

Structural Biology
Prof. Saugata Hazara
Department of Biotechnology
Indian Institute Technology – Roorkee

Lecture – 18
X-Ray Crystallography: Crystal Symmetry

Hi, everyone. Welcome to the course of structural biology. Today this is the continuation, where we will discuss symmetry as an overall concept and symmetry in crystallography.

(Refer Slide Time: 00:47)

Symmetry:

An object or function is symmetrical if a spatial transformation of it looks identical to the original

This is the original:  $\xrightarrow{\text{This is rotated by } 180^\circ}$  $\xrightarrow{\text{This is rotated by } 360^\circ}$ 



So, what is symmetry? Symmetry is called if an object or function is symmetrical if a spatial transformation looks identical to the original. Let us say this X is original. If I make a 180-degree rotation and come to this, I would say symmetry. But the interesting cases, if you see, you know that there is a 180-degree operation made. Still, because of the symmetrical nature of the structure, you do not understand it is a 180-degree rotation, a 360-degree rotation, or a 0-degree rotation.

So, what we need to see symmetry, we need a standard, concerning the standard your symmetry would be more clearly understood, let us say I put a red dot here. Now, when I perform 180 degrees, you see that the rotation happened, and now, this comes here, the red dot is not part of the system, not part of the symmetry, but its presence makes yourself clear. Similarly, a 360-degree rotation now would bring it here. This is a complex symmetrical representation with symmetries in some portions, and some are not symmetrical.

(Refer Slide Time: 03:37)

Symmetry Operations:

The symmetry of molecules is essential for understanding the structures and properties of organic and inorganic compounds in small scale but it is also important for macromolecules like protein, DNA etc

The properties of chemical compounds are often easily explained by consideration of symmetry

For example, the symmetry of a molecule determines whether the molecule has a permanent dipole moment or not

The theories that describe optical activity, infrared and ultraviolet spectroscopy, and crystal structure involve the application of symmetry considerations

Matrix algebra is the most important mathematical tool in the description of symmetry

What is symmetry operation? The symmetry of molecules is essential for understanding the structures and properties of organic and inorganic compounds. When we talk about small molecules, but it is also very important for macromolecules like protein DNA, especially we are studying X-ray crystallography, you will see the presence of symmetry, so I will tell you there are two types of symmetries.

One is crystallographic symmetry, and the other is non-crystallographic symmetry. What is non-crystallographic symmetry? First, a line could be drawn here if I am standing here. So, two homogeneous or symmetrical parts formed my body. That is what nature did. It did not come through the technical crystallography or the technique of other symmetry operations.

So, this is natural symmetry, or non-crystallographic symmetry, which comes when the atom is arranged in the crystal lattice that is crystallographic symmetry. It is very important to understand that you have the crystal, where these dots are in identical positions. So, what you could do, you could take one. But by solving the structure of the motif, one, you could apply symmetry operation, and then you do not have to solve 2, 3, and 4 individually. So, your work is reduced to 1 fourth.

That is the beauty of symmetry and its role in crystallography. The properties of chemical compounds are often easily explained by considering symmetry. Let us take an example the symmetry of a molecule determines whether the molecule has a permanent dipole moment or not. Sometimes we see molecules like a water molecule, like a carbon molecule being CH₃Cl, and the carbon molecule being CCl₄. So, in this way, the set of carbon molecules would have different dipoles based on their symmetry and positions. The theories that describe

optical activity infrared and ultraviolet spectroscopy and crystal structure involve the application of symmetry considerations the stretching if you have seen carbon dioxide in normal condition, but because the directions but if the directions are evenly stretched, then generation of dipole matrix. Algebra is the most important mathematical tool in symmetry description, and we will see some of the operations.

(Refer Slide Time: 08:27)

Symmetry Operators:

A spatial transformation can be expressed as an operator that changes the coordinates of every point in the object the same way
 Symmetry operators do not distort the object
 In other words, the distance between any two points is the same before and after being moved by the symmetry operation

Here is the operator for a 180° rotation around Z.

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

3x3 Matrix multiplication

$$\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} ax + by + cz \\ dx + ey + fz \\ gx + hy + iz \end{pmatrix}$$

equivalent positions

So, coming to the symmetry operators, a spatial transformation can be expressed as an operator that changes the coordinates of every point in the object the same way. The symmetry operator does not distort the object. In other words, the distance between any 2 points is the same before and after being moved by the symmetry operation. Here is the operator for a 180-degree rotation around the Z-axis. So, you see the around the Z-axis, it is the operation that happened.

So, x and y, there are changes x y z to -x, -y, z. So, these 2 are equivalent positions, and the concept comes from 3 into 3 matrix multiplication, which has a matrix form like this.

(Refer Slide Time: 09:36)

Elements of symmetry identified in the unit cell will be present in the crystal:

Center of symmetry (inversion)

Rotation

Mirror (reflection)

Translation

Glide

These are all referred to as symmetry operations

The symmetry elements identified in the unit cell will be present in the crystal. So, which would be the symmetry one, the center of symmetry, which we call inversion, rotation, and reflection, we will talk about their translation. The translation is movement and glide, which is a combination of reflection and translation. So, they are all referred to as symmetry operations.

(Refer Slide Time: 10:15)

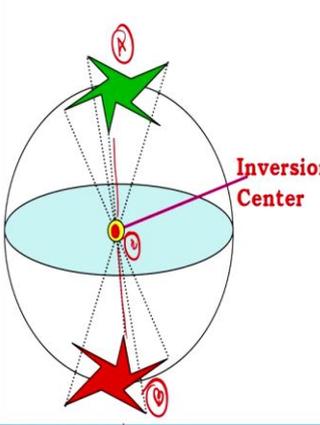
Inversion:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$


Now, let us see the symmetry inversion, where all the coordinates are changed x y z converted to $-x$ $-y$ $-z$. So, there would be a point, and if you measure, every position would be equidistant from that. So, inversion provides a point from where everything is inverted.

(Refer Slide Time: 11:01)

Inversion:



In the symmetry operation called inversion, lines are drawn from all points on the object through a point in the center of the object.

This is called a symmetry center (symbolized with the letter "i").

The lines each have lengths that are equidistant from the original points.

This is also about the same thing we have a point here, acting as the inversion center. All the distances are identical. So, in the symmetry operation, called inversion lines are drawn from all points on the object through a point in the center of the object called the inversion center. This is called a symmetry center, and 'i' could symbolize it. It is also called the inversion center. The lines each have lengths that are equidistant from the original points. So, each of the points would be equidistant from the two objects we get from the inversion operation.

(Refer Slide Time: 12:05)

Rotation:

$$\begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z \end{pmatrix}$$


Coming to rotation, here in rotation, we have angles. So, x y z, there is a change according to the x and y-axis. So, this is a representation of rotation.

(Refer Slide Time: 12:29)

Properties of rotation matrices:

Square, 2x2 or 3x3

The product of any two rotation matrices is a rotation matrix

The inverse equals the transpose $R^{-1} = R^T$

orthogonality

- The dot-product of any row or column with *itself* is one.
- The dot-product of any row or column with a *different* row or column is zero.

$|x|$ equals $|Rx|$, for any rotation R

In the rotation matrix, it could be two into two for 2D, it could be 3 into 3 for 3D. The product of any two rotation matrix is a rotation matrix. The inverse equals the transpose. So, the R inverse is equal to R transpose ($R^{-1} = R^T$). It maintains orthogonality that the dot product of any row or column in the matrix is one, and the dot product of any row or column with a different row or column is zero. The vector x, its absolute value equals Rx for any rotation R.

(Refer Slide Time: 13:21)

2-fold rotation:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

R

2-fold symbol

R

180° rotation. Called a 2-fold because doing it twice brings you back to where you started.

Equivalent positions in fractional coordinates:
 ~~x, y, z $-x, -y, z$~~

2-fold rotation, here, you see a change in the two axes. It is a 180-degree rotation. It is called twofold because doing it twice brings you back to the original where you have started. So, it would be the point from where the rotation performance has operated.

(Refer Slide Time: 14:33)

3-fold rotation:

$$\begin{pmatrix} \cos 120^\circ & -\sin 120^\circ & 0 \\ -\sin 120^\circ & \cos 120^\circ & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \cos 120^\circ - y \sin 120^\circ \\ x \sin 120^\circ + y \cos 120^\circ \\ z \end{pmatrix}$$

In fractional coordinates:

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ x-y \\ z \end{pmatrix}$$

Equivalent positions:

x, y, z $-y, x-y, z$ $-x+y, -x, z$

3-fold symbol

3 -fold rotation. As you see, in the matrix here, you will see the changes, and in the fractional coordinate, you will see from x it is converted to -y, y to x - y, z is not changed. It represents p3 symmetry, and the equivalent positions are x, y, z, and -y, x - y, z, and - x + y, -x, z.

(Refer Slide Time: 15:14)

4-fold rotation:

$$\begin{pmatrix} \cos 90^\circ & -\sin 90^\circ & 0 \\ -\sin 90^\circ & \cos 90^\circ & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \cos 90^\circ - y \sin 90^\circ \\ x \sin 90^\circ + y \cos 90^\circ \\ z \end{pmatrix}$$

In fractional coordinates (same as orthogonal coords):

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ x \\ z \end{pmatrix}$$

Equivalent positions:

x, y, z $-x, -y, z$
 $-y, x, z$ $y, -x, z$

4-fold symbol

6 fold → 60

4-fold rotation. Again, it is a p4 symmetry. So, if you see x, y, z, it seems to x change to -y. So, the position change, y change x, and z would be staying as z. So, it is 4-fold means it is 90 degrees. When it was 3-fold, it was 120 degrees.

(Refer Slide Time: 16:03)

Rotation:

Rotation produces patterns where the original motif is **Retained**.

Both original and rotation have the same "handedness".

They are CONGRUENT

6 turns of rotation

Each is 60°

6/360 = 60°

1
2
3
4
5

Rotation produces patterns where the original motif is retained. If you see the original motif, as I was talking about the hexagon, here, in each case, it is a 6-fold. So, 60-degree rotation and both original and rotation have the same handedness, congruent. So, we have 2-fold, 1-fold the same thing, 2-fold, 3-fold. So 1, 2, 3, 4, 6, 5. What happened to 5?

(Refer Slide Time: 17:14)

Rotation:

Rotational symmetry is expressed as a whole number (n) between 1 and ∞ . n refers to the number of times a motif is repeated during a complete 360° rotation

1 fold $\rightarrow 360/1 \rightarrow 360^\circ$

2 fold $\rightarrow 360/2 \rightarrow 180^\circ$

3 fold $\rightarrow 360/3 \rightarrow 120^\circ$

4 fold $\rightarrow 360/4 \rightarrow 90^\circ$

5 fold $\rightarrow 360/5 \rightarrow 72^\circ$

6 fold $\rightarrow 360/6 \rightarrow 60^\circ$

1

2

3

4

6

∞

Again, we will see that rotational symmetry is expressed as a whole number in between 1 and infinity in refers to the number of times a motif is repeated during a complete 360-degree rotation, which means if it is 1-fold, it is 360 degrees divided by one the rotation, 2-fold the rotation is 360 degree divided by 2 is 180 degree, 3-fold 360 degrees divided by three which is 120 degrees, 4-fold 360 degrees divided by 4 is 90 degrees, 5-fold have an idea is 72, 6-fold 360 degree by 6, 60 degrees in that way, you will get.

(Refer Slide Time: 18:36)

Rotation:

Rotation Axes (1, 2, 3, 4, or 6) – rotation of 360 (1), 180 (2), 120 (3), 90 (4), or 60°(6) around a rotation axis yields no change in orientation/arrangement

As I talked about, rotation axis 1,2,3,4, or 6 rotations of 360 degrees, 180 degrees, 120 degrees, 90 degrees, or 60 degrees around a rotation axis yields no change in orientation or arrangement.

(Refer Slide Time: 19:19)

1-Fold Rotation: A 1(E)-fold rotation operation implies either a 0° rotation or a 360° rotation, and is referred to as the *identity* operation.

2-Fold Rotation: A 2-fold(C2) rotation operation moves the object by $(360/2)^\circ = 180^\circ$. The symbol used to designate a 2-fold axis is a solid oval.

3-Fold Rotation. A 3-fold(C3) rotation operation moves the object by $(360/3)^\circ = 120^\circ$. The symbol used to designate a 3-fold axis is a solid equilateral triangle.

4-Fold Rotation. A 4-fold(C4) rotation operation moves the object by $(360/4)^\circ = 90^\circ$. The symbol used to designate a 4-fold axis is a solid square.

6-Fold Rotation. A 6-fold(C6) rotation operation moves the object by $(360/6)^\circ = 60^\circ$. The symbol used to designate a 6-fold axis is a solid hexagon.

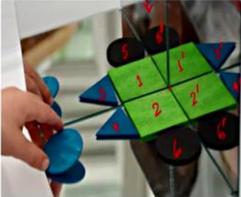
If you look here for a banana, you will understand more. There is 1-fold rotation, and 1-fold rotation operation implies either a 0-degree rotation or a 360 degrees rotation and is referred to as identity operation. 2-fold rotation, a 2-fold is C2 rotation operation moves the object by 360 / 2 180 degrees, the symbol used to designate 2-fold axis is a solid oval, if you see this is 2-fold. 3-fold rotation, a 3-fold or C3 rotation operation moves the object by 360 degrees by 3 120 degrees, the symbol used to designate a 3-fold is a solid equilateral, so, here 3-fold. 4-fold C4 rotation operation moves the object by 90 degrees, and the symbol is a solid square. So, this is 4-fold. 6-fold C6 rotation operation moves the object by 60 degrees, and it is a solid hexagon.

(Refer Slide Time: 21:04)

Reflection:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$$

Object
बस/90

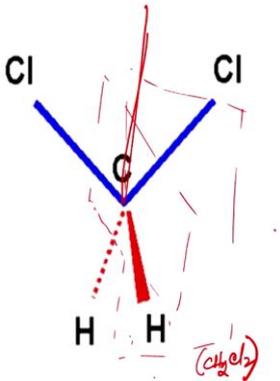


Swajati

A mirror would be changed from 1 axis x written x, y written y, and z goes to -z. This is one of the representations, you see the mirror plane, and this is a very beautiful representation.

(Refer Slide Time: 22:22)

Reflection:



The presented molecule contains two mirror planes

One is horizontal, on the plane of the paper, bisects the Cl-C-Cl bond

Other one is vertical, perpendicular to the plane of the paper, bisects H-C-H bond

Swajati

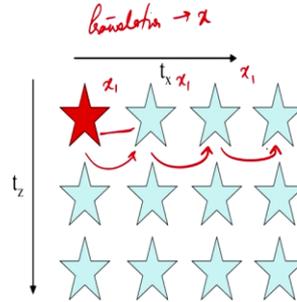
Reflection, if you take a compound like this, remember I talked about these compounds CH_2Cl_2 . So, the presented molecule contains two mirror planes. So, one is horizontal on the plane of the paper bisects the Cl-C-Cl bond, or the other is vertical, perpendicular to the plane of the paper bisects each C.

(Refer Slide Time: 23:27)

Translation:

Translation is an operation, denoted by t , that generates a pattern in regular identical intervals.

In 3D space operation of translations could be labelled as x , y and z .



The translation is an operation denoted by 't' that generates a pattern in regular identical intervals. So, if you see, suppose this is the distance in the x-axis if I say x_1 the same distance in the crystal, so, you get a translation of x , and you generate one motif. In a 3D space operation, a translation could be labeled as x , y , z . So, you have three axes and their movement.

(Refer Slide Time: 24:22)

glide plane:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} x + 1/2 \\ y \\ -z \end{pmatrix}$$

2 operation result

Object

Reflection + Translation

Object

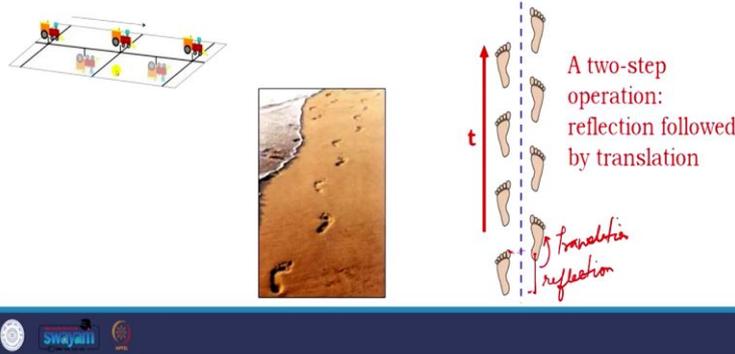
x

In the glide plane, you have one matrix, and you have a second matrix which tells you to have two operations leading to a result. So, x is x plus a half, y is y , z is $-z$. So, the glide plane is a combination of reflection and translation, reflection in the z -axis and then half translation.

(Refer Slide Time: 25:09)

Glide:

In geometry as well as crystallography, a **glide plane** which is also called as **transflection** is a symmetry operation describing how a **reflection** in a plane, followed by a **translation** parallel with that plane, may leave the crystal unchanged.

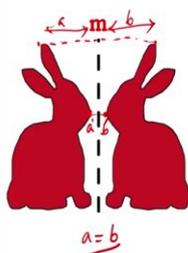


So, in geometry and crystallography, a glide plane, which is also called transflection is a symmetry operation describing how a reflection in a plane followed by a translation parallel with that plane may leave the crystal unchanged. A very good example is this, where you see a reflection. If you put a mirror, you will have a reflection, but the reflection would be putting the feet here, but the feet have now proceeded.

So, there is a reflection followed by a translation, a two-step operation reflection followed by a translation. Example of glide you will see when you go to any beach. You will see people walk generally. When people walk, they follow glide motion because you have your 1 foot. The other foot is a mirror plane. But so, it is a reflection, but it always proceeds. So, you have your first feet, your second feet going ahead, called glide.

(Refer Slide Time: 27:04)

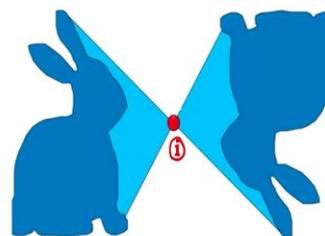
Reflection Versus Inversion:



Let us look at this comparison purely in 2 dimensions.

Reflection of a 2-dimensional object occurs across a plane (m)

After inversion everything is an equal and opposite distance through a single point i.



Let us take a comparison to understand reflection and inversion. For that, let us take at this comparison purely in 2 dimensions first. Reflection of a 2-dimensional object occurs across a plane mirror. So, you see, this is a reflection. The equidistance would be measured from the mirror axis a, b., which is always equal to b.

After inversion, everything is equal and opposite distance through a single point i.

(Refer Slide Time: 28:38)

Combination of Rotations:

Moving from 2 dimensional to 3 dimensional systems (real crystals) multiple rotation axes may be identified.

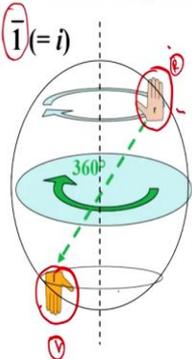
RULE: All symmetry operators must intersect at a single point.

-  2-fold rotation: 180° rotation
-  3-fold rotation: 120° rotation
-  4-fold rotation: 90° rotation
-  6-fold rotation: 60° rotation
-  mirror plane
- m** mirror plane

Now, we will discuss the combination of rotations. So, moving from 2 dimensions into 3 dimensions, the real system, multiple rotation axes may be identified. The rule is all symmetry operators must intersect at a single point. So, you have the rotations 2-fold, 3-fold, 4-fold, 6-fold, but along with that, you should have the mirror plane.

(Refer Slide Time: 29:15)

The combining of the single operations, rotation and inversion, generates a rotoinversion operation:



This may be viewed in one of two ways. Either, think of the diagram as two independent objects, a right hand in the upper hemisphere, and a left hand in the lower hemisphere.

The rotoinversion is the symmetry operation required to transpose one object onto the other.

In this operation, rotate the hand through 360° and invert.

2D inversion results in **congruent pairs**. 3D roto-inversion in **enantiomorph**ic pairs.

Combining single operation rotation and inversion generates a roto inversion operation, which is a 3-dimensional operation. So, you have this picture. Think of that diagram as two

independent objects. You have a right hand in the upper hemisphere and a left hand in the lower hemisphere. So, you have a right hand, and you have a left hand, the rotoinversion is the symmetry operation required to transpose one object into the other.

In this operation, rotate the hand through 360 degrees, and then you invert that. 2D inversion results in congruent pairs, whereas 3D roto-inversion in enantiomorph pairs. So, in 2D inversion result congruent pairs, rota-inversion in 3D enantiomorph pairs.

(Refer Slide Time: 31:33)

Congruent figures:

If the sides are the same length and the angles are equal, the **figures are congruent**

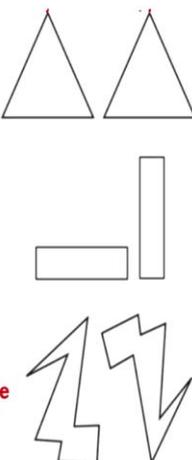
Each side and angle of one **figure** corresponds to a side or angle in the other

We call these corresponding parts

For instance, the top point of one triangle corresponds to the top point of the other triangle in a **congruent** pair.

Congruent figures have exactly the same size and shape

They have congruent sides and congruent angles



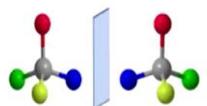
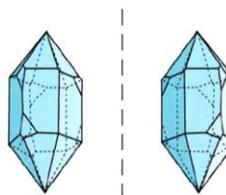
For a congruent figure or congruent pair, if the sides are the same length and the angles are equal, the figures are congruent. Each side and angle of one figure correspond to its side or angle to the other. For example, the top point of one triangle corresponds to the top point of the other triangle in a congruent pair. So congruent figures or congruent pairs have the same size and shape, and they have congruent sides and congruent angles.

(Refer Slide Time: 32:40)

Enantiomorph Pair:

Pair of compounds (crystals or molecules) that are mirror images on each other but are not identical.

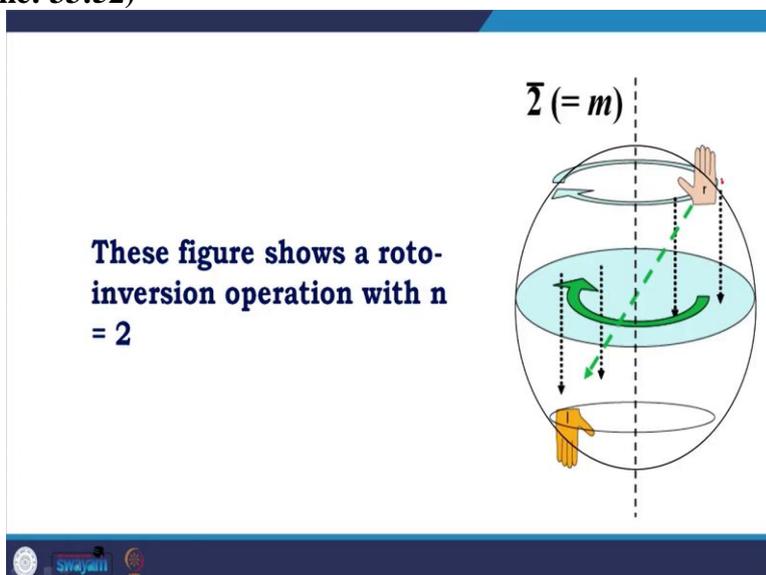
2D inversion results in **congruent pairs**. 3D roto-inversion in **enantiomorph pairs**



Now, what are enantiomorph figures and enantiomorph pairs? Pair of compounds, crystals, or molecules that are mirror images on each other but are not identical. So, you can see the pair of crystals, and they are in enantiomorph pair.

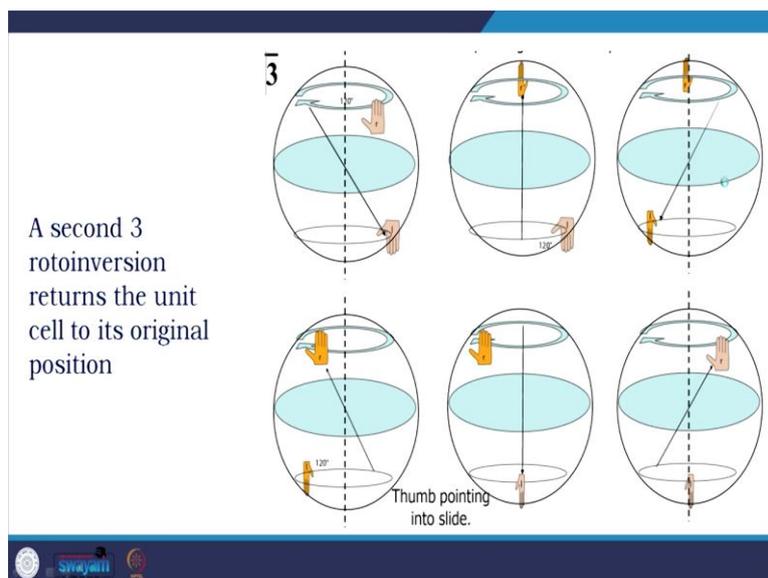
But now you understand that we have already shown you in the model that this is a chiral pair and not superimposed like hands. If you want to put them on top of each other, these two would not be superimposed. So that is the difference between a congruent pair and an enantiomorph pair.

(Refer Slide Time: 33:52)



Coming to another one, another roto-inversion. This shows a roto-inversion operation where $n = 2$, so you do a 360 degree, but not just the inversion as you are performing here. Instead of the combination of invert, you have 2-fold. That is the difference here.

(Refer Slide Time: 34:28)



Coming to a 3 roto-inversion, it returns the unit cell to its original position like you have here. You make a 120-degree angle here. Then what do you do? You do the next operation where you come here, and then you have the right hand and the left hand. So, because it is 3-fold, you are making 120-degree rotation with the inversion. So, you see the changes in the picture with a corresponding change of 120-degree angle with the inversion.

(Refer Slide Time: 35:22)

Total Symmetry operations and their symbols:

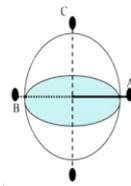
Symbol	Symmetry operation	Symmetry element
E	Identity (doing nothing)	----
C_n	Rotation by $360^\circ/n$	n-fold axis
σ (sigma)	Reflection	mirror plane
i	Inversion (through a center)	point
S_n	Improper rotation	n-fold axis and a mirror plane

So, total symmetry operation and the symbols. Symbol E is identity, which means doing nothing so, there is no symmetry element. C_n rotation by 360 degrees by n which is n-fold axis, 2-fold is 180, 3-fold is 120 like that. Sigma (σ) is reflection that demonstrates a mirror plane, i is a inversion, which is a point, and S_n is the improper rotation of the n-fold axis and a mirror plane.

(Refer Slide Time: 36:00)

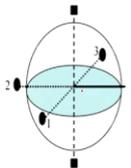
Simple Combination Systems:

Combining various axes of rotation to generate three dimensional patterns



2-fold rotation + 2-fold rotation

Vertical 2-fold axis (C) operates a 2-fold rotation on A
This generates a second, identical axis B.

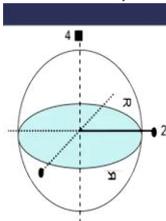


4-fold rotation + 2 x 2-fold rotation

In this example, the 4-fold axis generates three identical 2-fold axis

Simple combination system combining various axis of rotation to generate 3-dimensional patterns. So, 2-fold rotation plus 2-fold rotation is an operation 4-fold rotation + 2 into 2-fold rotation. Here, you have the vertical 2-fold axis in C operating at a 2-fold rotation on A, generating a point B with the identical axis. Similarly, here 4-fold axis generates 3 identical 2-fold axes.

(Refer Slide Time: 36:48)



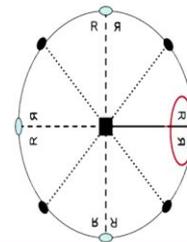
If we insert a "unit cell" we can track what happens as each symmetry operation is executed.

Viewing the image from above (down the 4-fold axis), 4-fold rotation of the original "R R" results the way figure is showing

Remember -thinking with respect only to rotation -this new pattern has two new independent sets of 2-fold rotation.

The first is highlighted by the marker 

This set, themselves generate the second set of 2-fold rotations indicated by the marker 



If we insert a unit cell, we can track what happens as each symmetry operation is executed. So, we are putting a unit cell viewing the image from above into the top 4-fold axis, which is 90-degree 4-fold rotation of the original R R motive results in the way we will see the change in the figure. Now, remember thinking with respect only to rotation, this new pattern has 2 new independent sets of 2-fold rotations.

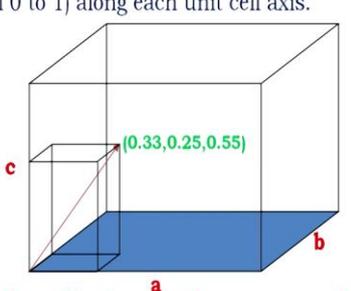
The first one we have highlighted and like this and this set themselves generates the second set of 2-fold rotation indicated by the black marker. So, we start from here, and then we have created initially we get a new pattern and then this new pattern generate itself the second set of 2-fold for rotations here.

(Refer Slide Time: 38:02)

Fractional Coordinates:

The crystallographic coordinate system is defined by the unit cell

The location of a point is defined by fraction of traveled (from 0 to 1) along each unit cell axis.



Fractional coordinates are always measured parallel to each axis. The axes are not necessarily 90° apart!

The crystallographic coordinate system is defined by the unit cell. The location of a point is defined by the fraction of travel from 0 to 1 along each unit cell axis. Here, we have a fractional axis 0.33, 0.25, 0.55. So, the fractional coordinates are always measured parallel to each axis, which are not necessarily 90 degrees apart.

(Refer Slide Time: 38:42)

The crystal lattice:

The crystal lattice is an example of translational symmetry

Equivalent positions are (x,y,z) and $(x+1,y+1,z+1)$, in fractional coordinates

Space groups that have no *other* translational symmetry operations are called "**primitive**". Space group letter "P"

Space groups have letters indicating the type of translational symmetry:

- C (**centered**)
- F (**face-centered**)
- I (**body-centered**)

The crystal lattice is an example of translational symmetry. Equivalent positions are x, y, z and $x+1, y+1, z+1$. So, one translation in fractional coordinates. Space groups that have no other translational symmetry operations are called primitive space groups and represented

Arrangement of lattice points in the Unit Cell & No. of Lattice points / Cell:

		Position of lattice points	Effective number of Lattice points / cell
1	P	8 Corners	$= [8 \times (1/8)] = 1$
2	I	8 Corners + 1 body centre	$= [1 \text{ (for corners)}] + [1 \text{ (BC)}] = 2$
3	F	8 Corners + 6 face centres	$= [1 \text{ (for corners)}] + [6 \times (1/2)] = 1 + 3 = 4$
4	A/ B/ C	8 corners + 2 centres of opposite faces	$= [1 \text{ (for corners)}] + [2 \times (1/2)] = 2$

$$8 \times \frac{1}{8}$$

$$1$$

$$1 + 1 = 2$$

$$1 + 3 = 4$$

$$1 + 2 \times \frac{1}{2} = 2$$

Arrangement of lattice points in the unit cell and number of lattice points per cell. So, if it is primitive, there are 8 corners; an effective number of lattice points per cell is 8 into 1 / 8, so 1. For I (body center), 8 corners and 1 point for one body center. So, 1 + 1 is 2. For F, if it had faces, so, 6 face and 8 corners, so, 1 + 3 = 4, and then for the C centered A, B, C, it has 2 centers of opposite faces. So, 1 for corners everyone has, and then 2 * 1/2 because it is either A or B or C. So, 1 + 2 * 1/2 = 2.

(Refer Slide Time: 42:27)

Tetragonal:

			P	I	F	C
2	Tetragonal	Square Prism (general height)	✓	✓		

Symmetry of tetragonal lattices:

$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

$$\frac{4}{m} \frac{2}{m} \frac{2}{m}$$

Now, look at the details of the 7 crystal systems, we talked about. So, here in the cube, it has primitive, body-centered, face centers, the conditions are $a=b=c$ and $\alpha = \beta = \gamma = 90$ degrees. The symmetry operations are $4 / m \bar{3} 2 / m$. For tetragonal, there is primitive and body-centered. So, here $a = b$ not equal to c , and $\alpha = \beta = \gamma = 90$ degree symmetry $4/m, 2/m, 2/m$.

(Refer Slide Time: 43:14)

Orthorhombic:

			P	I	F	C
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓

One convention $a < b < c$

Symmetry of orthorhombic lattices: $\frac{2}{m} \frac{2}{m} \frac{2}{m}$

$a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$

Orthorhombic has all the contributions primitive, body-centered, face-centered, c centered, a not equal to b not equal to c. The hence the basis angle $\alpha = \beta = \gamma = 90$ degree symmetry $2/m, 2/m, 2/m$.

(Refer Slide Time: 43:33)

Hexagonal:

			P	I	F	C
4	Hexagonal	120° Rhombic Prism	✓			

$a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Note: there is only one type of hexagonal lattice (the simple one)

Symmetry of tetragonal lattices: $\frac{6}{m} \frac{2}{m} \frac{2}{m}$

A single unit cell (marked in blue) along with a 3-unit cells forming a hexagonal prism

Hexagonal, you will note here only primitive for the hands $a = b$ not equal to c angles $\alpha = \beta = 90$ -degree, $\gamma = 120$ degrees, as I told you, there is only one type of hexagonal lattice the simple the primitive one. A single unit cell marked in blue and 3 unit cell forms a hexagonal prism if you see the symmetry $6 / m, 2 / m, 2 / m$.

(Refer Slide Time: 44:10)

Trigonal:

			P	I	F	C
5	Trigonal	Parallelepiped (Equilateral, Equiangular)	✓			

Rhombohedral

$a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$

Symmetry of trigonal lattices: $\bar{3} \frac{2}{m}$

Trigonal it could also call us rhombohedral it has only primitive again. In case of trigonal $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$, symmetry $\bar{3} \frac{2}{m}$

(Refer Slide Time: 44:29)

Monoclinic:

			P	I	F	C
6	Monoclinic	Parallogramic Prism	✓			✓

Note the position of a, b, c

One convention
 $a < b < c$ $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ \neq \beta$

Conventionally b is chosen as the 'unique' axis

Symmetry of Monoclinic lattices: $\frac{2}{m}$

Monoclinic primitive and C centered, here $a \neq b \neq c$ for the sides and $a < b < c$, $\alpha = \gamma = 90^\circ \neq \beta$, the symmetry is $\frac{2}{m}$ only.

(Refer Slide Time: 44:50)

Triclinic:

7	Triclinic	Parallelepiped (general)	P	I	F	C
			✓			

$a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$

Symmetry of Triclinic lattices:

$\bar{1}$

Triclinic is primitive, a not equal to b not equal to c, alpha not equal to beta not equal to gamma. It is only 1 bar is the symmetry operation.

(Refer Slide Time: 45:03)

Hexagonal class

Unit Cell Shape	Crystal System	Unit Cell Symmetry
cubic	cubic (isometric)	$4/m\bar{3}2/m$
tetragonal	tetragonal	$4/m2/m2/m$
hexagonal	hexagonal	$6/m2/m2/m$
orthorhombic	orthorhombic	$2/m2/m2/m$
monoclinic	monoclinic	$2/m$
triclinic	triclinic	$\bar{1}$

So, as I told you, unit cell shaped cubic, tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic. Crystal systems according to cubic, tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic. Here you see 6, but we have 7 because of the hexagonal class of 2 rhombohedral and hexagonal forms.

(Refer Slide Time: 45:32)

Point group symmetry:

Inorganic crystals usually have perfect shape which reflects their internal symmetry

Point groups are originally used to describe the symmetry of crystal

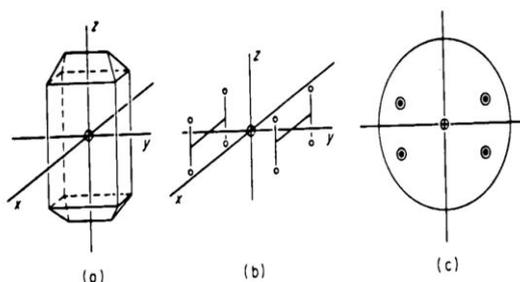
Point group symmetry does not consider Translation

Included symmetry elements are rotation, mirror plane, center of symmetry, roto-inversion.

The point group symmetry in the inorganic crystal is usually a perfect shape reflected in their internal symmetry. Point groups are originally used to describe the symmetry of crystals. Point group symmetry does not consider translation. Included symmetry elements are rotation, mirror plane, center of symmetry, and roto-inversion.

(Refer Slide Time: 45:59)

Point group symmetry diagrams:

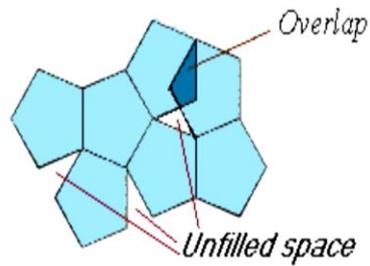


- a) Crystal with symmetry mmm
- b) Set of points related by symmetry mmm
- c) Plane representation of the symmetry mmm

So, when you see crystal with symmetry mmm the mirror plane, set of points related by symmetry mmm and plane represented for the symmetry mmm the mirror. So, point group symmetry diagrams.

(Refer Slide Time: 46:15)

N-fold axes with $n=5$ or $n>6$ does not occur in crystals:



Adjacent spaces must be completely filled (no gaps, no overlaps).

I talked about N-fold axes where $n =$ five or n greater than 6 does not occur in the crystal because in those cases, there are overlaps and unfilled space that are not favorable for the formation of the crystals. So, the adjacent spaces must be filled to get perfect symmetry which comes in the $n = 2$, $n = 3$, $n = 4$, and $n = 6$.

(Refer Slide Time: 48:07)

230 space groups, 32 point groups, 14 Bravais lattice, and 7 crystal systems

Overall, there are 230 space groups, 32 point groups, 14 Bravais lattice, and 7 crystal systems discussed.

(Refer Slide Time: 48:18)

Selective environment in Enzymes:

Selectivity/Biasness

But now, we have to talk about selective involvement in enzymes or proteins, which is our focus. We already talked about chirality. We talk about the amino acids maintain chirality. So, you cannot get d amino acids. You only get l amino acids here. I will talk about an interesting story. So, you look at this person standing or waiting at the bus stop. The bus appears at the bus stop two doors. You could say front door and back door the guy could level both the doors it has an equal chance now, suddenly the guy has observed the driver there is a beautiful driver. So, now, the equally valid chances of the front door and back door to him the preference become the front door. Similarly, the choice depends on the chiral environment in an enzyme or protein special in the enzyme where it goes for the catalytic reaction.

(Refer Slide Time: 49:42)

Space Groups in Proteins:

Only 65 space groups for chiral molecules

TABLE 4.II
Enantiomorphic space groups

System	Class	Space group symbols
Triclinic	1	$P1$
Monoclinic	2	$P2, P2_1, C2$
Orthorhombic	222	$C222, P222, P2_12_12_1, P2_12_12, P222_1, C222_1, F222, I222, I2_12_12_1$
Tetragonal	4	$P4, P4_1, P4_2, P4_3, I4, I4_1$
	422	$P422, P4_22, P4_122, P4_12_12, P4_222, P4_22_12, P4_32_12, P4_322, I422, I4_122$
Trigonal	3	$P3, P3_1, P3_2, R3$
	32	$P312, P321, P3_121, P3_112, P3_212, P3_221, R32$
Hexagonal	6	$P6, P6_5, P6_4, P6_3, P6_2, P6_1$
	622	$P622, P6_122, P6_222, P6_322, P6_422, P6_522$
Cubic	23	$P23, F23, I23, P2_13, I2_13$
	432	$P432, P4_132, P4_232, P4_332, F432, F4_132, I432, I4_132$

230
65

And also, when you are considering here, I told you the 230 space group is reduced to 65 for protein because of its chiral involvement. So, we have talked about basic symmetry. We have talked about how those symmetries are operated using matrix operation. We have discussed the importance of those symmetries spatially; we understand well when they are in 2d. Still, when it comes to combination, it isn't easy to understand, but they are the ones that are present here.

So, we talked about the combination, we talked about the operation how that gives to a system of Bravais lattice, which is having 14 crystals to a 7 crystal system which is there, the space groups we talked about and we ended up understanding the fact that in protein there are 65 space group instead of 230 because of the chiral environment present in protein from here, we will shift from direct space or real space to a reciprocal space. We will talk about Miller indices in the next class. Thank you very much.