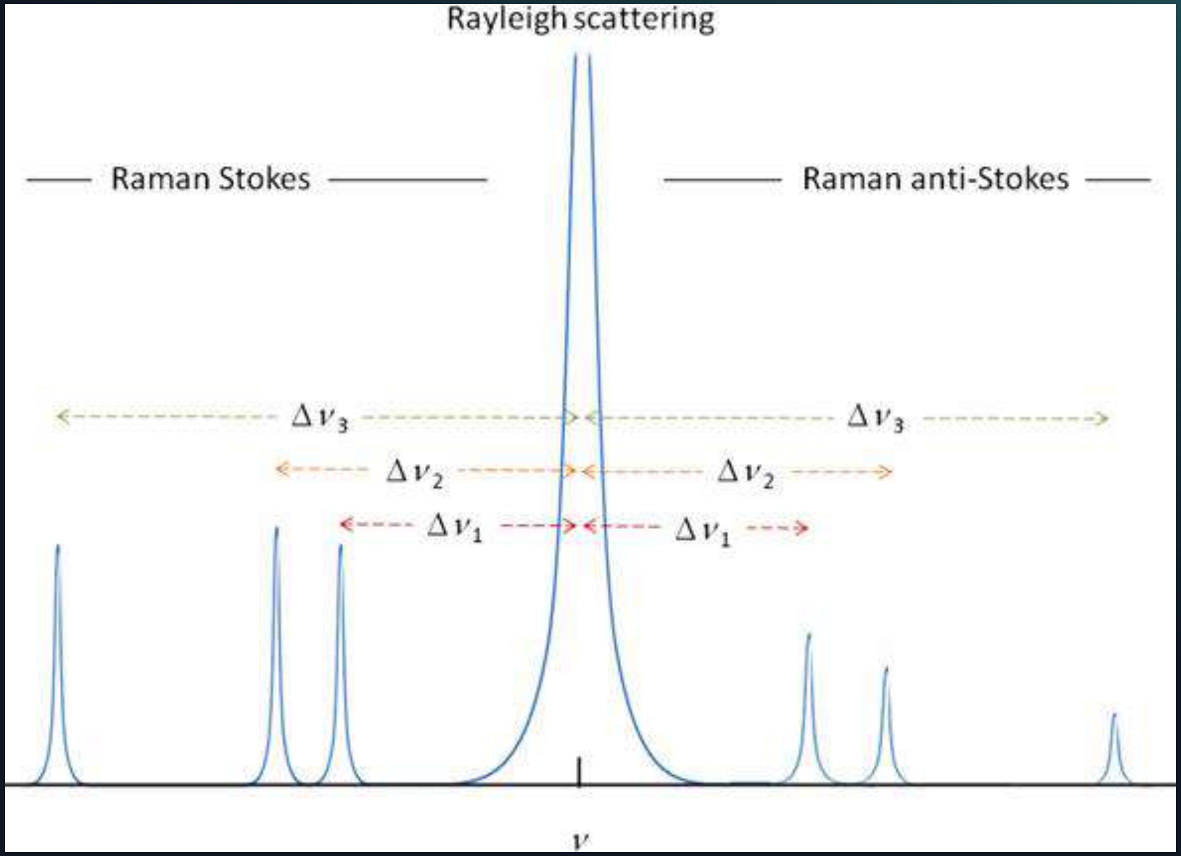
Where I_0 and λ are the intensity and wavelength of the incoming light, respectively, R is the sample to detector distance, φ is the scattering angle and α is the sample polarizability.

It follows that the Raman intensity:

- rapidly increases as the wavelength of the monochromatic light source decreases;
- is zero on a direction parallel to the direction of the source radiation and maximum when the Raman scattering is collected orthogonal to the direction of the light source.

Raman Spectrum

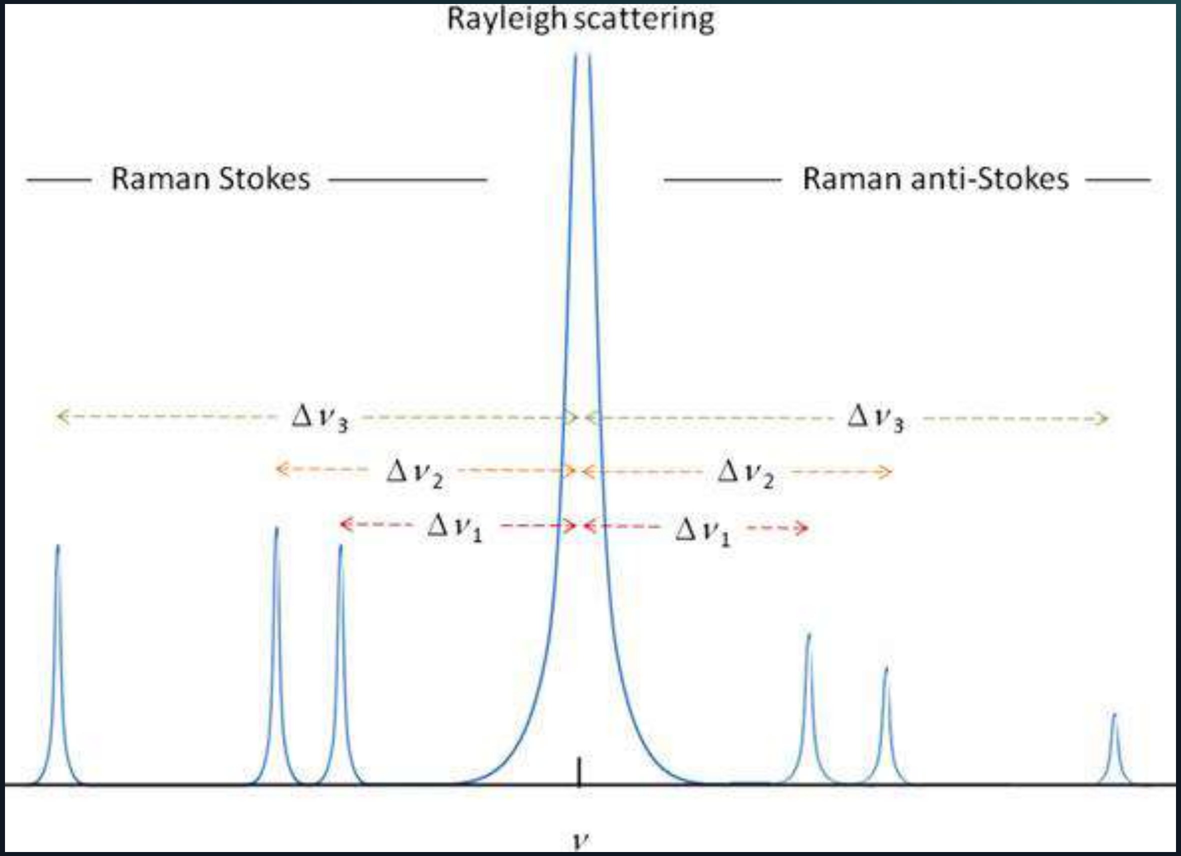
- A typical Raman spectrum is characterized by:
  - Rayleigh line → it is the most intense peak, placed at λ of the of the light source
  - Stokes lines → photons emitted with lower energy that the incoming ones
  - anti-Stokes lines → photons emitted with higher energy that the incoming ones
- Stokes and anti-Stokes lines are symmetrical with respect to the Rayleigh scattering line.
- In addition, in standard conditions, the Stokes lines are more intense than the anti-Stokes ones.



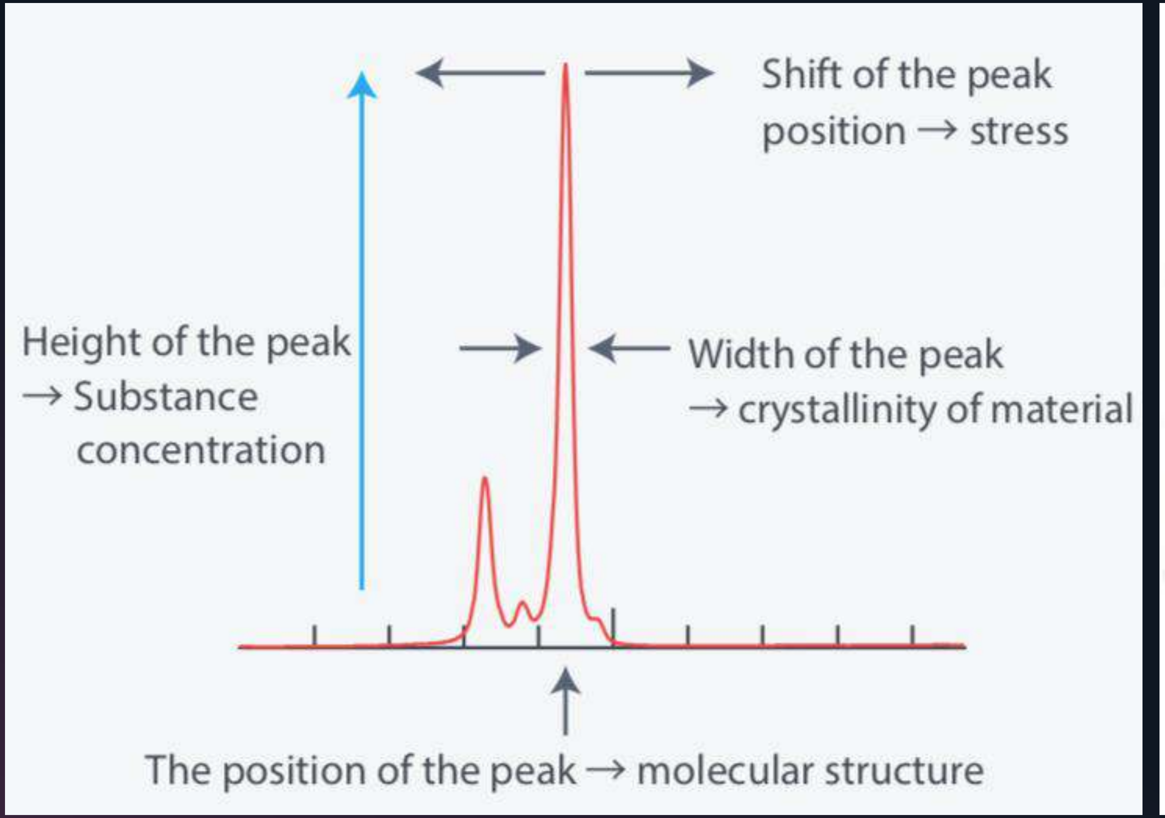
Raman Spectrum

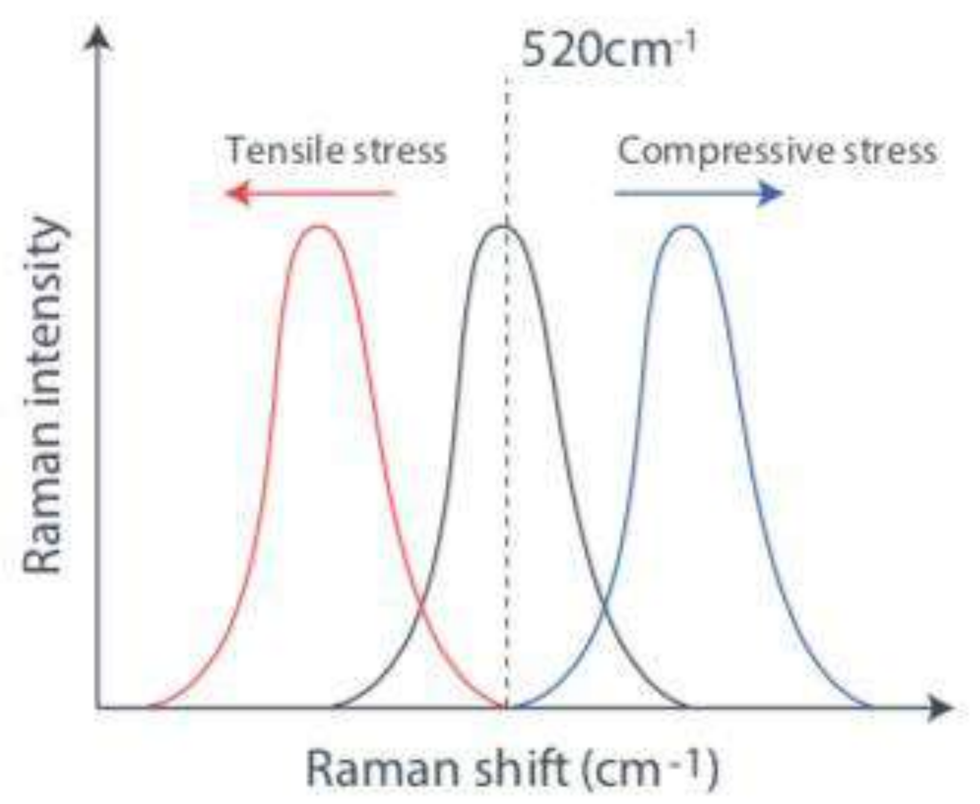
As seen from the theory previously explained:

- the Rayleigh line does not carry any information on the sample and it is usually removed from the spectra by acquisition software.
- Stokes (and anti-Stokes) lines are related to the vibrational energy levels of the molecule/crystal under analysis.
- In addition, anti-Stokes lines are often not easily detectable (very low intensity). However, they can provide information of the temperature of the sample by comparison of the Stokes/anti-Stokes intensities.



Information from Raman spectra





Raman/IR relationship

Since the (anti-)Stokes lines carry information on the vibrational modes of molecules and phonon of crystals, we can compare the Raman signals to the infrared ones, because:

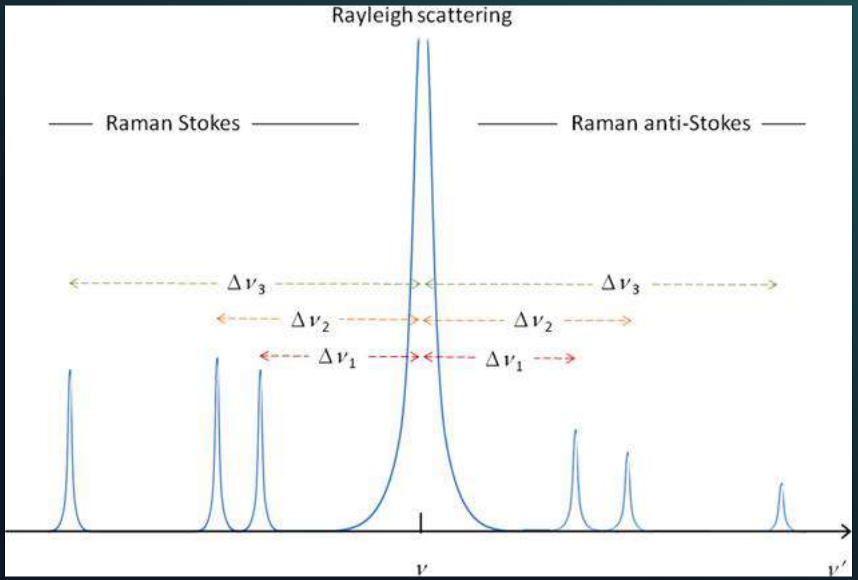
$$h\nu_f = h\nu_i - h\nu_m$$

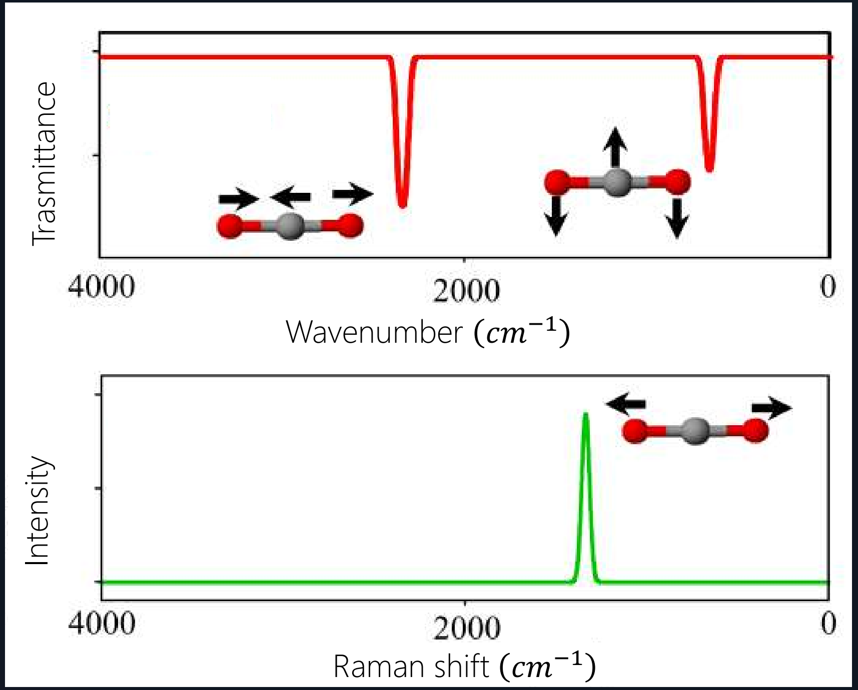
It is just required to centre (i.e., shift) the Raman spectrum on the Rayleigh (excitation) line. In fact, several Raman spectra reports in abscissa a quantity called **Raman shift**, which is the frequency (wavelength) shift of the inelastically scattered photons.

In addition, there is the so-called rule of mutual exclusion:

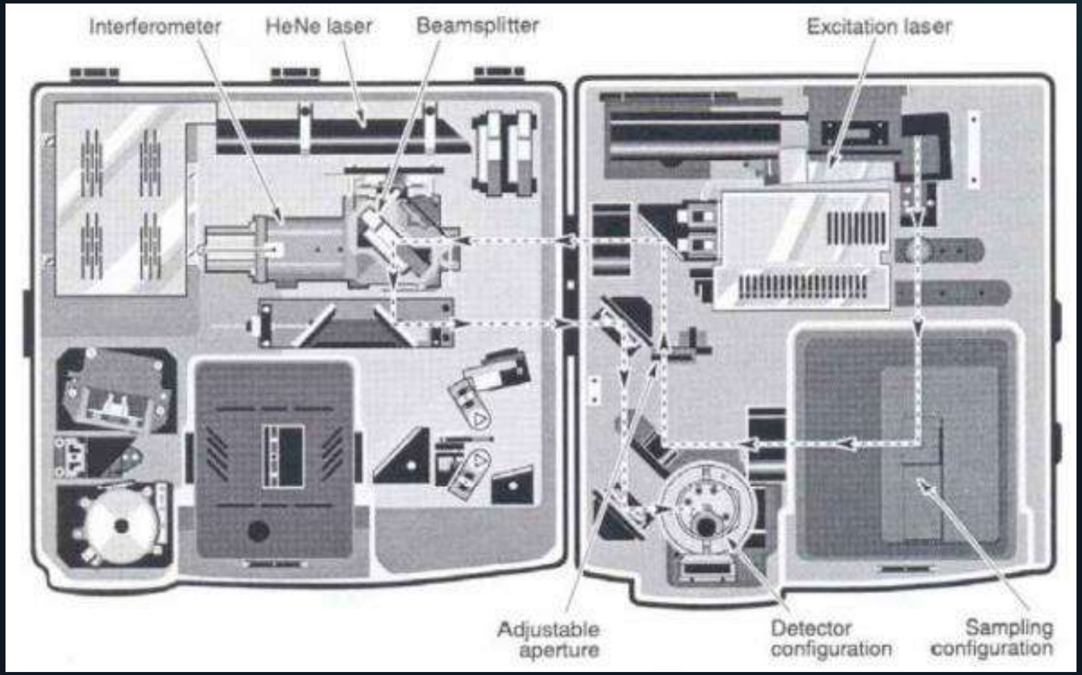
"If a molecule/crystal possesses an inversion centre, then there can not be normal modes/phonons that are simultaneously active in both Raman and infrared spectroscopies.".

Thus, **the two techniques are complementary**.

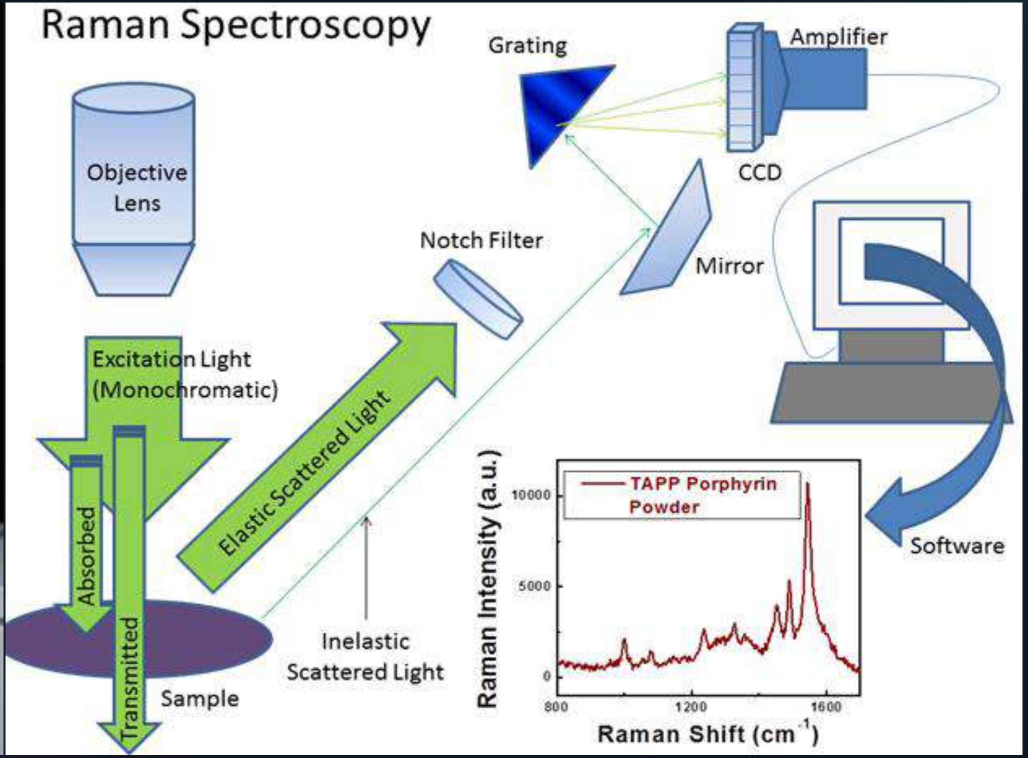




Benchtop Raman instrument



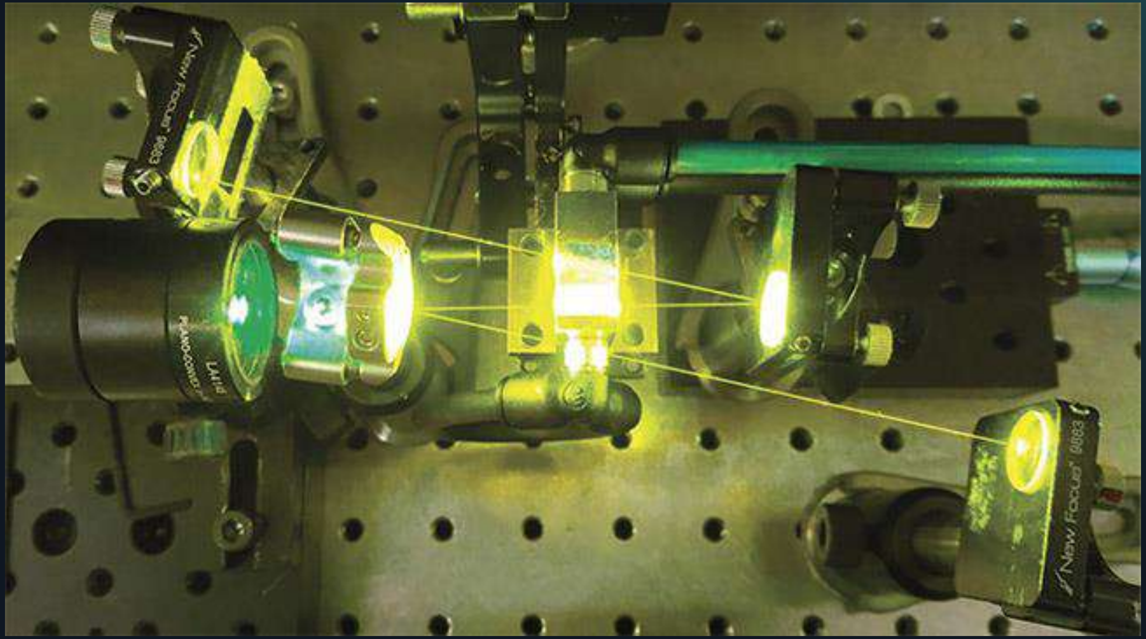
Confocal Raman microscopes



Light sources for Raman spectroscopy

Monochromatic light sources are employed:

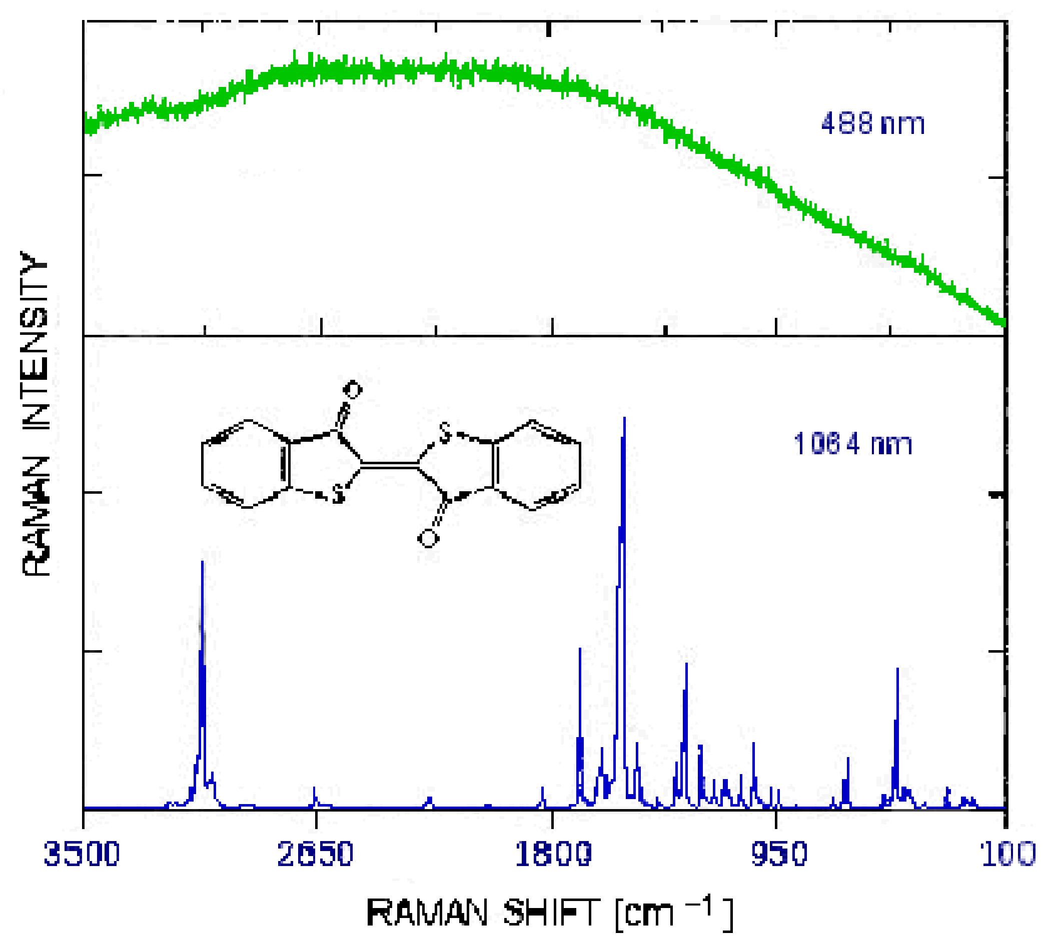
- UV Laser, 244 or 325 nm
- Argon Laser, 488.0 nm or 514.5 nm
- He-Ne Laser, 632.8 nm
- Ruby Laser, 694.3 nm
- Nd-YAG (Nd-doped Yttrium-Aluminum-Garnet), 1064 nm



Light sources for Raman spectroscopy

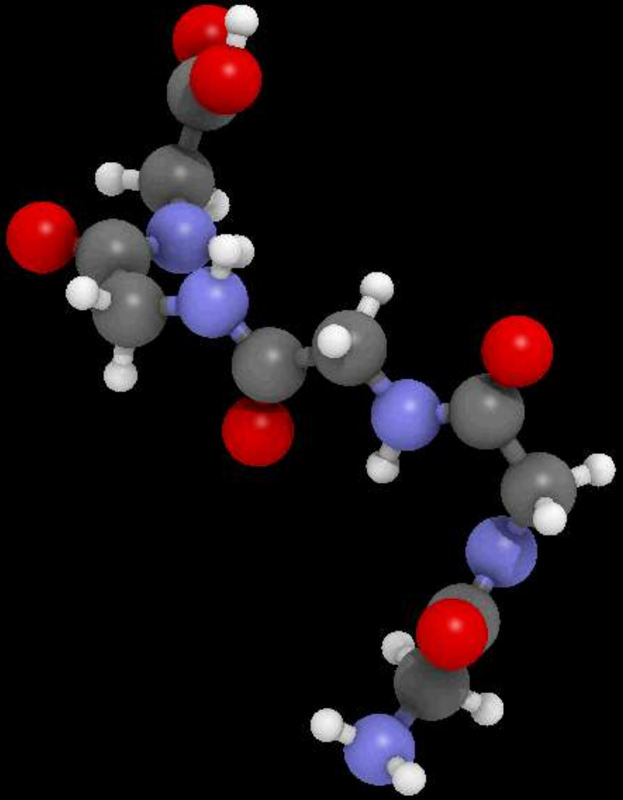
The laser frequency (and hence the associated energy) is an important factor that has to be carefully considered because it can both affect the overall quality of the final spectrum and alter the sample. In general:

- Raman intensity is proportional to the fourth power of the source frequency
- High-frequency lasers, with high irradiating energy, such as UV lasers may activate undesired electronic transitions in the sample, which generate fluorescence and hinder the interpretation of the spectra
- High-frequency lasers may irreversibly damage the sample (photobleaching, …), with alteration of the results.



Infrared spectroscopy *vs* Raman spectroscopy

	Infrared spectroscopy	Raman
Physical effect	ABSORBANCE Variation of the dipole moment in the molecule/solid during the vibration (strong in bonds such as O – H, N – H)	ANELASTIC SCATTERING Variation of the polarizability of the molecule/solid (strong in covalent bonds)
Sample preparation	Optimal thickness (transmission), powdered samples dispersed in a medium (usually KBr) or contact with the sample	No contact, sample as is (in portable systems or confocal Raman microscopes)
Advantages	Rich spectra, presenting many peaks	Sharper peaks (easy identification), it is possible to analyse water solutions and it is possible to use glass sample holders
Disadvantages	Strong and very broad adsorption from water, strong adsorption from glass and CO_2	Fluorescence, photobleaching
Suitable materials	Mostly organic samples (polymers, proteins), but also minerals and materials presenting groups as SiO_4, CO_3, PO_4, SO_4, etc.	Almost no limits in the material choice
Frequency range	4000 – 400 cm^{-1}	4000 – 50 cm^{-1}
Light sources	Nerst filaments, tungsten filaments, Globar	Monochromatic lasers in the UV, visible or near infrared regions



Simulation methods

Basics and applications

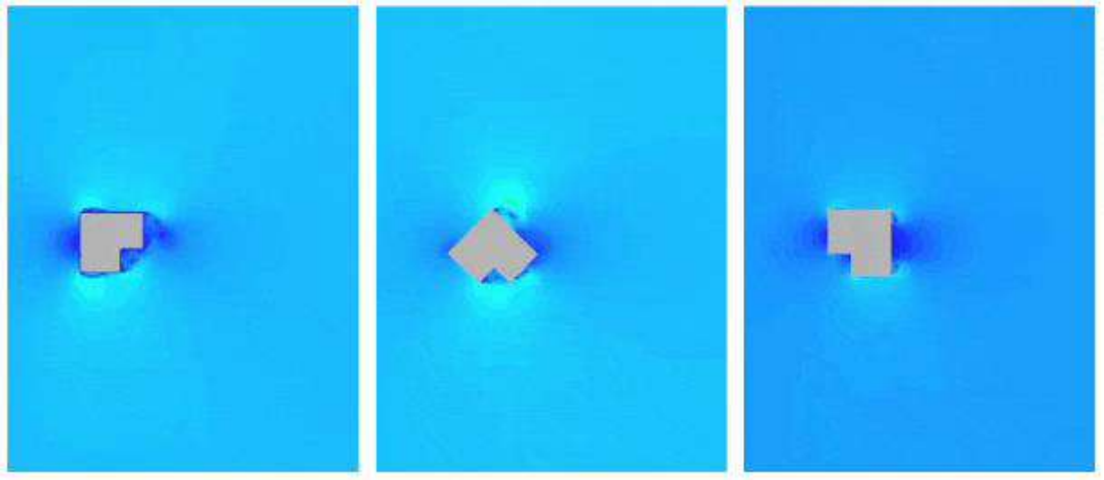
Simulation: what do we mean?

- A simulation is a research or teaching technique that reproduces actual events and processes under test conditions. They are typically performed with computers, from laptops up to large-scale facilities.
- Developing a simulation is often a highly complex mathematical process. Initially a set of rules, relationships, and operating procedures are specified, along with other variables.
- The interaction of these phenomena create new situations, even new rules, which further evolve as the simulation proceeds.

Use of simulations to:

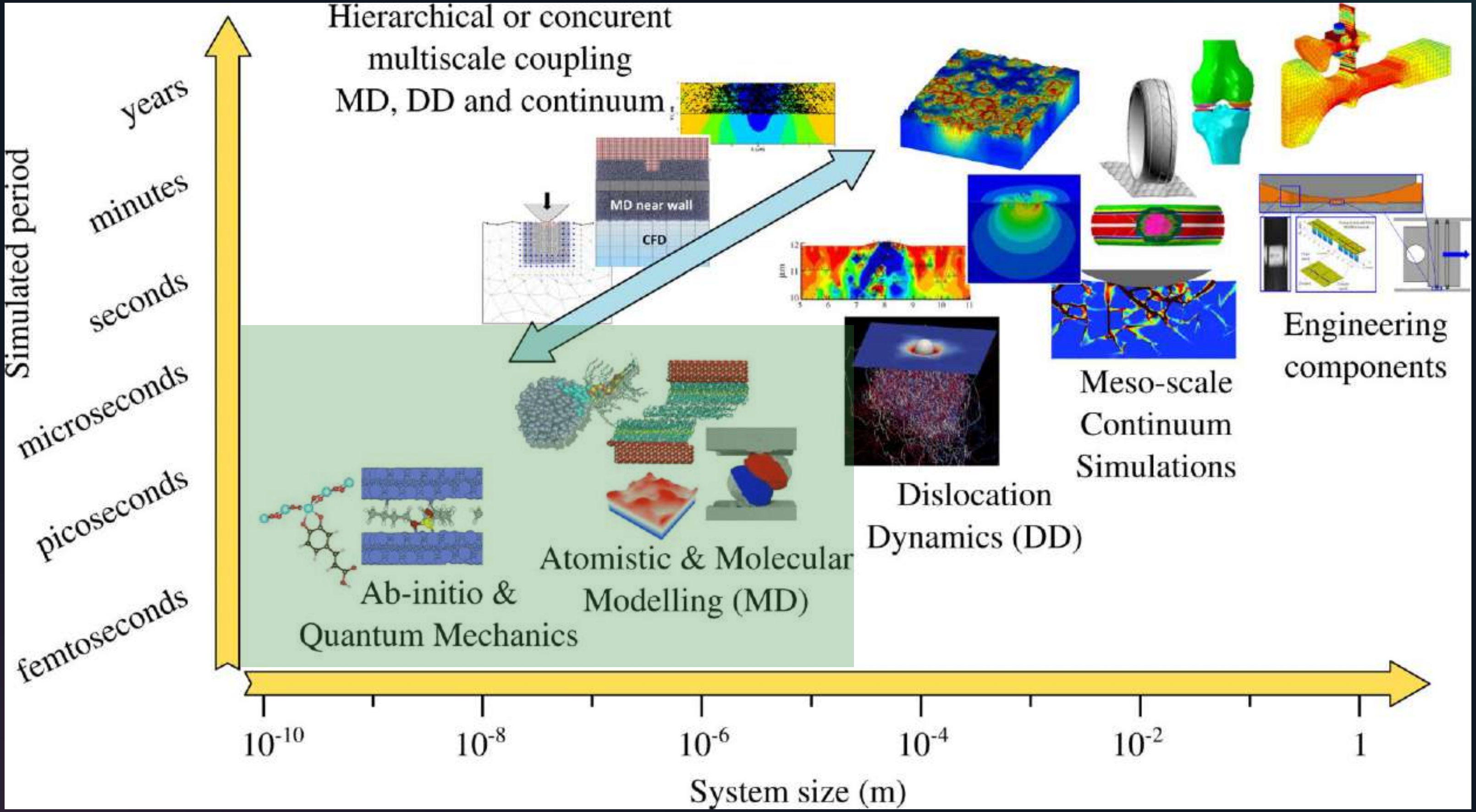
- Predict phenomena
- Provide further details on a phenomenon

Real-world wind tunnel test



Virtual wind tunnel test

Simulations: time and space scales

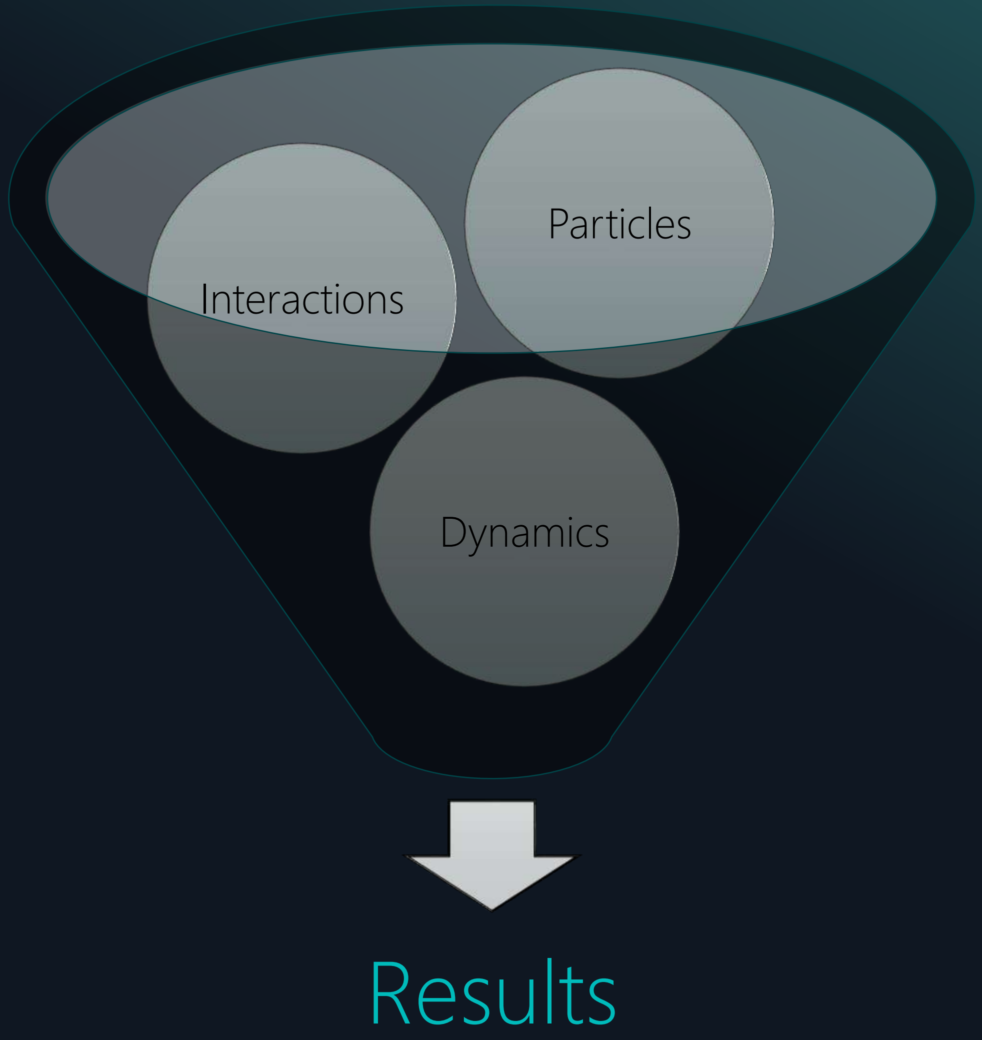


Different laws for different scales!

Simulations: the system

To describe a system, we need four fundamental information

- **System description**: what and how many are the fundamental units, or «particles»?
- **System condition**: where are the particles and what are their velocities?
- **Interaction**: what is the mathematical form for the forces acting between the particles?
- **Dynamical equation**: what is the mathematical form for evolving the system in time?

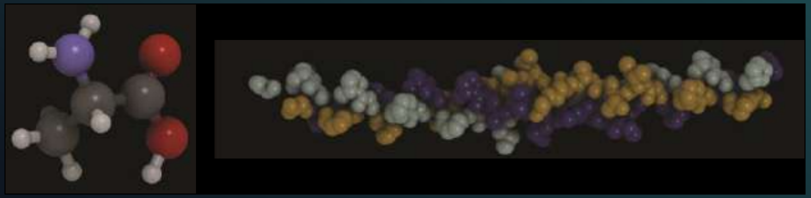


Simulations: the system

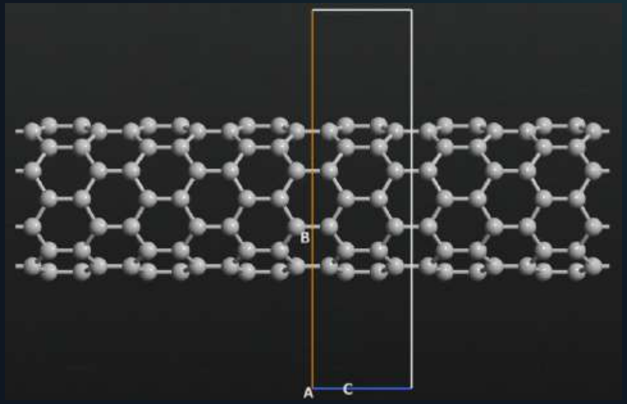
Define the smallest particle in the system:

- Nuclei and electrons?
- Atoms («charged spheres»)?
- Grains
- …

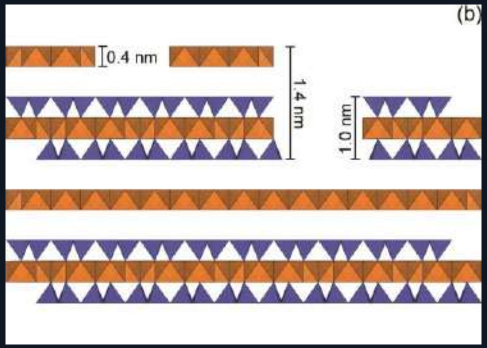
0D – Atoms and molecules



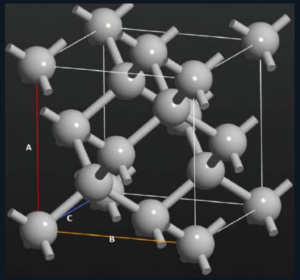
1D – Polymers and nanotubes



2D – Surfaces



3D – Crystals

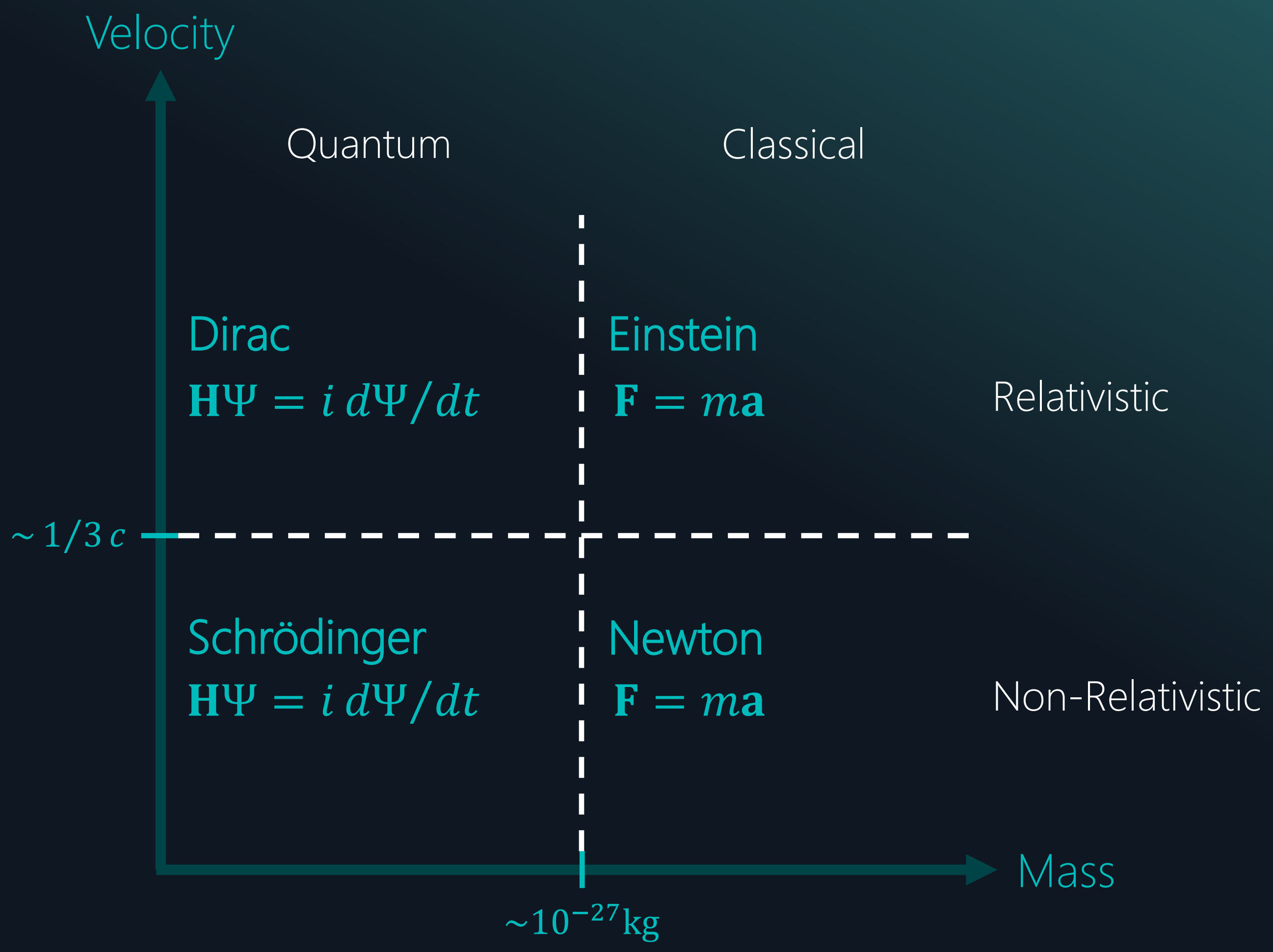


Systems: the dynamical equation

- Four regimes, according to the mass and velocity of the particles
- «Heavy», «slow» particles can be described with sufficient accuracy by Newtonian law – atomistic simulations – force fields methods
- Light particles (hydrogen, electrons) must be treated by quantum mechanics

Classical mechanics → Deterministic

Quantum mechanics → Probabilistic



Velocity

Quantum

Classical

Dirac

$\mathbf{H}\Psi = i\, d\Psi/dt$

Einstein

$\mathbf{F} = ma$

Relativistic

$\sim 1/3\, c$

Schrödinger

$\mathbf{H}\Psi = i\, d\Psi/dt$

Newton

$\mathbf{F} = ma$

Non-Relativistic

Mass

$\sim 10^{-27}\mathrm{kg}$

Quantum mechanics

The (time-dependent) Schrödinger equation

$$\mathbf{H}(\mathbf{r},t)\Psi(\mathbf{r},t) = i\frac{d\Psi(\mathbf{r},t)}{dt}$$

H is the Hamiltonian operator, sum of the kinetic and potential operators: $\mathbf{H}(\boldsymbol{r},t) = \mathbf{T}(\mathbf{r}) + \mathbf{V}(\mathbf{r},t)$.

Ψ is the wavefunction, whose square gives the probability of observing a particle at position **r** and time *t*.

For a time-independent (bound) system, the Schrödinger equation provides the total energy:

$$\mathbf{H}(\mathbf{r})\Psi(\mathbf{r}) = E(\mathbf{r})\Psi(\mathbf{r})$$

Or

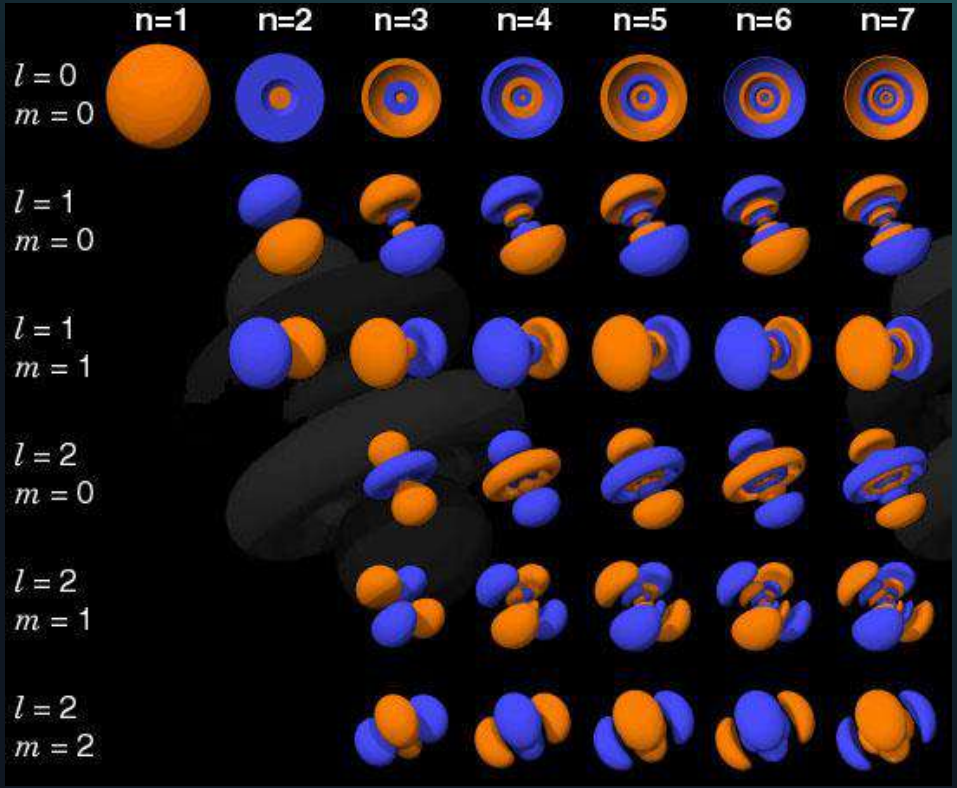
$$E(\mathbf{r}) = \langle\Psi(\mathbf{r})|\mathbf{H}(\mathbf{r})|\Psi(\mathbf{r})\rangle$$

Erwin Schrödinger
1887 – 1961
Nobel Prize in Physics 1933

Quantum mechanics

$$\mathbf{H}(\mathbf{r})\Psi(\mathbf{r}) = E(\mathbf{r})\Psi(\mathbf{r})$$

- This is an eigenvalue-eigenvector equation, used to solve a many-body problem (several nuclei and electrons).
- *Ab initio* (First principle) approach → no parametrization, the only necessary knowledge is the number of particles and their initial position and velocity.
- It is commonly assumed that the electrons are moving, whereas the nuclei are still (Born-Oppenheimer approximation)
- It can not be solved analytically for a number of particles $N > 2$, hence it requires **numerical solutions**.



Analytical solutions of the Schrödinger equation for the hydrogen atom → the electronic orbitals and the quantum numbers

- *n* = size (energy) of the orbital
- *l* = type of the orbital
  - l = 0 → *s* orbital
  - l = 1 → *p* orbital
  - l = 2 → *d* orbital
  - l = 3 → *f* orbital
- *m* = orientation of the orbital

Quantum mechanics methods

Wavefunctions

Hartree-Fock (Wavefunction Theory)

MP2-CI

Electron density

Density Functional Theory

Time-Dependent-DFT

Important note: the methods are formally exact, but the solution is necessarily approximated

The variational theorem

No approximate wave function can have lower energy than the exact ground state energy of the system

$$E_{\text{ground}} \leq \langle \phi | \mathbf{H} | \phi \rangle$$

↓

Criterion to iteratively construct the approximate wave function

The basis set

The basis set is a set of known functions (*atomic orbitals*) used to construct the unknown *molecular* (or *crystalline*) *orbitals*

⬇

The expansion of the molecular orbitals in terms of atomic orbitals is not an approximation if the basis set is *complete* (infinite number of functions) → obviously, this is not possible

Requested features for a basis set

- Representative of the physics of the problem → good accuracy with few functions
- Able to generate a complete basis set
- Hierarchical → each hierarchy level should have a certain level of accuracy
- Computational efficient
- Universal → suitable for different methods (HF, DFT, …) and properties (energy, forces, vibrations, etc.)
- Available for all atoms

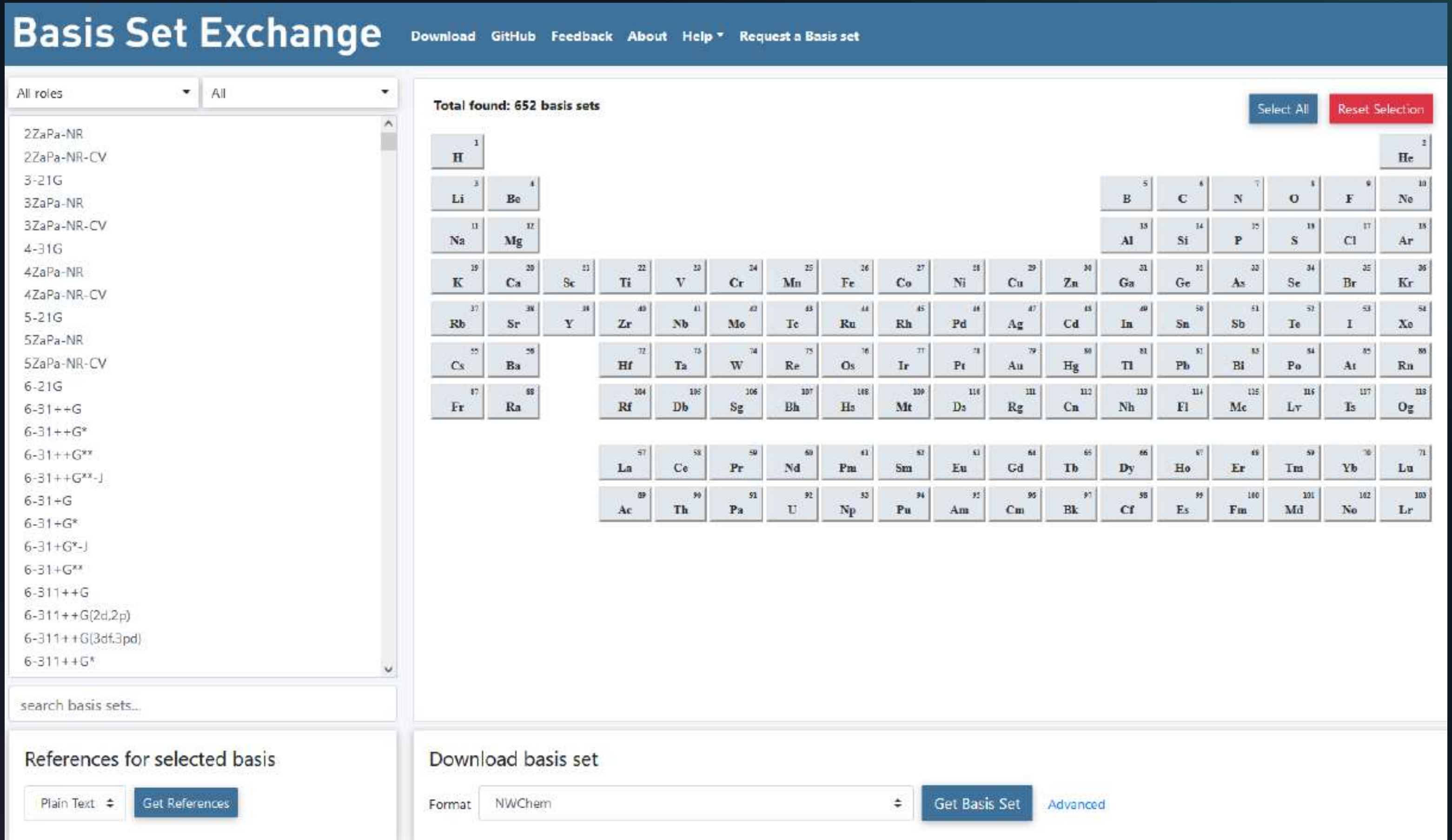
The basis set

Different types of basis sets:

- Slater-type orbitals (STO)
- Gaussian-type orbitals (GTO)
- Atomic natural orbitals (ANO)
- Effective core pseudopotentials (ECP)
- Plane waves (PW)
- …

Basis sets are tested and validated against experimental data:

- Chemical bonding
- Reactions
- Molecular/crystal structures
- …



All roles | All

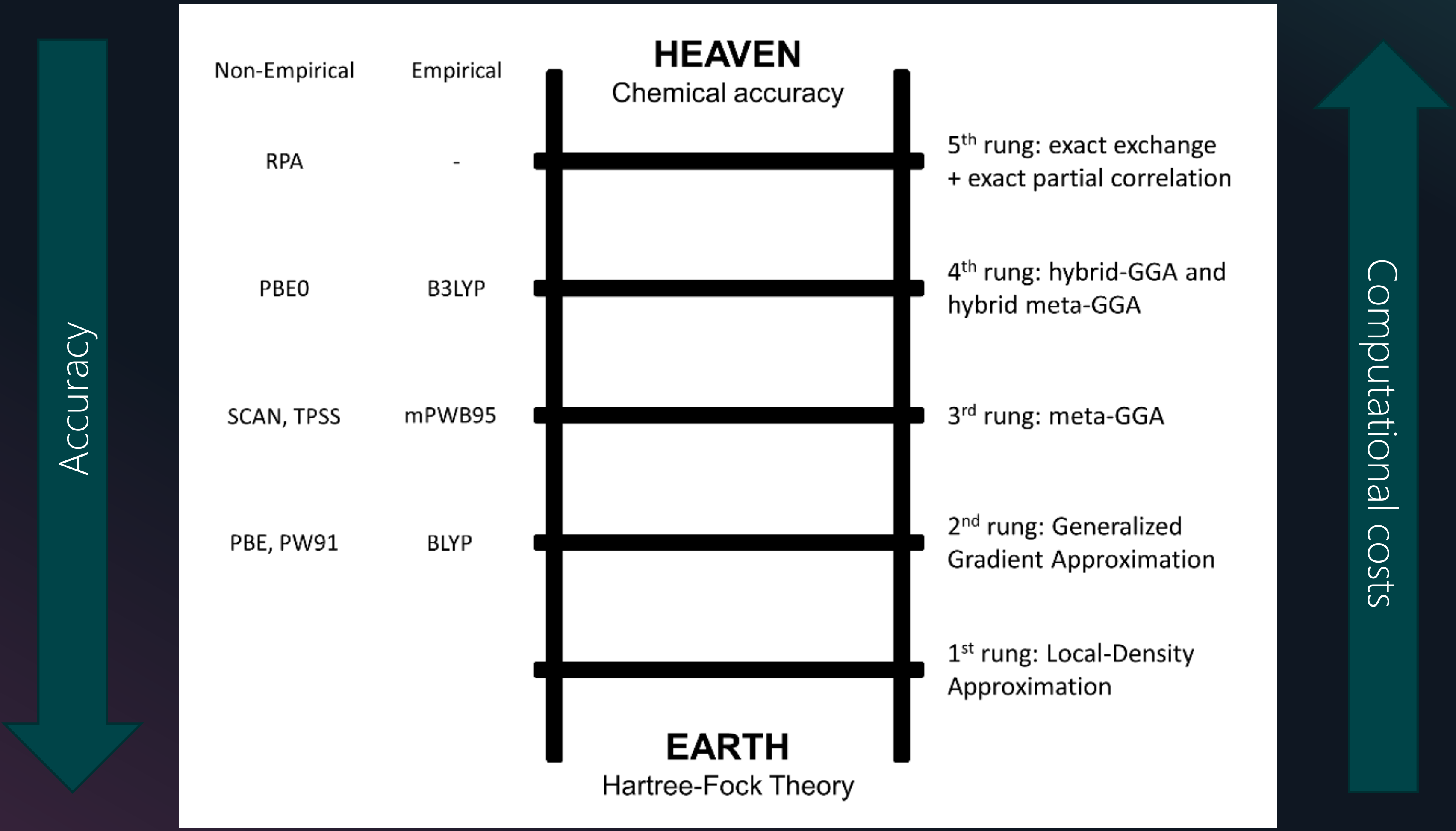
Total found: 652 basis sets

Plain Text

Format NWChem

https://www.basissetexchange.org/

DFT functionals



Non-Empirical	Empirical	
RPA	-	5th rung: exact exchange + exact partial correlation
PBE0	B3LYP	4th rung: hybrid-GGA and hybrid meta-GGA
SCAN, TPSS	mPWB95	3rd rung: meta-GGA
PBE, PW91	BLYP	2nd rung: Generalized Gradient Approximation
		1st rung: Local-Density Approximation

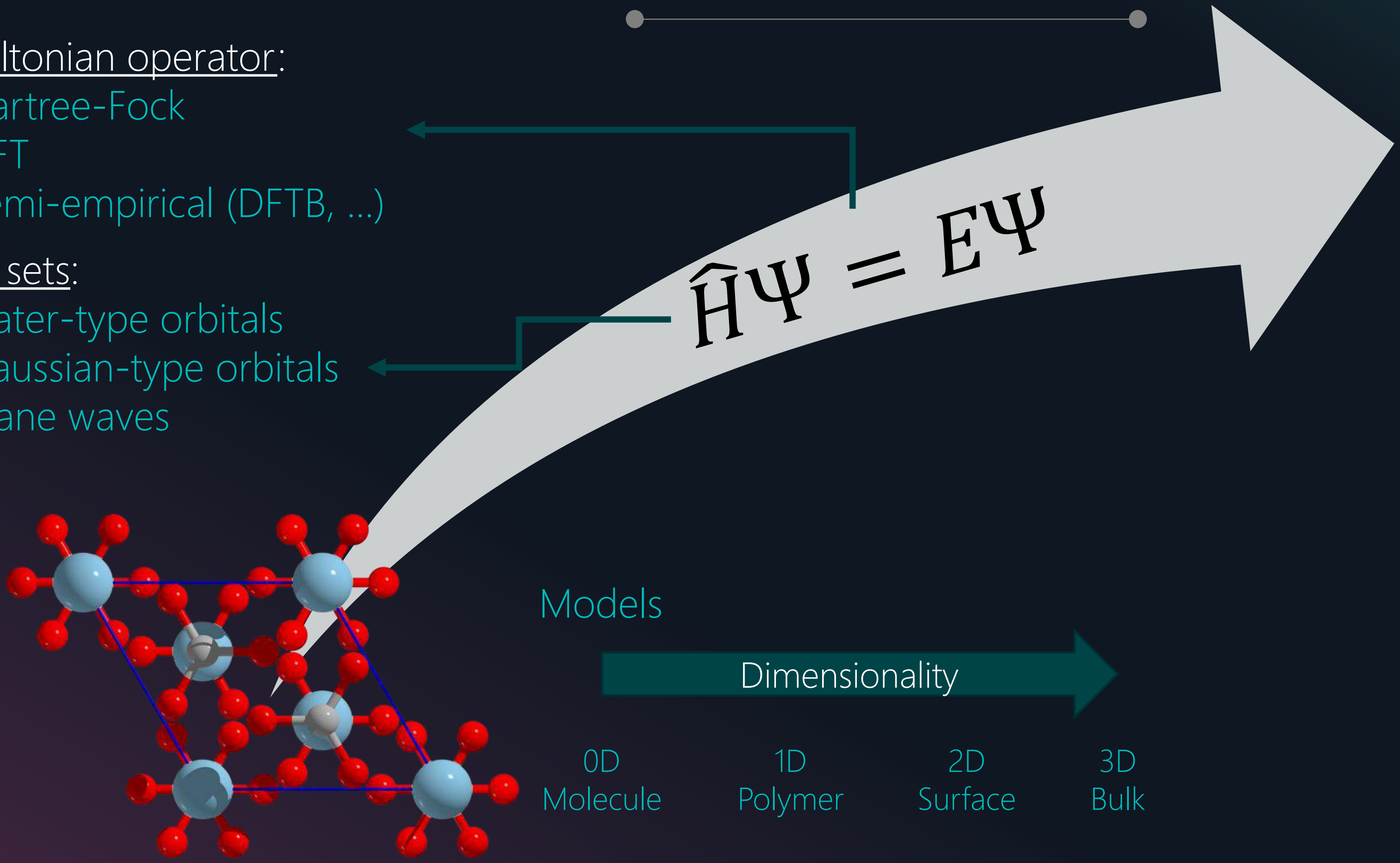
Mixing all together

Hamiltonian operator:

- Hartree-Fock
- DFT
- Semi-empirical (DFTB, …)

Basis sets:

- Slater-type orbitals
- Gaussian-type orbitals
- Plane waves
- …



$$\hat{H}\Psi = E\Psi$$

Models

Dimensionality

0D
Molecule

1D
Polymer

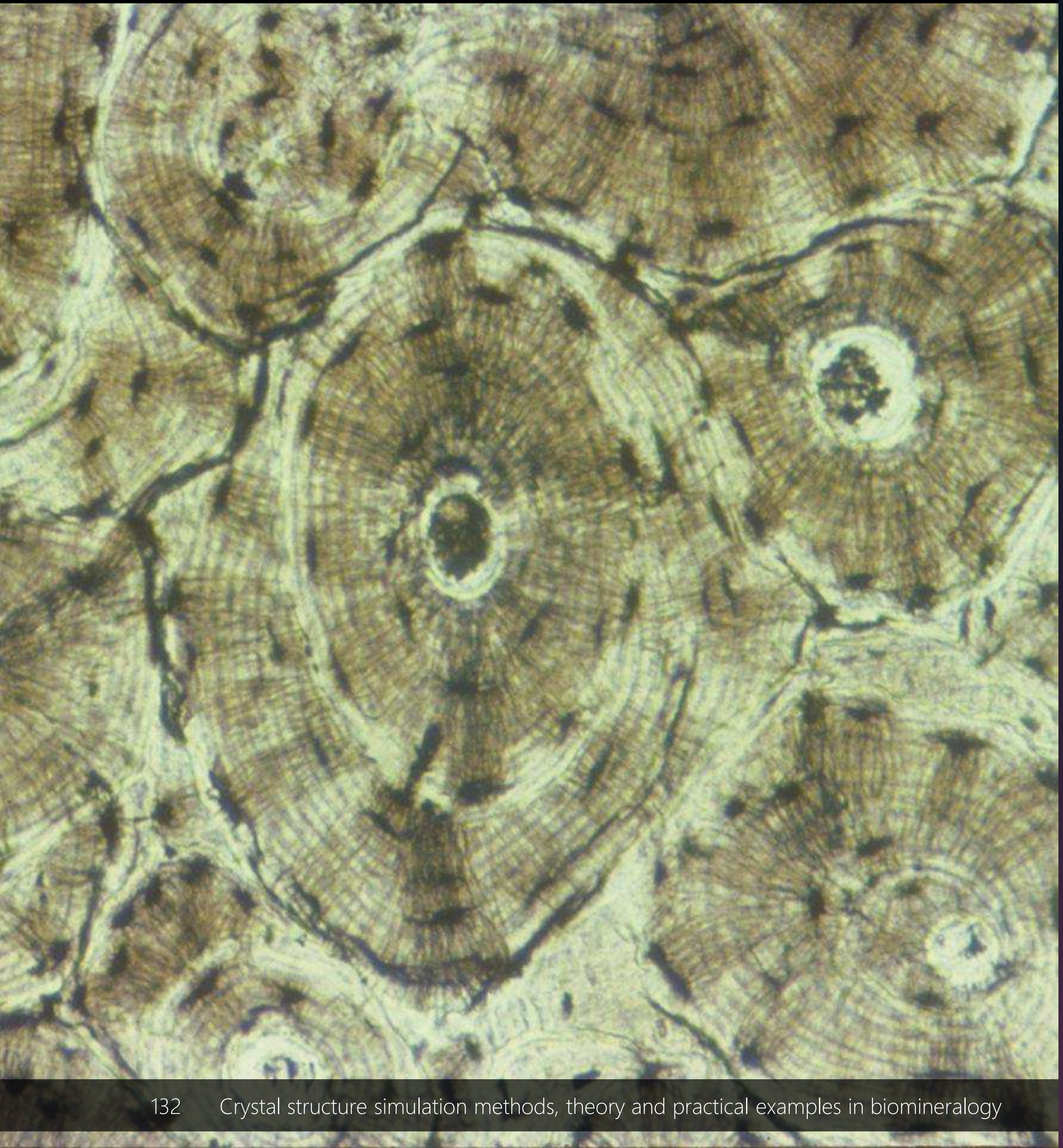
2D
Surface

3D
Bulk

Results:

- Crystal-chemistry
- Electronic properties
- Optical properties
- Thermodynamics
- Elastic properties
- Surface properties
- …

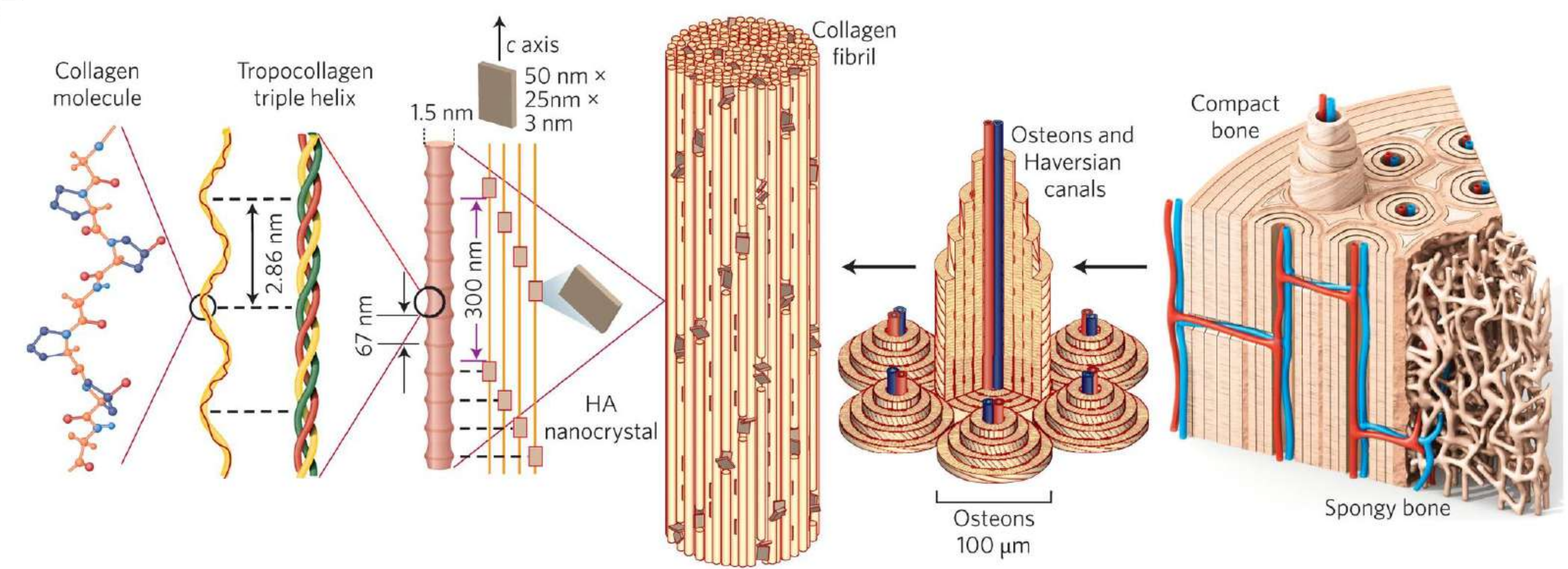
Bone tissue. Compact bone viewed under an optical microscope.



Crystallography & biomineralogy

Some examples from Nature

Bone tissue hierarchy

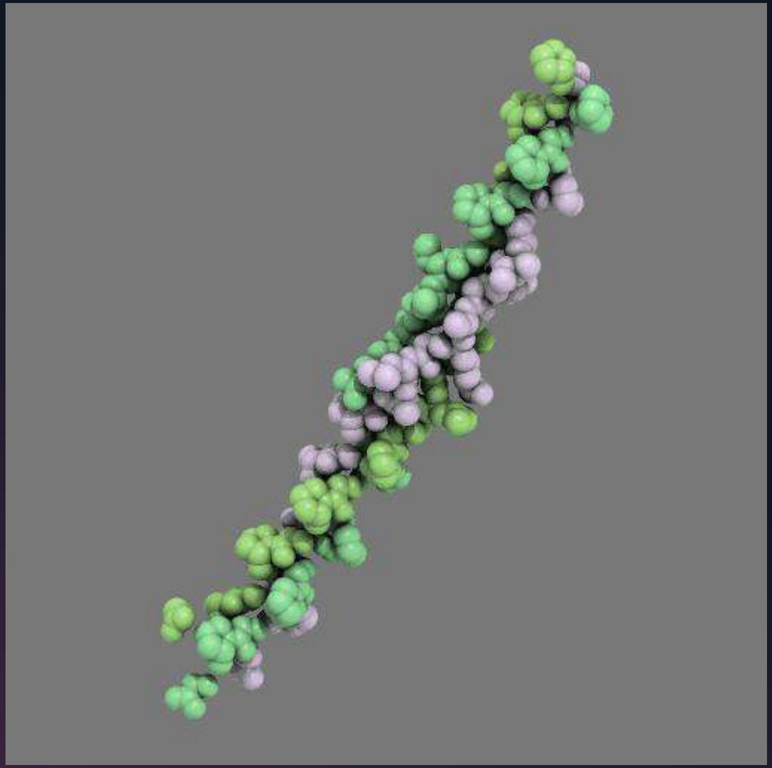


In bone, macroscale arrangements involve both compact/cortical bone at the surface and spongy/trabecular bone in the interior. Compact bone is composed of osteons and Haversian canals, which surround blood vessels. Osteons have a lamellar structure, with individual lamella consisting of fibres arranged in geometrical patterns. The fibres comprise several mineralized collagen fibrils, composed of collagen protein molecules (tropocollagen) formed from three chains of amino acids and nanocrystals of hydroxyapatite (HA), and linked by an organic phase to form fibril arrays.

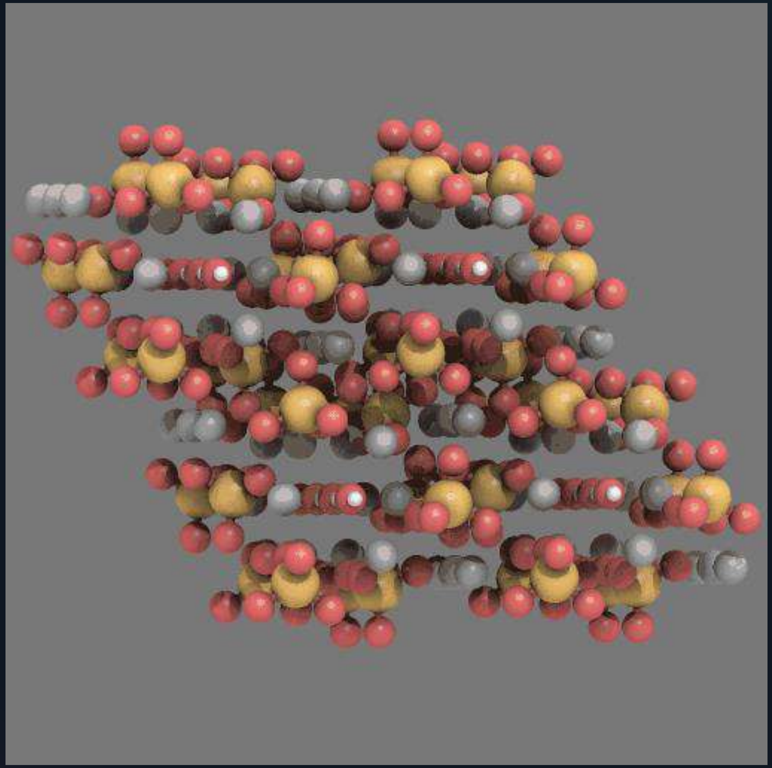
Source: Wegst, U. G., Bai, H., Saiz, E., Tomsia, A. P., & Ritchie, R. O. (2015). Bioinspired structural materials. Nature materials, 14(1), 23–36. https://doi.org/10.1038/nmat4089

Bone tissue building blocks

Collagen triple helix

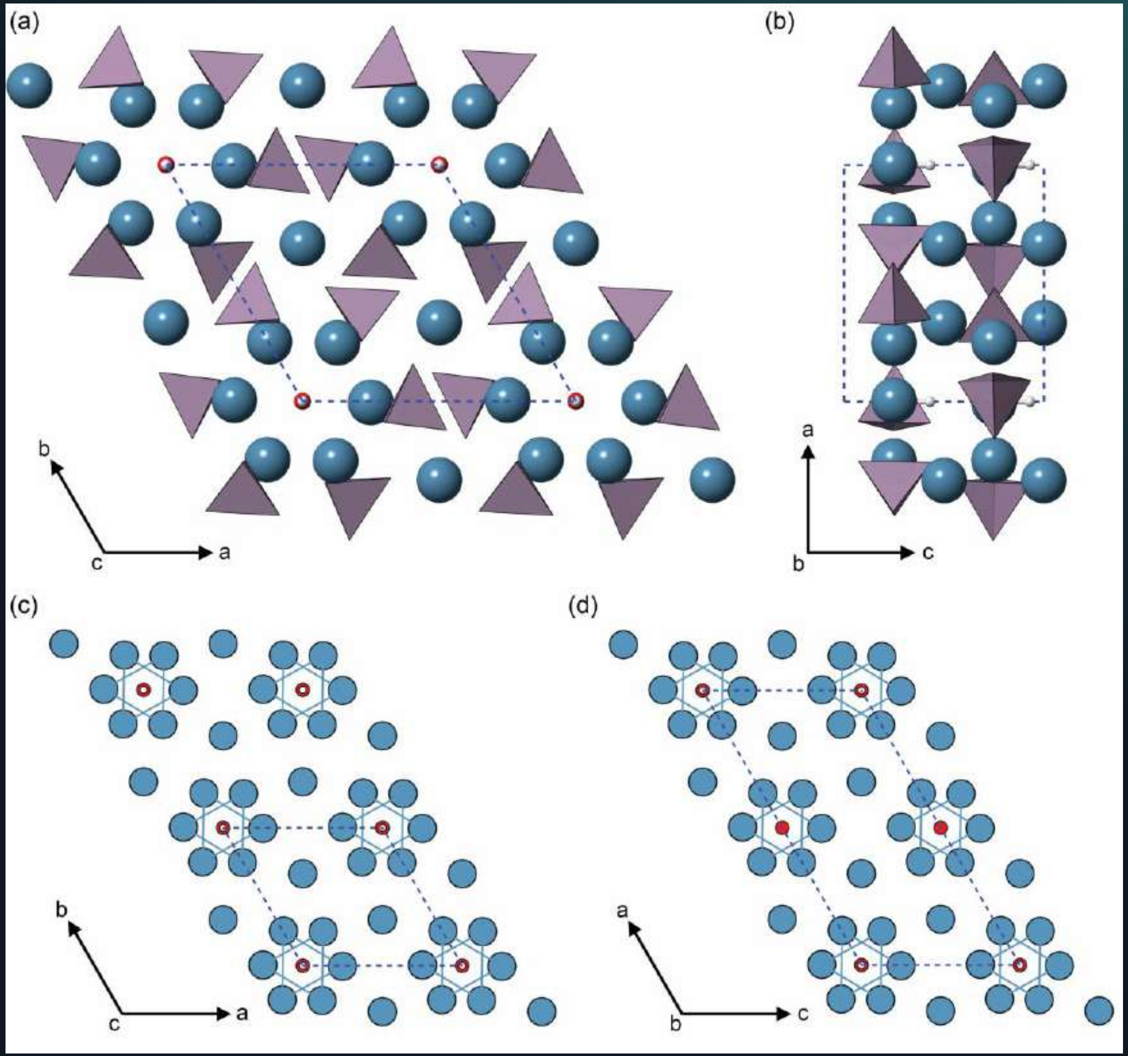


Biological apatite nanocrystals



Hydroxylapatite

- Other names: HA, OHAp
- Unit cell formula: $Ca_{10}(PO_4)_6(OH)_2$ ($Z = 2$)
- Crystal system: Hexagonal
- Space group: $P6_3/m$



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Hydroxylapatite CIF card

```
Hughes J M, Cameron M, Crowley K D
American Mineralogist 74 (1989) 870-876
Structural variations in natural F, OH, and Cl apatites
Locality: Holly Springs, Georgia, USA
_database_code_amcsd 0001257
9.4166 9.4166 6.8745 90 90 120 P6_3/m
atom       x      y      z occ Biso B(1,1) B(2,2) B(3,3) B(1,2) B(1,3) B(2,3)
Ca1      2/3    1/3 .00144          .00408 .00408 0.0033 .00204      0      0
Ca2  -.00657 .24706    .25          .00308 .00353 .00417 .00156      0      0
P     .36860 .39866    .25          .00223 .00250 0.0034 .00127      0      0
O1     .4850  .3289    .25          0.0036 0.0044 0.0059  .0027      0      0
O2     .4649  .5871    .25          0.0035 0.0031 0.0105  .0016      0      0
O3     .2580  .3435  .0703          0.0050 0.0096 0.0070 .00505 -.0025 -.0041
O(H)       0      0  .1979  .5      0.0030 0.0030  0.012  .0015      0      0
H          0      0    .04  .5  3.3
```

Hydroxylapatite

- Other names: HA, OHAp
- Unit cell formula: $Ca_{10}(PO_4)_6(OH)_2$ (Z = 2)
- Crystal system: Hexagonal
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Fractional occupancy → probability to find an atom at a specific site

Modelling can not handle partial occupancies!

Hydroxylapatite CIF card

```
Hughes J M, Cameron M, Crowley K D
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atom       x      y      z occ Biso B(1,1) B(2,2) B(3,3) B(1,2) B(1,3) B(2,3)
Ca1      2/3    1/3 .00144          .00408 .00408 0.0033 .00204      0      0
Ca2  -.00657 .24706    .25          .00308 .00353 .00417 .00156      0      0
P     .36860 .39866    .25          .00223 .00250 0.0034 .00127      0      0
O1     .4850  .3289    .25          0.0036 0.0044 0.0059  .0027      0      0
O2     .4649  .5871    .25          0.0035 0.0031 0.0105  .0016      0      0
O3     .2580  .3435  .0703          0.0050 0.0096 0.0070 .00505 -.0025 -.0041
O(H)       0      0  .1979  .5      0.0030 0.0030  0.012  .0015      0      0
H          0      0    .04  .5  3.3
```

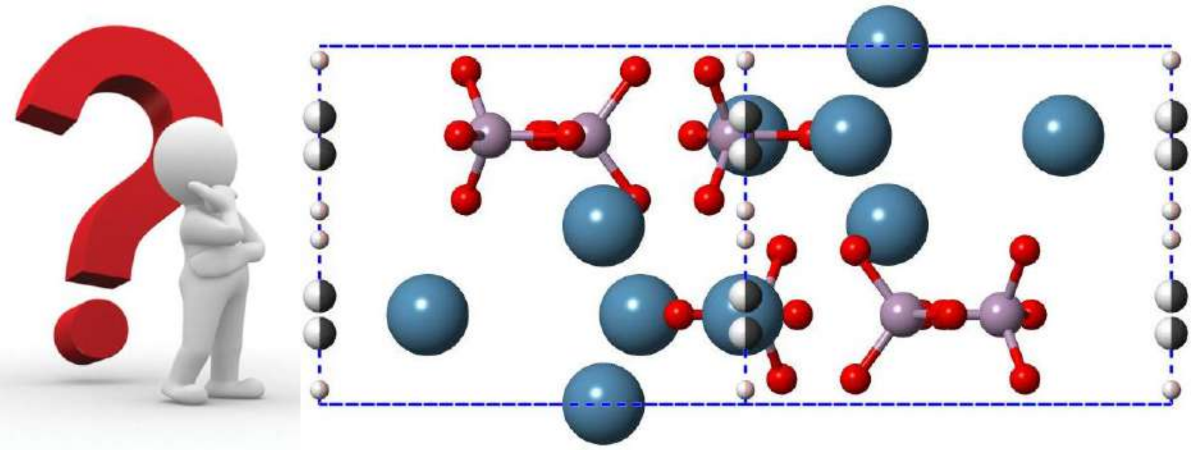

Hughes, J. M., Cameron, M. & Crowley, K. D. (1989). *American Mineralogist* **74**, 870-876.

Hydroxylapatite

- Other names: HA, OHAp
- Unit cell formula: $Ca_{10}(PO_4)_6(OH)_2$ ($Z = 2$)
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- Space group: $P6_3/m$

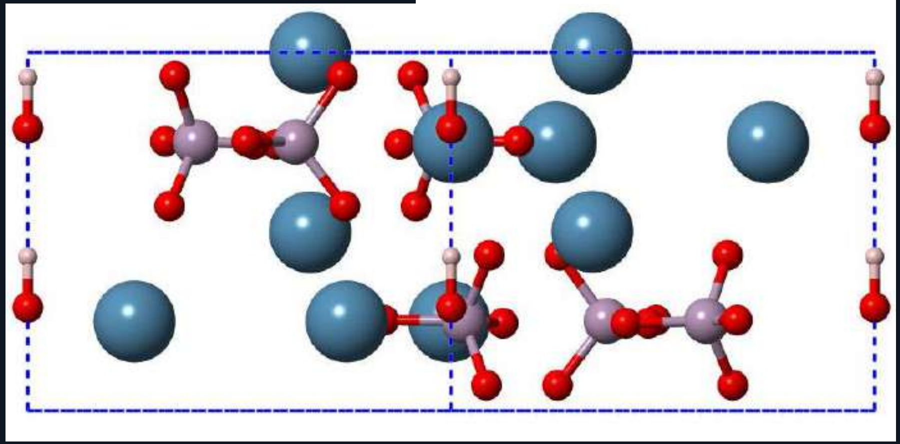
Fractional occupancy → probability to find an atom at a specific site

Modelling can not handle partial occupancies!

Lower the symmetry: $P6_3/m \rightarrow P6_3/m$

Hydroxylapatite CIF card

```
data_ohap_DFT_B3LYP
[...omissis...]
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
   Ca1      Ca 1.0000      0.3333    0.6667    0.9999
   Ca2      Ca 1.0000      0.6667    0.3333    0.9986
   Ca3      Ca 1.0000      0.2471    0.9951    0.2494
     P      P  1.0000      0.3966    0.3667    0.2507
    O1      O  1.0000      0.3245    0.4833    0.2527
    O2      O  1.0000      0.5880    0.4656    0.2444
    O3      O  1.0000      0.3347    0.2513    0.0716
    O4      O  1.0000      0.6528    0.7432    0.9341
  O(H)      O  1.0000      0.0000    0.0000    0.7884
     H      H  1.0000      0.0000    0.0000    0.9296
```



Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 410-416.

Hydroxylapatite

Simulations of the crystal structures of the mineral

- DFT
- All-electron GTO basis set
- Hybrid functional B3LYP

All-electron basis set

Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 410-416.

Pseudopotential basis set

Corno, M., Busco, C., Civalleri, B. & Ugliengo, P. (2006). *Physical Chemistry Chemical Physics* **8**, 2464-2472.

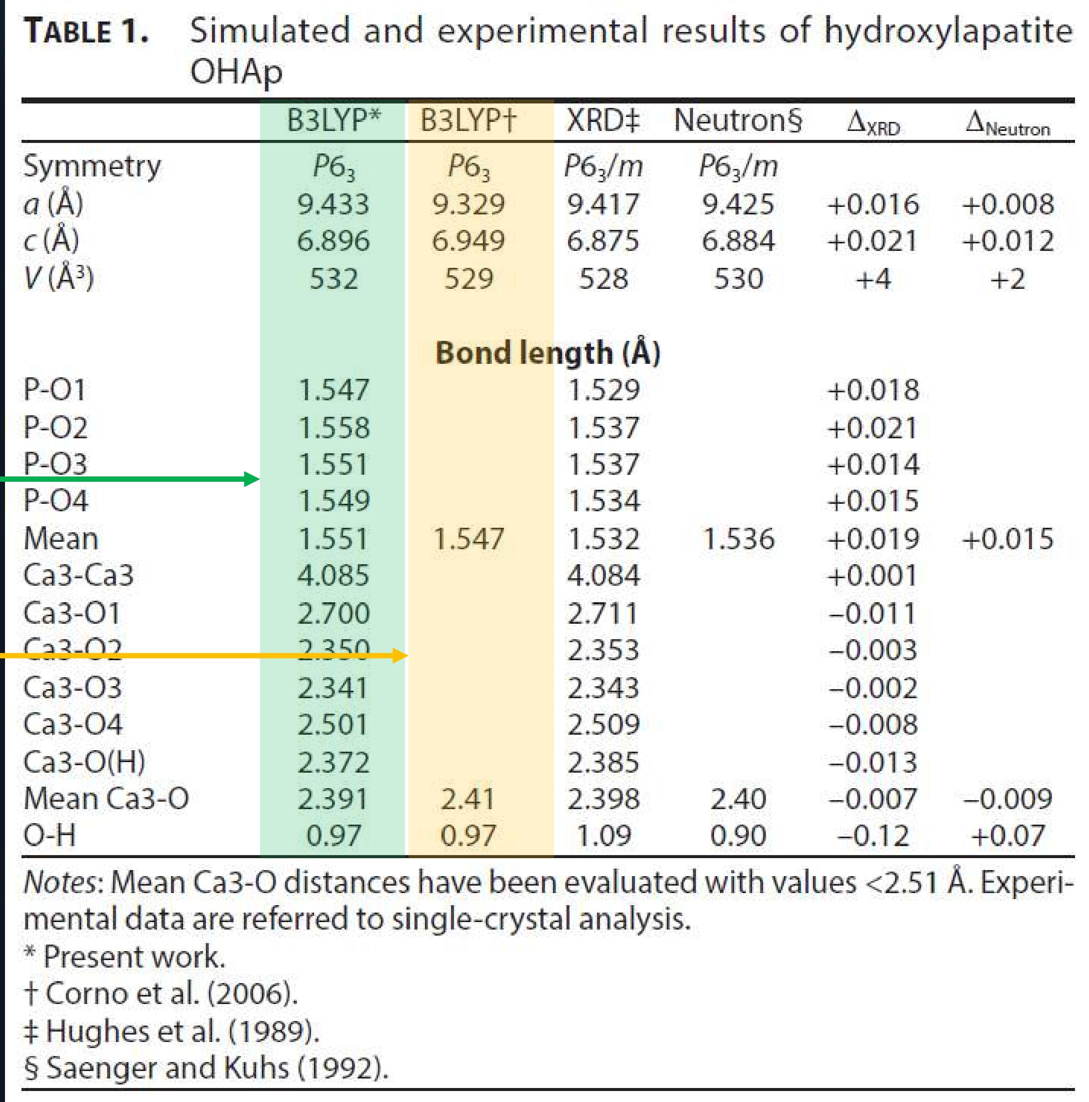


TABLE 1. Simulated and experimental results of hydroxylapatite OHAp

	B3LYP*	B3LYP†	XRD‡	Neutron§	Δ_{XRD}	$\Delta_{Neutron}$
Symmetry	$P6_3$	$P6_3$	$P6_3/m$	$P6_3/m$		
a (Å)	9.433	9.329	9.417	9.425	+0.016	+0.008
c (Å)	6.896	6.949	6.875	6.884	+0.021	+0.012
V (Å^3)	532	529	528	530	+4	+2
			Bond length (Å)			
P-O1	1.547		1.529		+0.018	
P-O2	1.558		1.537		+0.021	
P-O3	1.551		1.537		+0.014	
P-O4	1.549		1.534		+0.015	
Mean	1.551	1.547	1.532	1.536	+0.019	+0.015
Ca3-Ca3	4.085		4.084		+0.001	
Ca3-O1	2.700		2.711		−0.011	
Ca3-O2	2.350		2.353		−0.003	
Ca3-O3	2.341		2.343		−0.002	
Ca3-O4	2.501		2.509		−0.008	
Ca3-O(H)	2.372		2.385		−0.013	
Mean Ca3-O	2.391	2.41	2.398	2.40	−0.007	−0.009
O-H	0.97	0.97	1.09	0.90	−0.12	+0.07

Notes: Mean Ca3-O distances have been evaluated with values <2.51 Å. Experimental data are referred to single-crystal analysis.

* Present work.

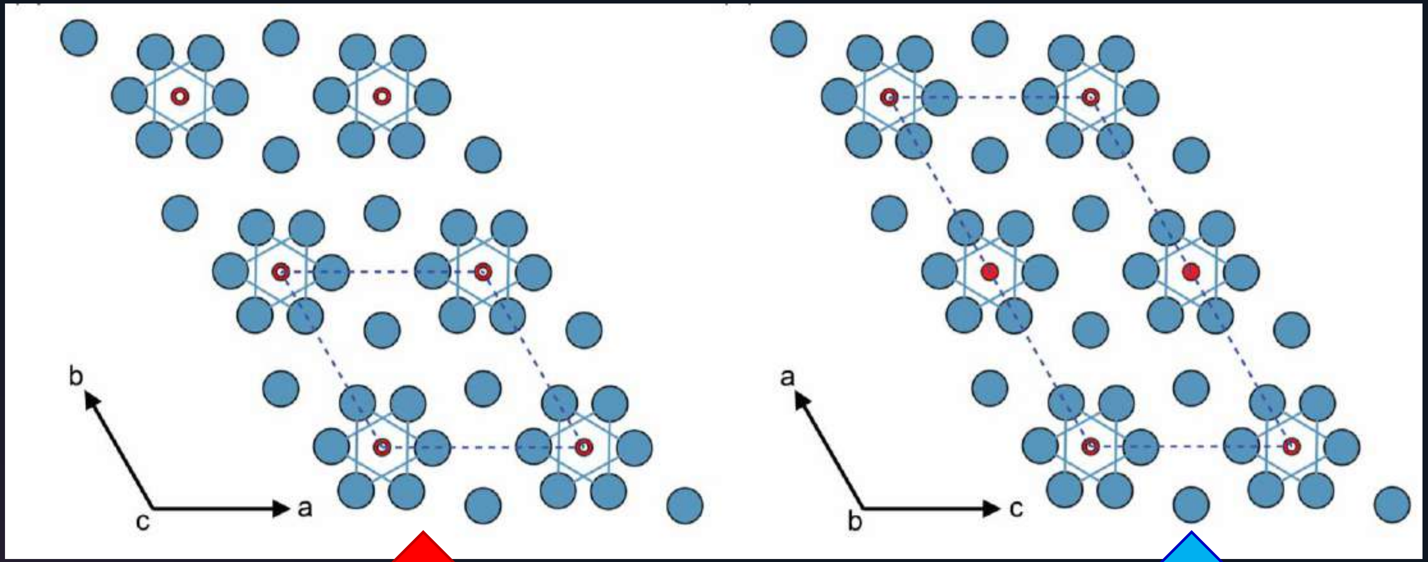
† Corno et al. (2006).

‡ Hughes et al. (1989).

§ Saenger and Kuhs (1992).

Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 410-416.

Stability of hydroxylapatite



Hexagonal
$P6_3/m$

Monoclinic
$P2_1$

Hexagonal ca. 200 °C

Monoclinic RT

Suda H., Yashima M., Kakihana M., Yoshimura M., Journal of Physical Chemistry, *99* (17), 6752-6754, 1995.

How can we observe hexagonal OHAp in bone tissues?

Stability of hydroxylapatite

Entropy stabilization

- Calcium deficiency
- Cationic substitutions
- Anionic substitutions
- …

$$(\mathrm{Ca}, X)_{10}(\mathrm{PO}_4, Y)_6(\mathrm{OH}, Z)_2$$

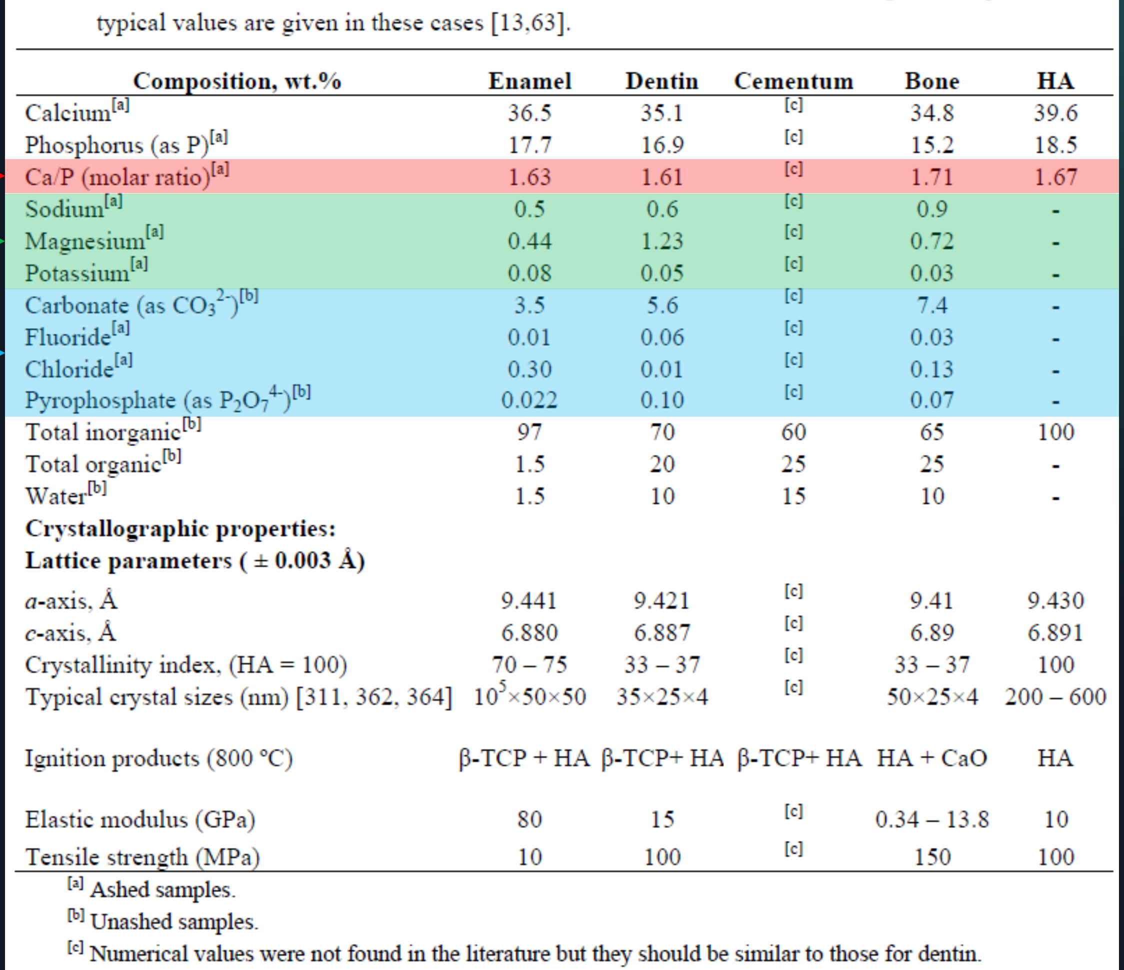


Table 1. Comparative composition and structural parameters of inorganic phases of adult human calcified tissues. Due to the considerable variation found in biological samples, typical values are given in these cases [13,63].

Composition, wt.%	**Enamel**	**Dentin**	**Cementum**	**Bone**	**HA**
Calcium[a]	36.5	35.1	[c]	34.8	39.6
Phosphorus (as P)[a]	17.7	16.9	[c]	15.2	18.5
Ca/P (molar ratio)[a]	1.63	1.61	[c]	1.71	1.67
Sodium[a]	0.5	0.6	[c]	0.9	-
Magnesium[a]	0.44	1.23	[c]	0.72	-
Potassium[a]	0.08	0.05	[c]	0.03	-
Carbonate (as CO_3^{2-})[b]	3.5	5.6	[c]	7.4	-
Fluoride[a]	0.01	0.06	[c]	0.03	-
Chloride[a]	0.30	0.01	[c]	0.13	-
Pyrophosphate (as $P_2O_7^{4-}$)[b]	0.022	0.10	[c]	0.07	-
Total inorganic[b]	97	70	60	65	100
Total organic[b]	1.5	20	25	25	-
Water[b]	1.5	10	15	10	-
Crystallographic properties:					
Lattice parameters (± 0.003 Å)					
a-axis, Å	9.441	9.421	[c]	9.41	9.430
c-axis, Å	6.880	6.887	[c]	6.89	6.891
Crystallinity index, (HA = 100)	70 – 75	33 – 37	[c]	33 – 37	100
Typical crystal sizes (nm) [311, 362, 364]	$10^5 \times 50 \times 50$	$35 \times 25 \times 4$	[c]	$50 \times 25 \times 4$	200 – 600
Ignition products (800 °C)	β-TCP + HA	β-TCP+ HA	β-TCP+ HA	HA + CaO	HA
Elastic modulus (GPa)	80	15	[c]	0.34 – 13.8	10
Tensile strength (MPa)	10	100	[c]	150	100

[a] Ashed samples.

[b] Unashed samples.

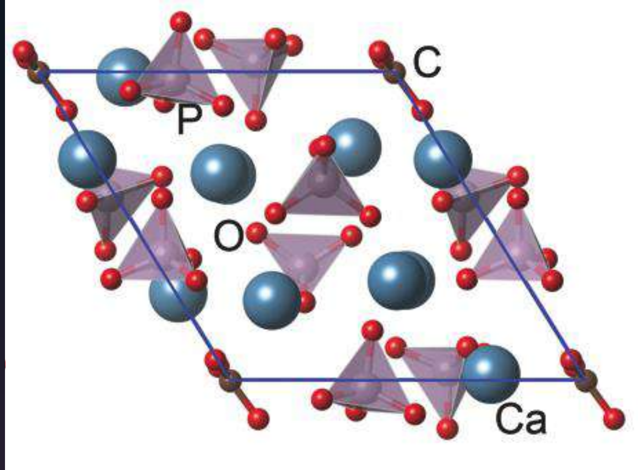
[c] Numerical values were not found in the literature but they should be similar to those for dentin.

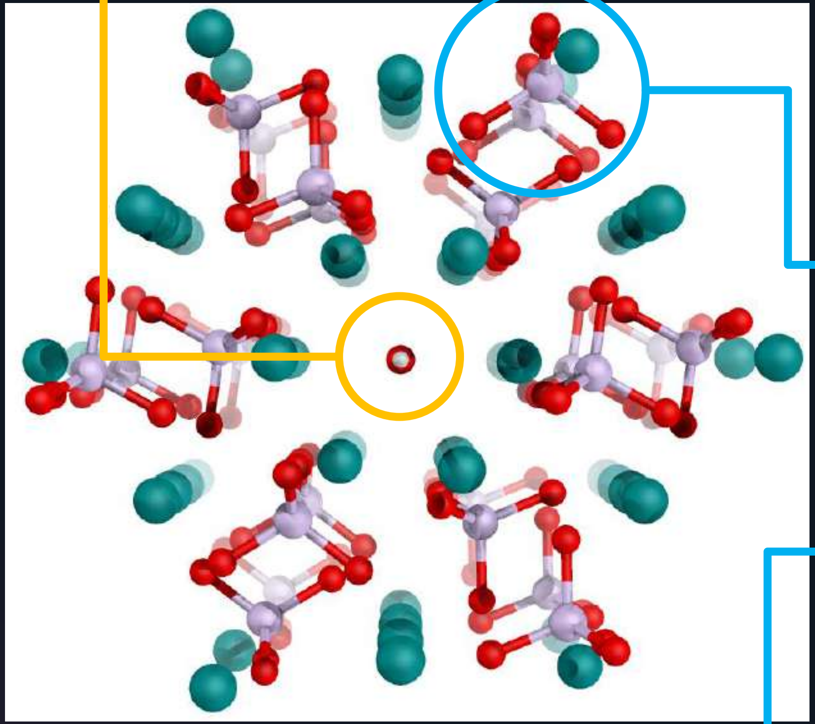
Dorozhkin, S. V., Calcium Orthophosphates in Nature, Biology and Medicine. *Materials* 2009, *2*, 399-498.

Carbonate ion substitutions
Carbonated hydroxylapatite (COHAp)

Type-A substitution

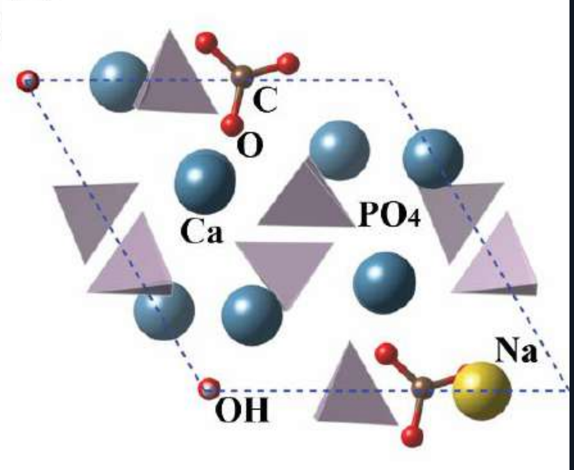
CO_3^{2-} / $2OH^-$





Type B defect

$CO_3^{2-} + Na^+$ / $PO_4^{3-} + Ca^{2+}$



Type AB defect

$2CO_3^{2-}$ / $PO_4^{3-} + OH^-$

Type-A COHAp

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + CO_3^{2-} \rightarrow [Ca_{10}(PO_4)_6CO_3OH]^- + OH^-}$$

Different ways to restore the charge neutrality

$$\mathrm{[Ca_{10}(PO_4)_6CO_3OH]^- \xrightarrow{-OH^-} Ca_{10}(PO_4)_6CO_3}$$

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + HCO_3^- \rightarrow Ca_{10}HPO_4(PO_4)_5CO_3OH + OH^-}$$

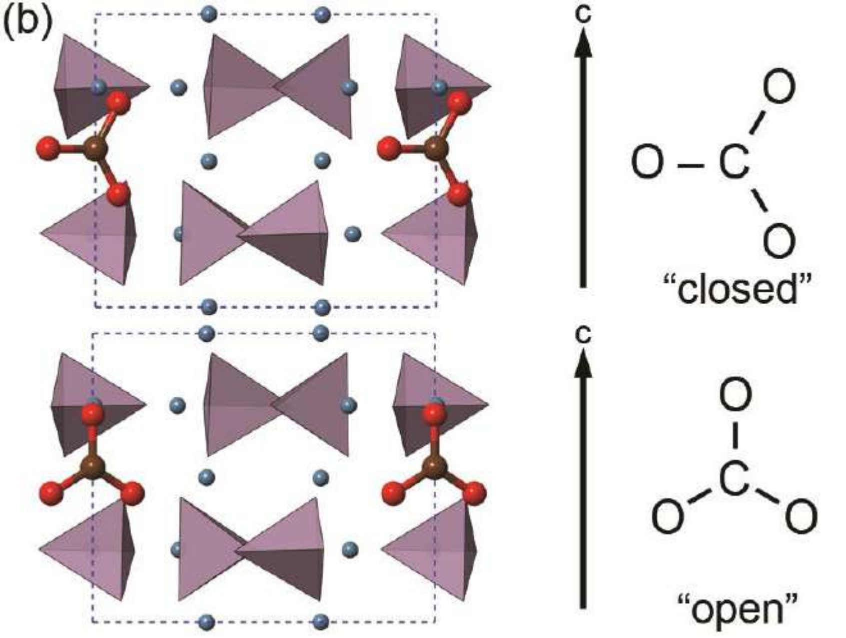
The overall reaction chosen in our simulations is

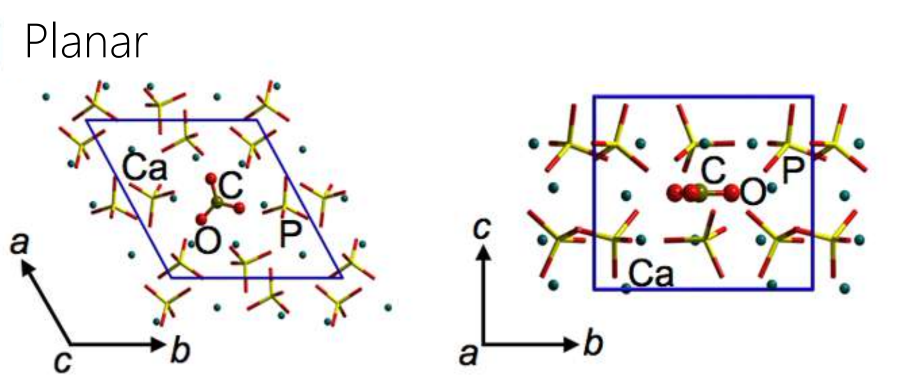
$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + CO_3^{2-} \rightarrow Ca_{10}(PO_4)_6CO_3 + 2OH^-}$$

Type-A COHAp

Questions and uncertainties:

- Orientation of the carbonate group within the unit cell?
  - «closed» configuration (A1)
  - «open» configuration (A2)
  - «planar» configuration
- At the experimental level (XRD), space group $P\bar{3}$. How could it be?



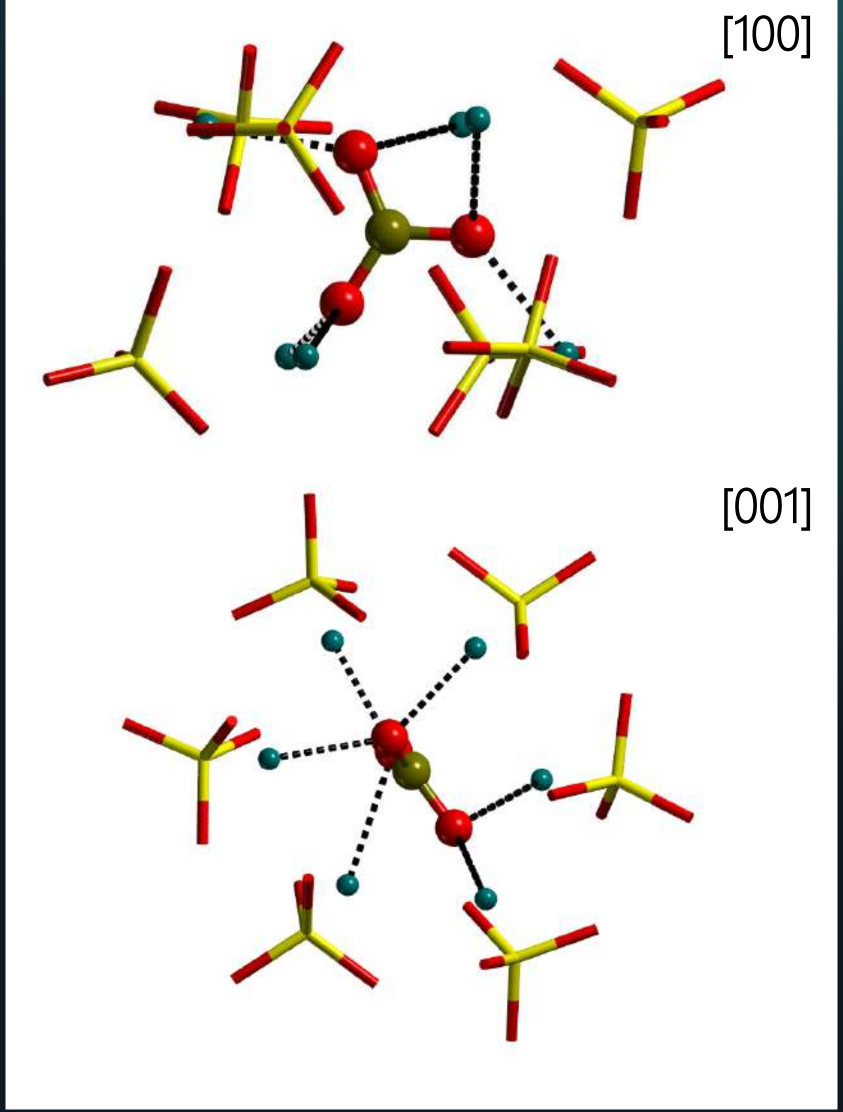


Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 410-416.
Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 752-759.

Type-A COHAp

CO_3^{2-} configuration:

- «closed» configuration (space group *P*1) is the most stable one;
- «open» configuration (space group *P*1) spontaneously switch to the «closed» one;
- «planar» configuration (space group *P*3) is stable upon constrained geometry optimization, but with very high energy (+166 kJ/mol) with respect to the «closed» configuration. In addition, it is phononically unstable (negative vibrational frequencies).



Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 410-416.
Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 752-759.

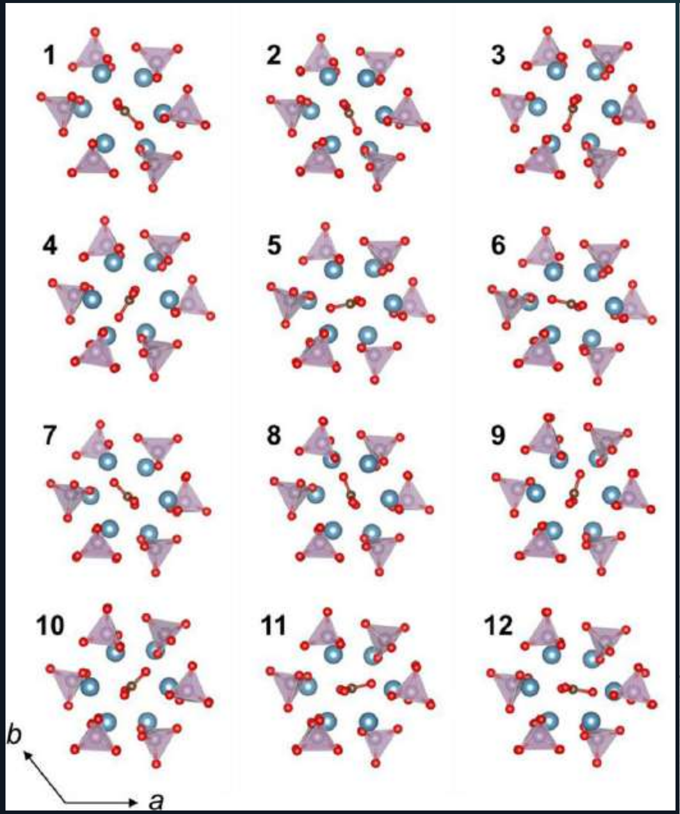
Type-A COHAp

Explanation of the experimental space group $P\bar{3}$:

- Very low energy difference between configurations where there carbonate ion is rotated within the hexagonal calcium channel;
- Configurations with odd numbers, where the C – O bond perpendicular to the c-axis points between two $\mathrm{PO_4^{3-}}$ groups, have the lowest energy difference (0.62 kJ/mol);
- Configurations with odd numbers, where the C – O bond perpendicular to the c-axis points towards a single $\mathrm{PO_4^{3-}}$ group, have the highest energy difference (2.85 kJ/mol);
- *Ab initio* molecular dynamics (AIMS) showed that, at 300 K, the carbonate ion is almost free to rotate within the channel.

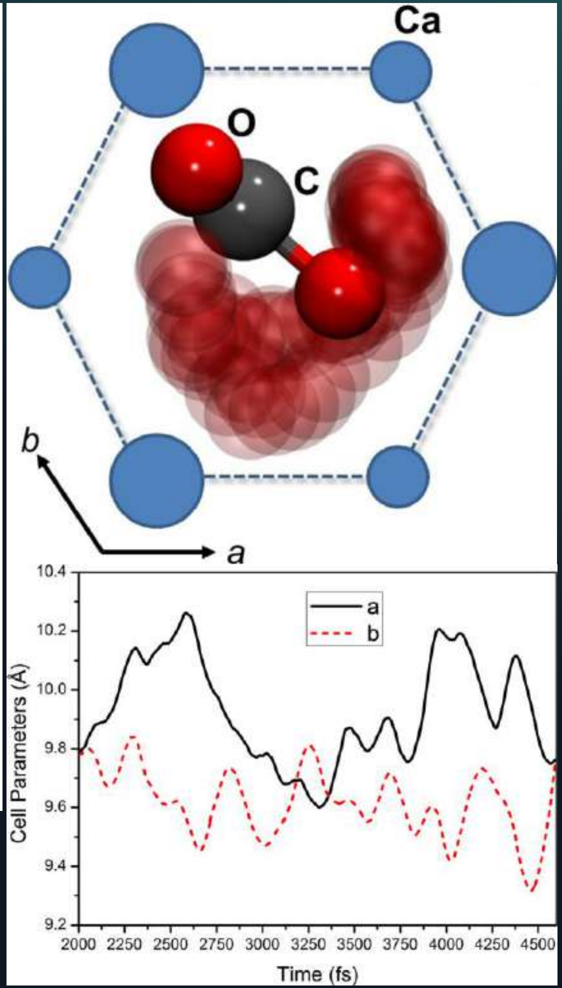
The experimental structure is a geometrical mean of the most stable configurations

«Static» simulations



Max Δ*E* = 2.85 kJ/mol

«Dynamic» simulations



Peccati, F., Corno, M., Delle Piane, M., Ulian, G., Ugliengo, P. & Valdrè, G. (2014). *Journal of Physical Chemistry C* **118**, 1364-1369.

Type-B COHAp

$$Ca_{10}(PO_4)_6(OH)_2 + CO_3^{2-} \rightarrow [Ca_{10}(PO_4)_5CO_3(OH)_2]^+ + PO_4^{3-}$$

Different ways to restore the charge neutrality

$$[Ca_{10}(PO_4)_5CO_3(OH)_2]^+ \xrightarrow{-Ca^{2+}+Na^+} Ca_9Na(PO_4)_5CO_3(OH)_2$$

$$[Ca_{10}(PO_4)_5CO_3(OH)_2]^+ \xrightarrow{+OH^-} Ca_{10}(PO_4)_5CO_3(OH)_3$$

$$[Ca_{10}(PO_4)_5CO_3(OH)_2]^+ \xrightarrow{-Ca^{2+}+H^+} Ca_9H(PO_4)_5CO_3(OH)_2$$

The overall reaction chosen in our simulations is

$$Ca_{10}(PO_4)_6(OH)_2 + CO_3^{2-} + Na^+ \rightarrow Ca_9Na(PO_4)_5CO_3(OH)_2 + PO_4^{3-} + Ca^{2+}$$

Type-B COHAp

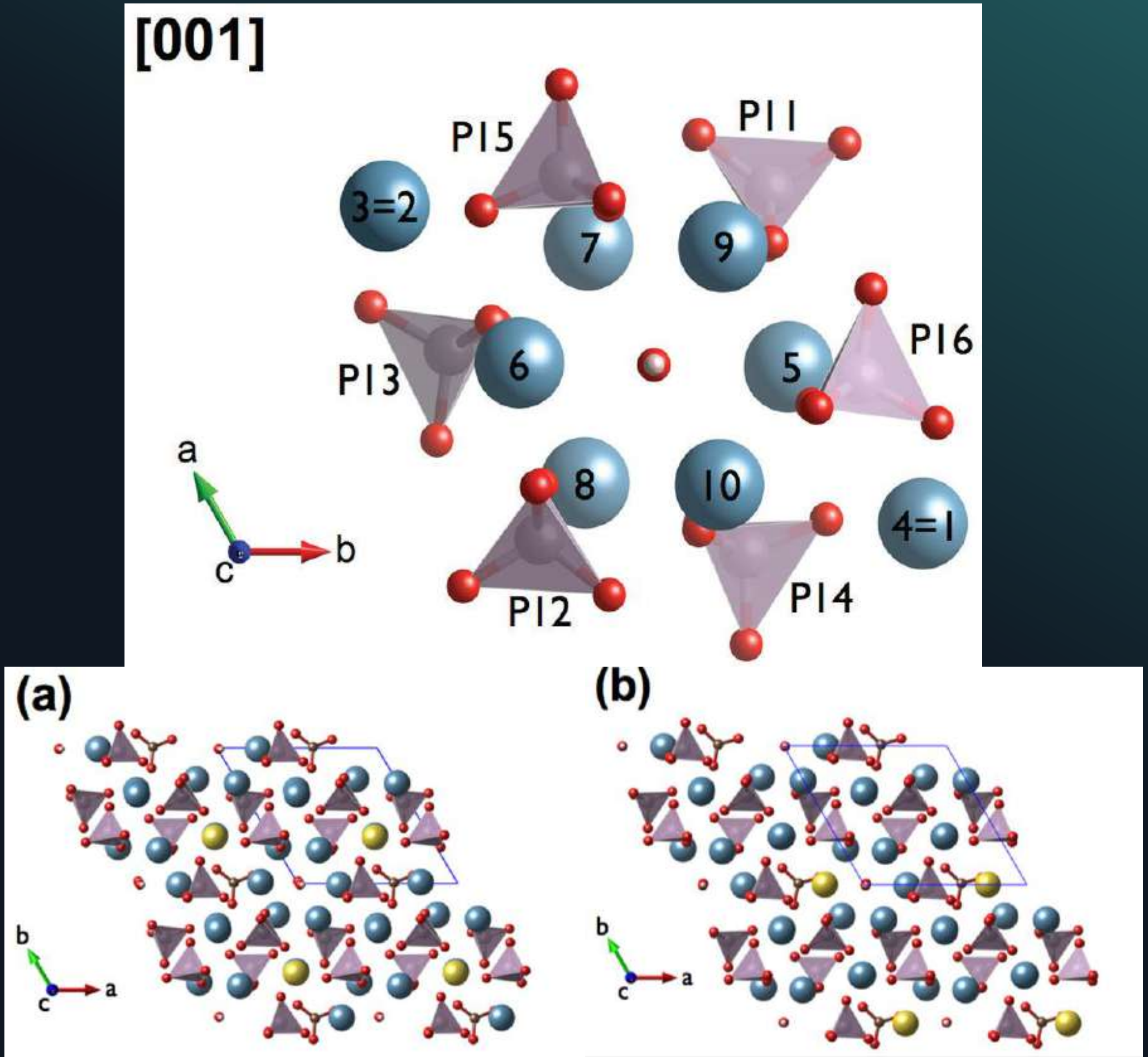
Where do we put the carbonate and sodium ions?

- 6 PO_4^{3-} sites that are symmetry-equivalent;
- 3 different Ca^{2+} sites (2 Ca1, 2 Ca2 and 6 Ca3).

In our approach:

- we substituted a single phosphate group (**site P13**) with the carbonate ion, then
- we made 10 different models, each one with a Na^+/Ca^{2+} substitution in a specific cationic site.

Each model belongs to the space group *P*1



Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2014). *American Mineralogist* **99**, 117-127.

Type-B COAHp

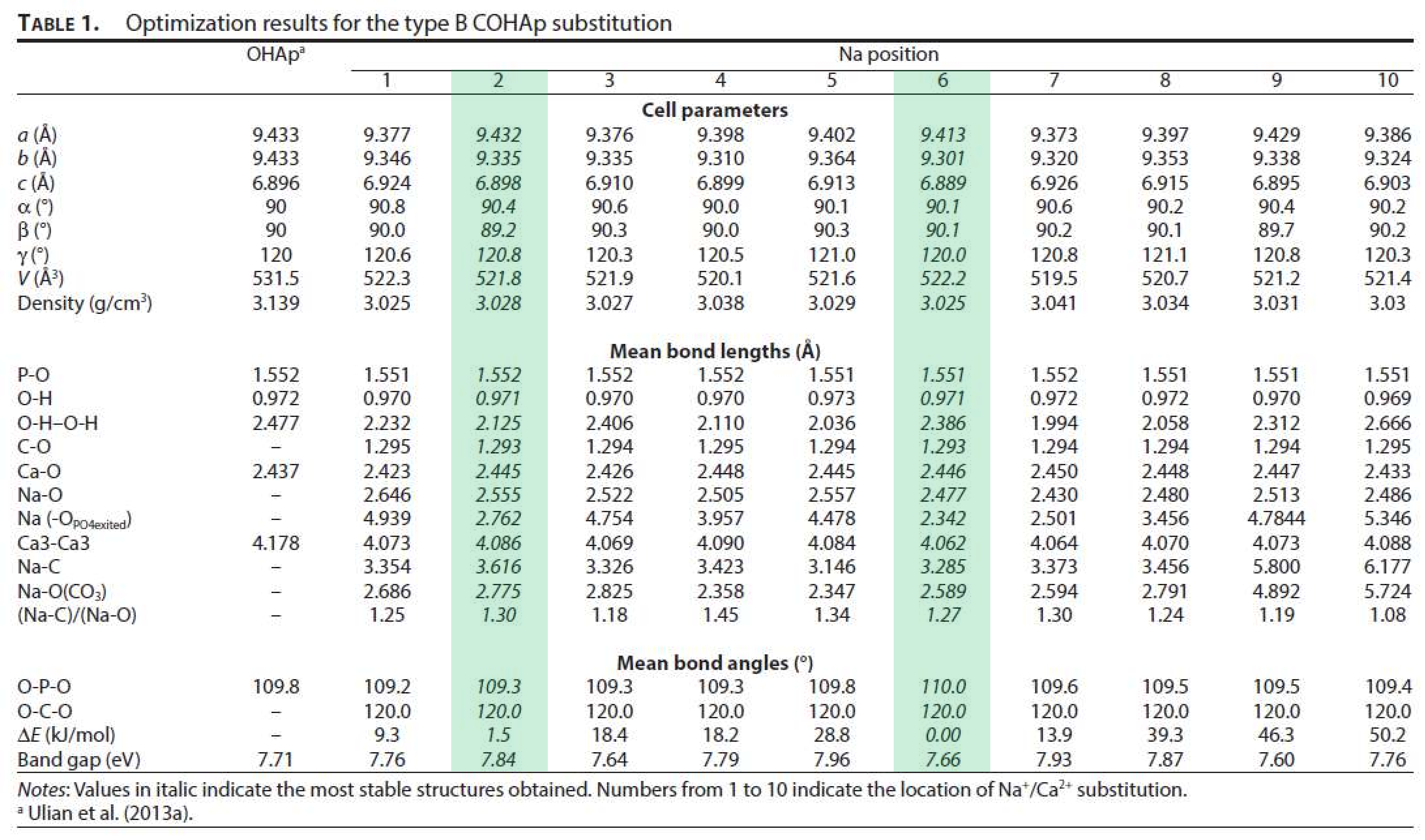


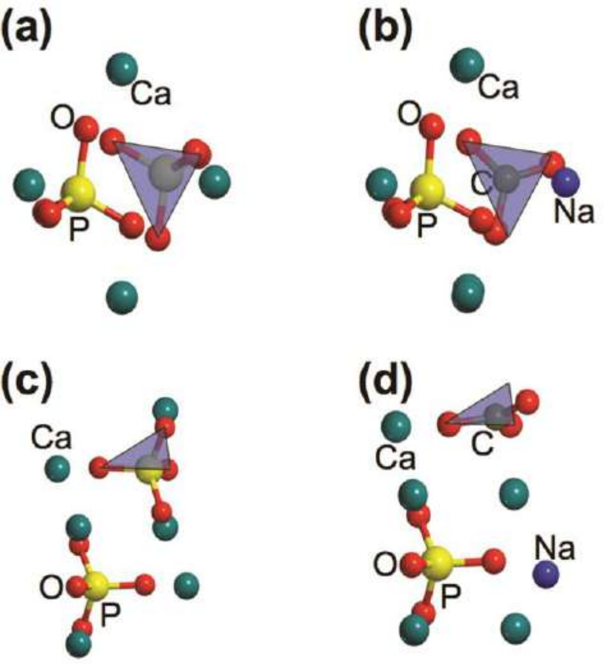
Table 1. Optimization results for the type B COHAp substitution

	OHAp[a]	Na position									
		1	2	3	4	5	6	7	8	9	10
Cell parameters											
a (Å)	9.433	9.377	*9.432*	9.376	9.398	9.402	*9.413*	9.373	9.397	9.429	9.386
b (Å)	9.433	9.346	*9.335*	9.335	9.310	9.364	*9.301*	9.320	9.353	9.338	9.324
c (Å)	6.896	6.924	*6.898*	6.910	6.899	6.913	*6.889*	6.926	6.915	6.895	6.903
α (°)	90	90.8	*90.4*	90.6	90.0	90.1	*90.1*	90.6	90.2	90.4	90.2
β (°)	90	90.0	*89.2*	90.3	90.0	90.3	*90.1*	90.2	90.1	89.7	90.2
γ (°)	120	120.6	*120.8*	120.3	120.5	121.0	*120.0*	120.8	121.1	120.8	120.3
V ($Å^3$)	531.5	522.3	*521.8*	521.9	520.1	521.6	*522.2*	519.5	520.7	521.2	521.4
Density (g/cm^3)	3.139	3.025	*3.028*	3.027	3.038	3.029	*3.025*	3.041	3.034	3.031	3.03
Mean bond lengths (Å)											
P-O	1.552	1.551	*1.552*	1.552	1.552	1.551	*1.551*	1.552	1.551	1.551	1.551
O-H	0.972	0.970	*0.971*	0.970	0.970	0.973	*0.971*	0.972	0.972	0.970	0.969
O-H–O-H	2.477	2.232	*2.125*	2.406	2.110	2.036	*2.386*	1.994	2.058	2.312	2.666
C-O	–	1.295	*1.293*	1.294	1.295	1.294	*1.293*	1.294	1.294	1.294	1.295
Ca-O	2.437	2.423	*2.445*	2.426	2.448	2.445	*2.446*	2.450	2.448	2.447	2.433
Na-O	–	2.646	*2.555*	2.522	2.505	2.557	*2.477*	2.430	2.480	2.513	2.486
Na ($-O_{PO4exited}$)	–	4.939	*2.762*	4.754	3.957	4.478	*2.342*	2.501	3.456	4.7844	5.346
Ca3-Ca3	4.178	4.073	*4.086*	4.069	4.090	4.084	*4.062*	4.064	4.070	4.073	4.088
Na-C	–	3.354	*3.616*	3.326	3.423	3.146	*3.285*	3.373	3.456	5.800	6.177
Na-O(CO_3)	–	2.686	*2.775*	2.825	2.358	2.347	*2.589*	2.594	2.791	4.892	5.724
(Na-C)/(Na-O)	–	1.25	*1.30*	1.18	1.45	1.34	*1.27*	1.30	1.24	1.19	1.08
Mean bond angles (°)											
O-P-O	109.8	109.2	*109.3*	109.3	109.3	109.8	*110.0*	109.6	109.5	109.5	109.4
O-C-O	–	120.0	*120.0*	120.0	120.0	120.0	*120.0*	120.0	120.0	120.0	120.0
Δ*E* (kJ/mol)	–	9.3	*1.5*	18.4	18.2	28.8	*0.00*	13.9	39.3	46.3	50.2
Band gap (eV)	7.71	7.76	*7.84*	7.64	7.79	7.96	*7.66*	7.93	7.87	7.60	7.76

Notes: Values in italic indicate the most stable structures obtained. Numbers from 1 to 10 indicate the location of Na^+/Ca^{2+} substitution.

[a] Ulian et al. (2013a).

Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2014). *American Mineralogist* **99**, 117-127.



- Rotation of the carbonate group
- Stability when Na^+ is near the vacant oxygen atom

Type-AB COAHp

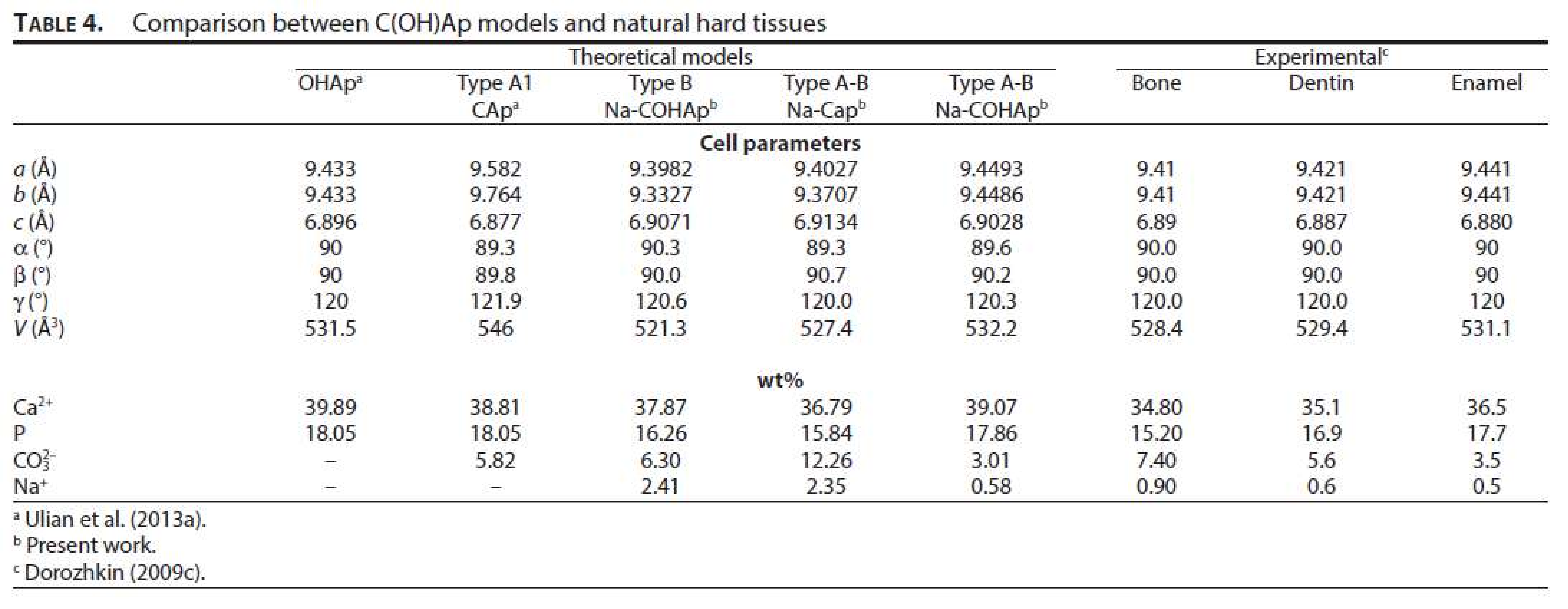


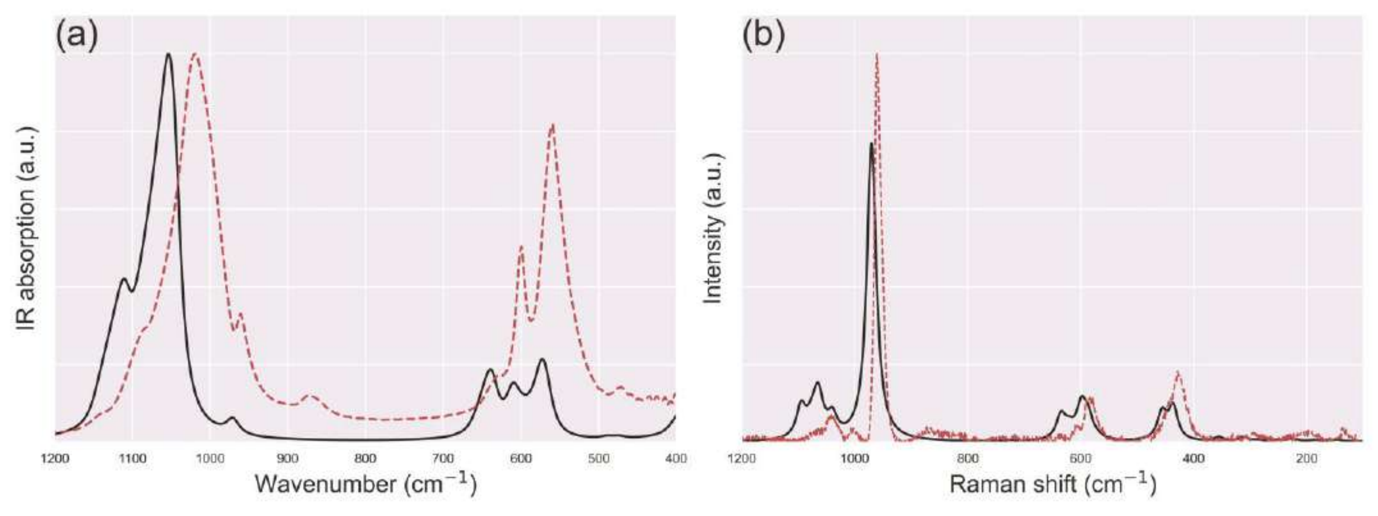
TABLE 4. Comparison between C(OH)Ap models and natural hard tissues

	Theoretical models					Experimental[c]		
	OHAp[a]	Type A1 CAp[a]	Type B Na-COHAp[b]	Type A-B Na-Cap[b]	Type A-B Na-COHAp[b]	Bone	Dentin	Enamel
				Cell parameters				
a (Å)	9.433	9.582	9.3982	9.4027	9.4493	9.41	9.421	9.441
b (Å)	9.433	9.764	9.3327	9.3707	9.4486	9.41	9.421	9.441
c (Å)	6.896	6.877	6.9071	6.9134	6.9028	6.89	6.887	6.880
α (°)	90	89.3	90.3	89.3	89.6	90.0	90.0	90
β (°)	90	89.8	90.0	90.7	90.2	90.0	90.0	90
γ (°)	120	121.9	120.6	120.0	120.3	120.0	120.0	120
V (Å^3)	531.5	546	521.3	527.4	532.2	528.4	529.4	531.1
				wt%				
Ca^{2+}	39.89	38.81	37.87	36.79	39.07	34.80	35.1	36.5
P	18.05	18.05	16.26	15.84	17.86	15.20	16.9	17.7
CO_3^{2-}	–	5.82	6.30	12.26	3.01	7.40	5.6	3.5
Na^+	–	–	2.41	2.35	0.58	0.90	0.6	0.5

[a] Ulian et al. (2013a).
[b] Present work.
[c] Dorozhkin (2009c).

Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2014). *American Mineralogist* **99**, 117-127.

OHAp IR spectrum



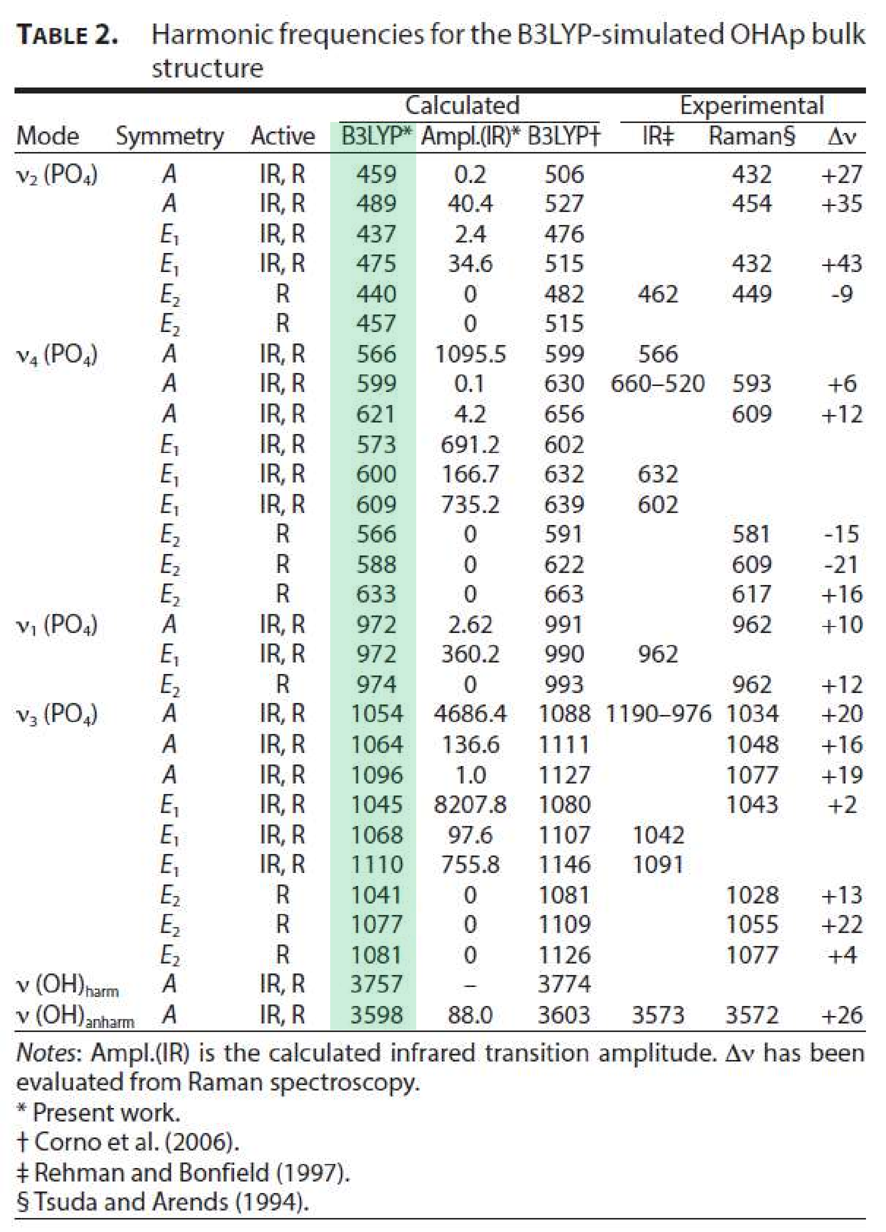


TABLE 2. Harmonic frequencies for the B3LYP-simulated OHAp bulk structure

			Calculated			Experimental		
Mode	Symmetry	Active	B3LYP*	Ampl.(IR)*	B3LYP†	IR‡	Raman§	Δν
ν_2 (PO$_4$)	A	IR, R	459	0.2	506		432	+27
	A	IR, R	489	40.4	527		454	+35
	E_1	IR, R	437	2.4	476			
	E_1	IR, R	475	34.6	515		432	+43
	E_2	R	440	0	482	462	449	-9
	E_2	R	457	0	515			
ν_4 (PO$_4$)	A	IR, R	566	1095.5	599	566		
	A	IR, R	599	0.1	630	660–520	593	+6
	A	IR, R	621	4.2	656		609	+12
	E_1	IR, R	573	691.2	602			
	E_1	IR, R	600	166.7	632	632		
	E_1	IR, R	609	735.2	639	602		
	E_2	R	566	0	591		581	-15
	E_2	R	588	0	622		609	-21
	E_2	R	633	0	663		617	+16
ν_1 (PO$_4$)	A	IR, R	972	2.62	991		962	+10
	E_1	IR, R	972	360.2	990	962		
	E_2	R	974	0	993		962	+12
ν_3 (PO$_4$)	A	IR, R	1054	4686.4	1088	1190–976	1034	+20
	A	IR, R	1064	136.6	1111		1048	+16
	A	IR, R	1096	1.0	1127		1077	+19
	E_1	IR, R	1045	8207.8	1080		1043	+2
	E_1	IR, R	1068	97.6	1107	1042		
	E_1	IR, R	1110	755.8	1146	1091		
	E_2	R	1041	0	1081		1028	+13
	E_2	R	1077	0	1109		1055	+22
	E_2	R	1081	0	1126		1077	+4
ν (OH)$_{\text{harm}}$	A	IR, R	3757	–	3774			
ν (OH)$_{\text{anharm}}$	A	IR, R	3598	88.0	3603	3573	3572	+26

Notes: Ampl.(IR) is the calculated infrared transition amplitude. Δν has been evaluated from Raman spectroscopy.
* Present work.
† Corno et al. (2006).
‡ Rehman and Bonfield (1997).
§ Tsuda and Arends (1994).

Ulian, G., Valdrè, G., Corno, M. & Ugliengo, P. (2013). *American Mineralogist* **98**, 752-759.

COHAp – carbonate ion IR/Raman peaks

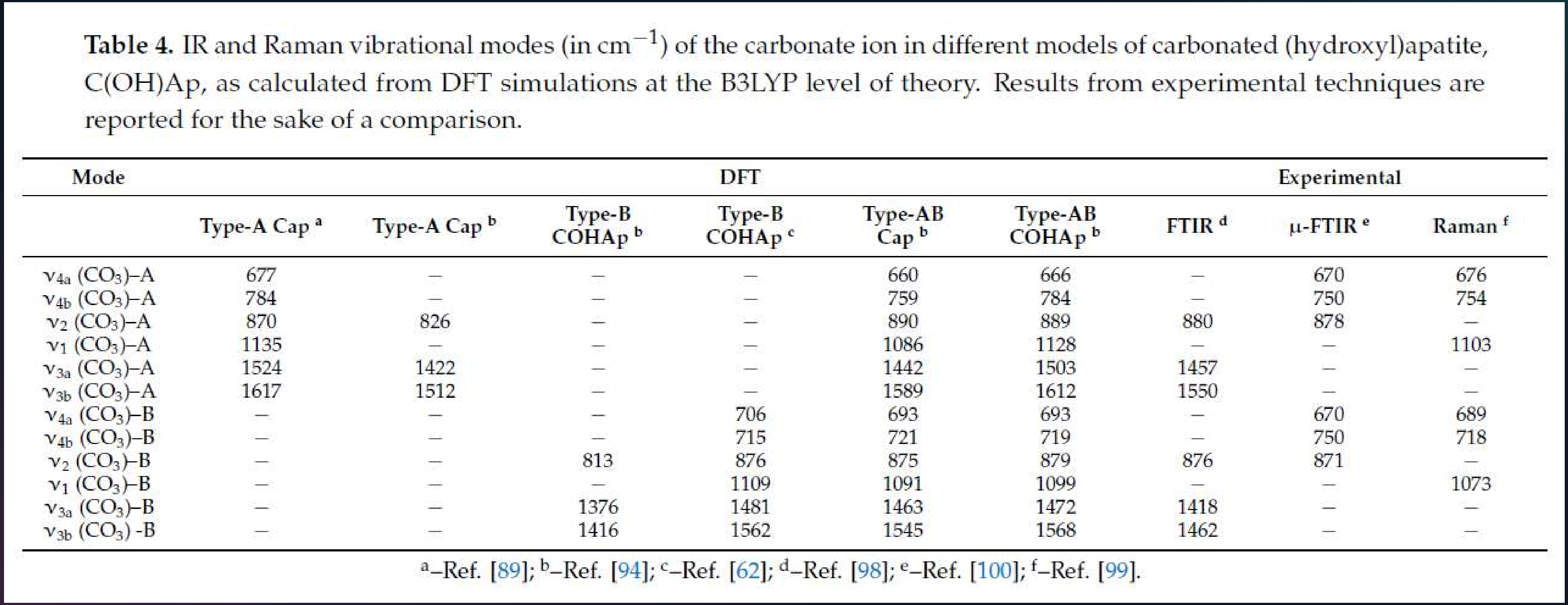


Table 4. IR and Raman vibrational modes (in cm^{-1}) of the carbonate ion in different models of carbonated (hydroxyl)apatite, C(OH)Ap, as calculated from DFT simulations at the B3LYP level of theory. Results from experimental techniques are reported for the sake of a comparison.

Mode	DFT						Experimental		
	Type-A Cap [a]	Type-A Cap [b]	Type-B COHAp [b]	Type-B COHAp [c]	Type-AB Cap [b]	Type-AB COHAp [b]	FTIR [d]	μ-FTIR [e]	Raman [f]
ν_{4a} (CO_3)–A	677	–	–	–	660	666	–	670	676
ν_{4b} (CO_3)–A	784	–	–	–	759	784	–	750	754
ν_2 (CO_3)–A	870	826	–	–	890	889	880	878	–
ν_1 (CO_3)–A	1135	–	–	–	1086	1128	–	–	1103
ν_{3a} (CO_3)–A	1524	1422	–	–	1442	1503	1457	–	–
ν_{3b} (CO_3)–A	1617	1512	–	–	1589	1612	1550	–	–
ν_{4a} (CO_3)–B	–	–	–	706	693	693	–	670	689
ν_{4b} (CO_3)–B	–	–	–	715	721	719	–	750	718
ν_2 (CO_3)–B	–	–	813	876	875	879	876	871	–
ν_1 (CO_3)–B	–	–	–	1109	1091	1099	–	–	1073
ν_{3a} (CO_3)–B	–	–	1376	1481	1463	1472	1418	–	–
ν_{3b} (CO_3) -B	–	–	1416	1562	1545	1568	1462	–	–

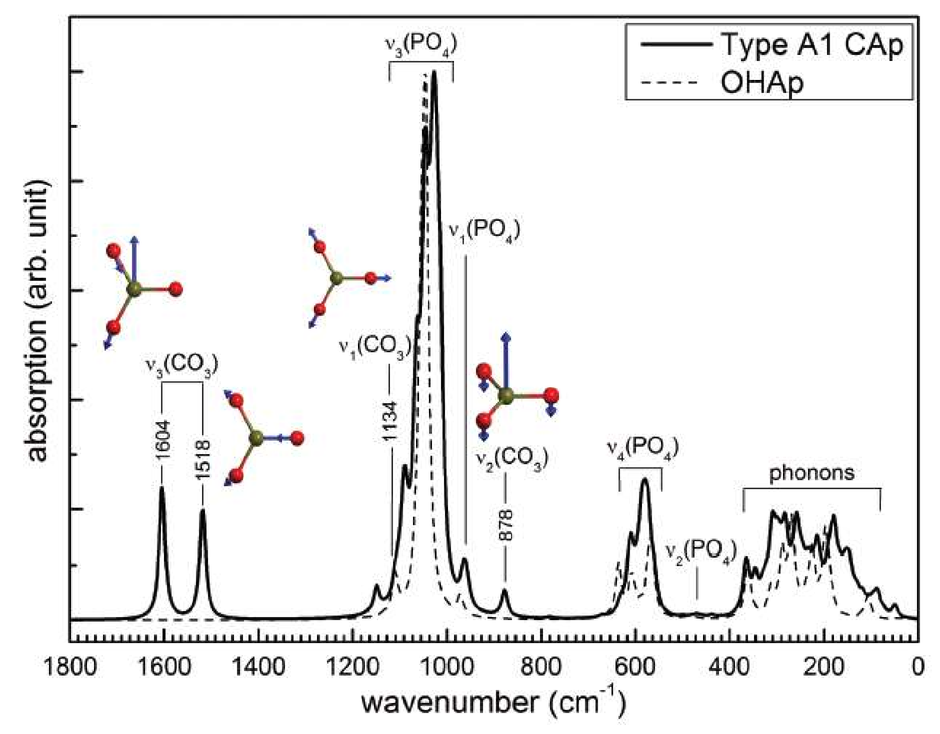
[a]–Ref. [89]; [b]–Ref. [94]; [c]–Ref. [62]; [d]–Ref. [98]; [e]–Ref. [100]; [f]–Ref. [99].

Different position of the signals depending on the site occupied by the carbonate ion!

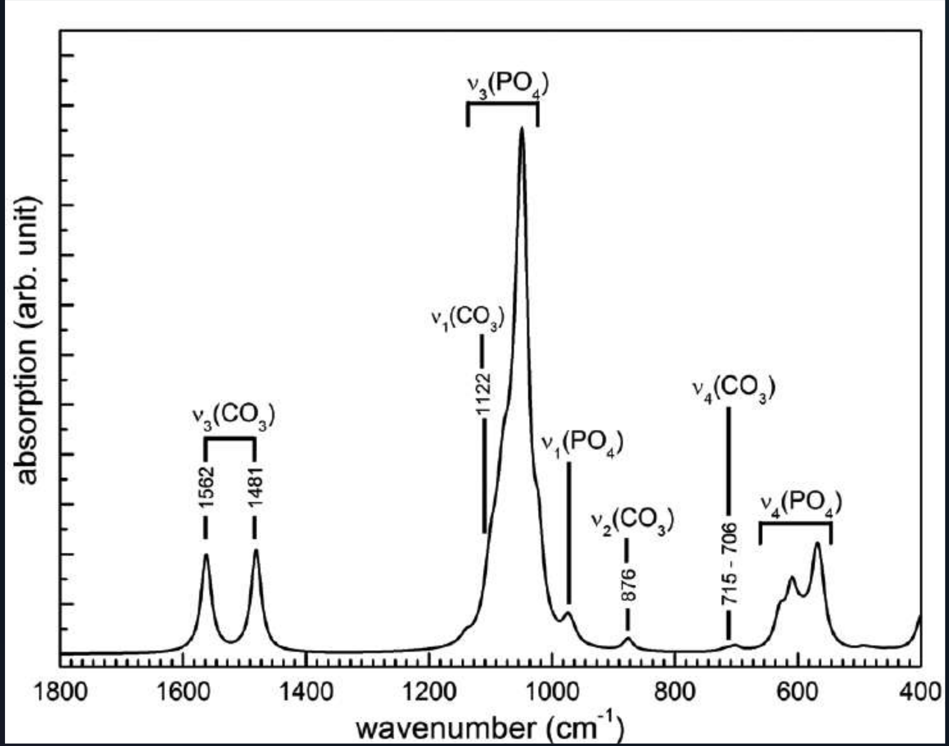
COHAp IR spectrum

Simulated spectra at DFT/B3LYP level of theory

Type-A COHAp

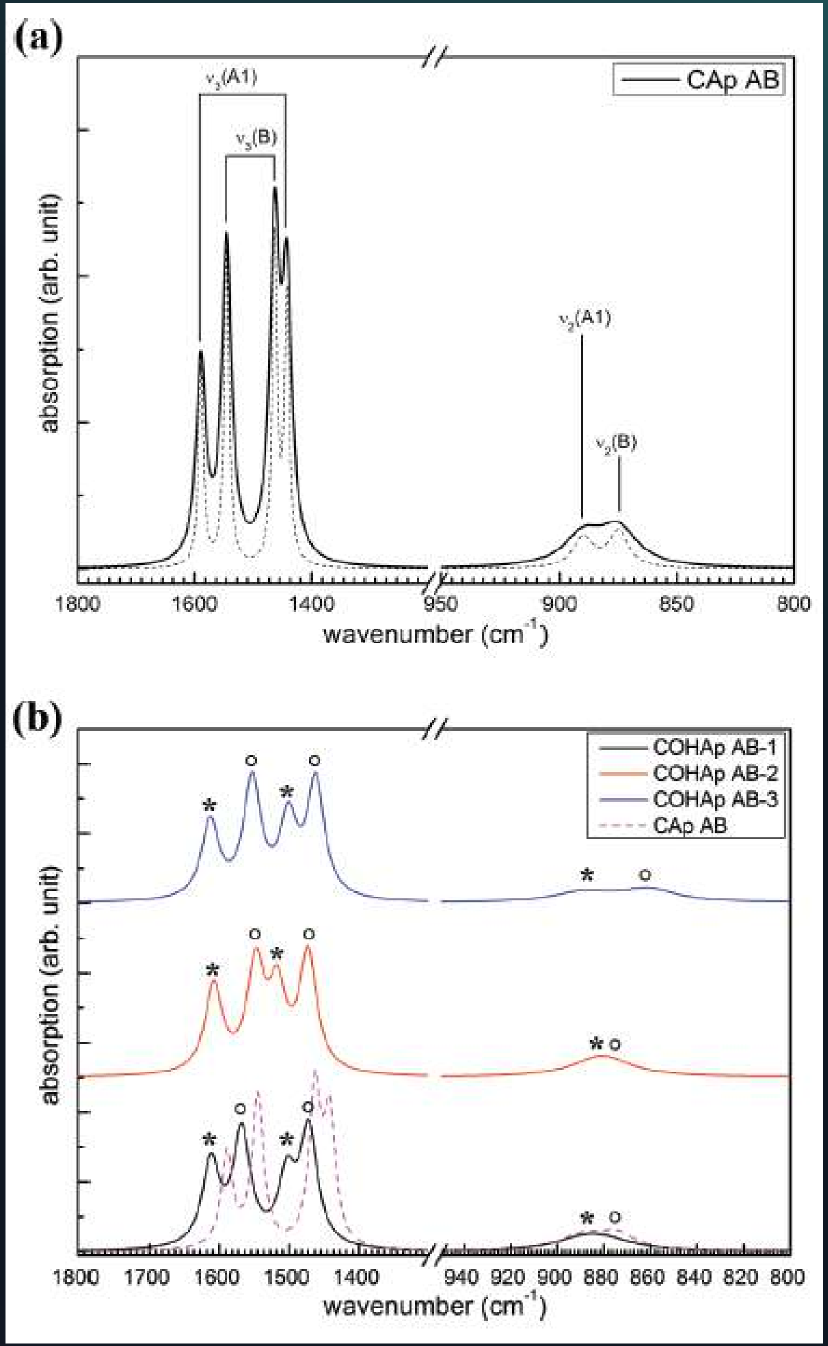


Type-B COHAp

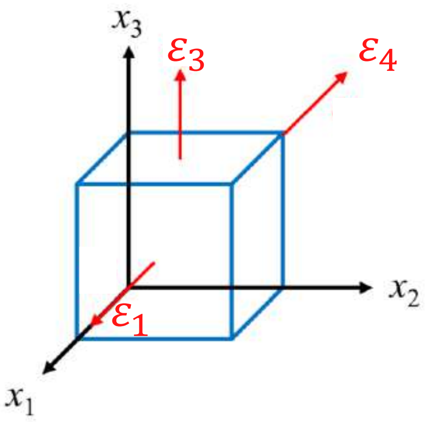


Type-AB IR COHAp spectra

- Convolution of the carbonate ion signals
- Peaks shifted according to the site occupied – different models tested!



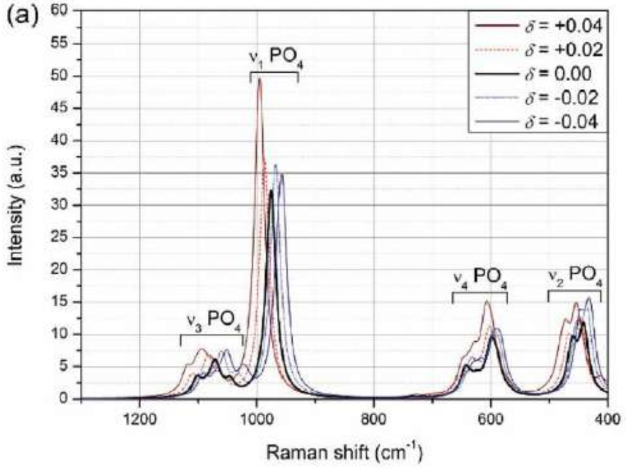
OHAp – Raman & stress/strain

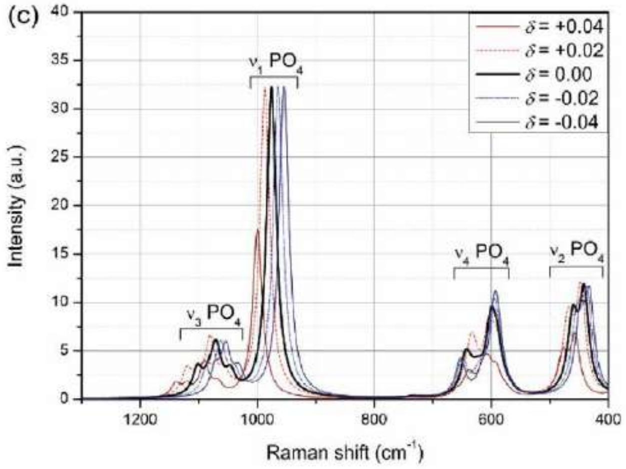


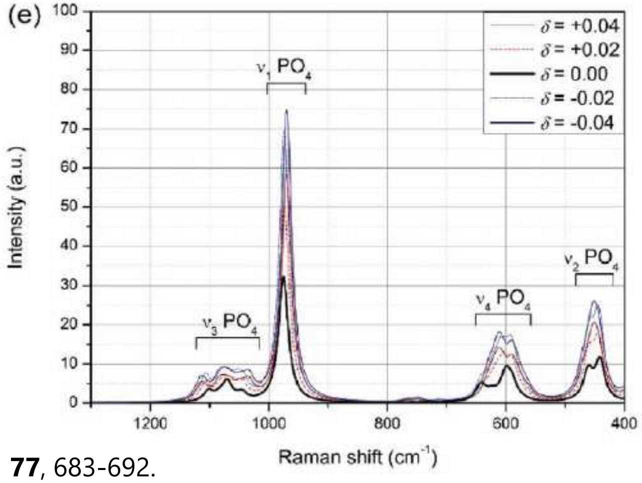
$$\varepsilon_1 = \delta\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$$

$$\varepsilon_3 = \delta\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$\varepsilon_4 = \delta\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}$$







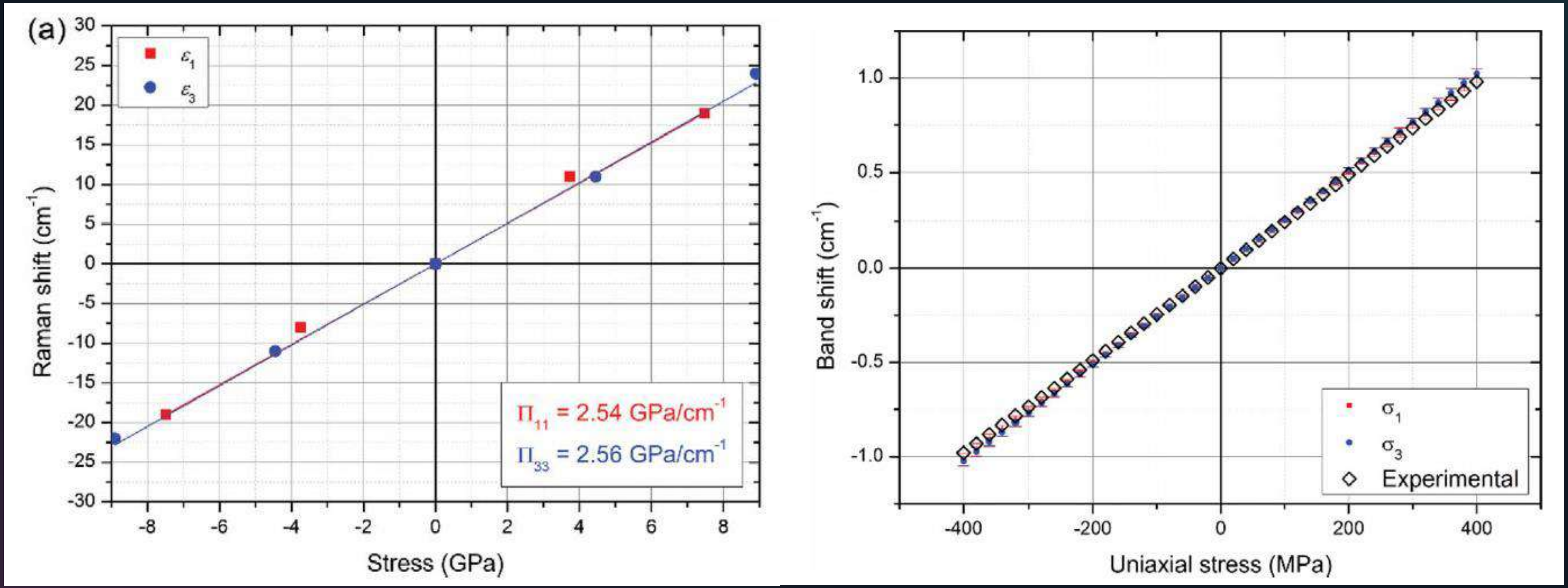
ε_1 = strain (compression/expansion) along **a**-axis

ε_3 = strain (compression/expansion) along **c**-axis

ε_4 = (shear) strain along **ab**-plane

Ulian, G. & Valdrè, G. (2018). *Journal of the Mechanical Behavior of Biomedical Materials* **77**, 683-692.

OHAp – Raman & stress/strain



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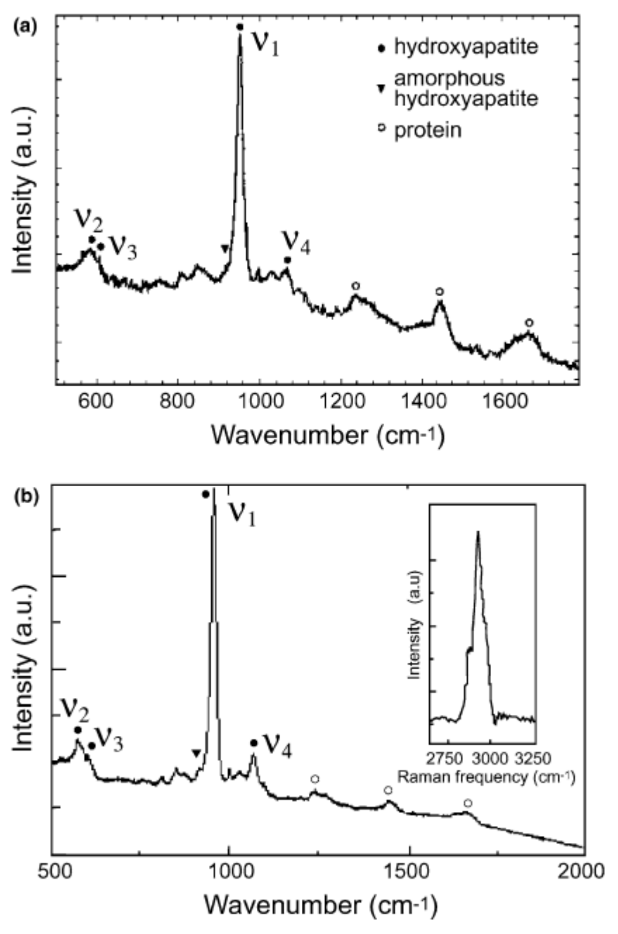
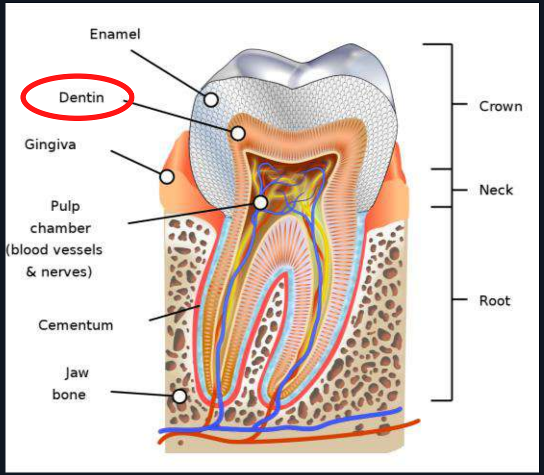
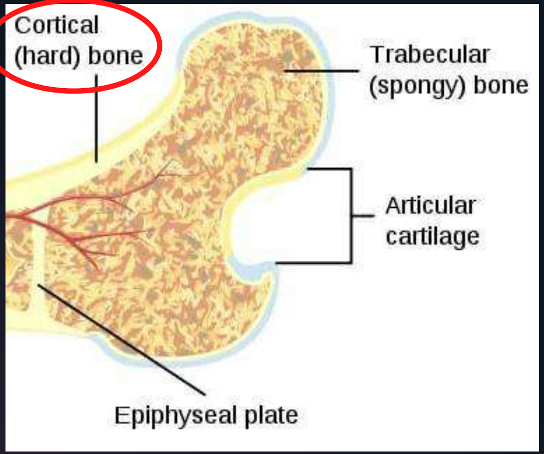
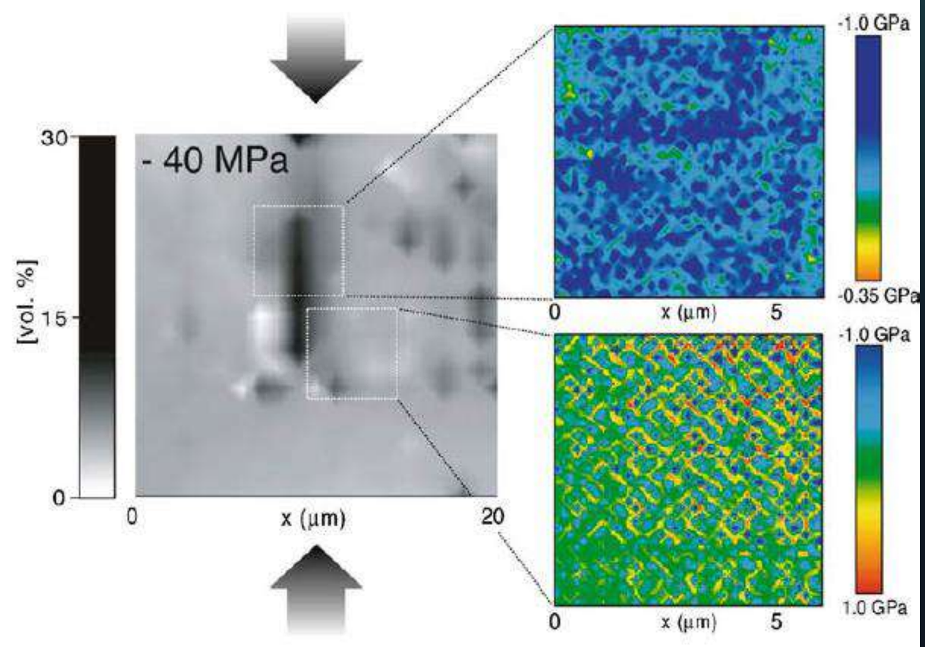
OHAp – Raman & stress/strain







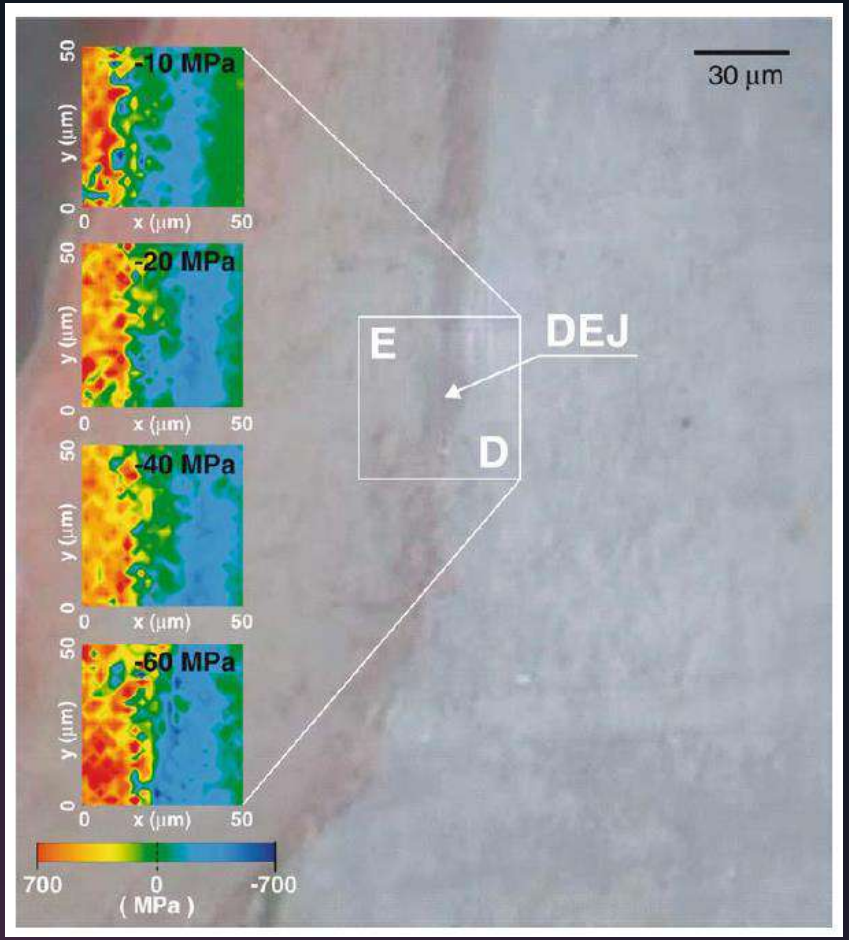


Collagen volume fraction map in cortical bone and maps of the microscopic stresses stored in apatite crystals as collected in confocal configuration.

Criss-cross stress field suggests the presence of a peculiar fibrous structure, with orientation inclinedwith respect to the longitudinal axis of the bovine femur

Pezzotti, G. (2005). *Analytical and Bioanalytical Chemistry* **381**, 577-590.

OHAp – Raman & stress/strain



Pezzotti, G. (2005). *Analytical and Bioanalytical Chemistry* **381**, 577-590.

Dentin-enamel joint (DEJ)

Optical micrograph of the DEJ and microscopic stress maps from a selected area under different compressive remote stress fields.

The microstress maps in apatite were made by monitoring the spectral shift of the sharp 960 cm^{-1} band of (crystalline) hydroxylapatite.

- Tensile stress in the enamel
- Compression stress on the dentin core
- The interface is stress-free