Symmetry, Stereochemistry And Application
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Lecture No-53
Brief Introduction to Crystallographic Symmetry

Welcome back to the course entitled symmetry stereochemistry and applications. This is the last week of this course and as discussed in the previous week in this week we will talk about some of the aspects of crystallographic symmetry and we will try to understand the difference between molecular symmetry and crystallographic symmetry. See as this course is dedicated for symmetry and its application stereochemistry etcetera.

I felt that a brief introduction to crystallographic symmetry will be highly useful for all of you in your future courses. So, what you know about crystals?

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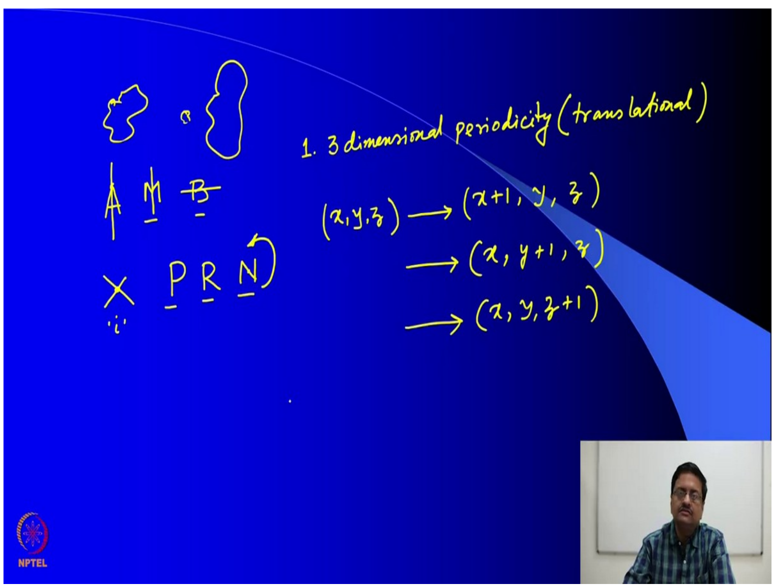

A crystal is a 3 dimensional array of objects and the object can have any shape any size and so on. So, the objects can be symmetrical like the letter A which has a mirror plane the letter M which also has a mirror plane or symmetric like a letter B which has a mirror plane or maybe something like a letter X which has an inversion center i. So, the objects can be symmetric by itself or there may be asymmetric objects like P, R these letters do not have any symmetry as such.

The letter N which actually has a 2 fold axis which if you rotate one 180 degree about the 2 fold axis it maintains the symmetry. So, you can have some objects without symmetry and some objects which have symmetry. Now the question is how these objects are arranged in 3 dimension this arrangement of objects in 3 dimension is the first point of symmetry that we encounter in X-ray crystallography.

So, the first point is the, 3 dimensional periodicity. So, this 3 dimensional periodicity means if you suppose have one object at x, y, z that is the coordinate of the center of gravity of that object. Then you should have one unit translation along x, y and z one object one unit translation along y and one unit translation along z and object that means whatever you have in this room here is translated along x you have one object along y you have another object and you translate it along z you have another object.

So, this 3D, 3 dimensional radio periodicity it is translational periodicity and this translational periodicity is the first point of symmetry that one should think of in any crystalline lattice because of this translational periodicity being implemented there comes a certain number of restrictions and those restrictions will lead to restrictions in the number of crystallographic symmetry elements and the point groups that can be considered in case of crystallographic symmetry.

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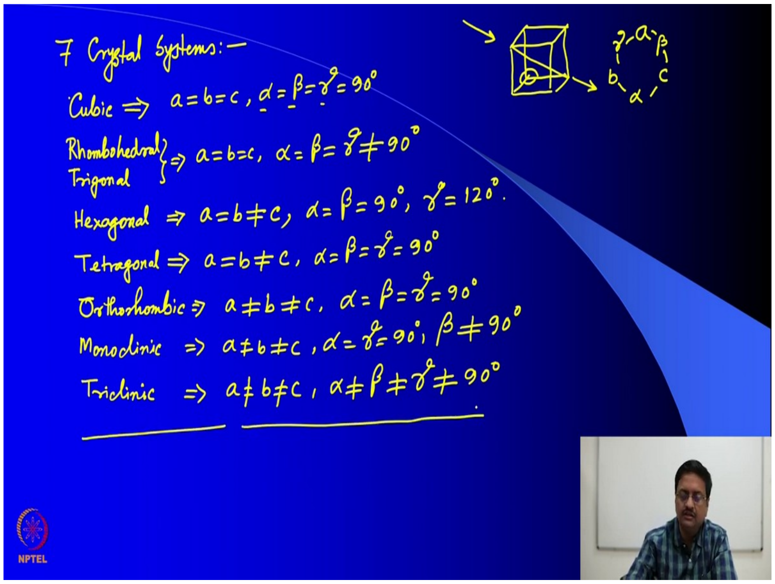

Some of you may be aware of different types of crystal systems. There are 7 different types of crystal systems in 3 dimension. And if we start from the highest symmetric which is cubic in case of cubic lattice the lattice parameter a equal to b equal to c and alpha equal to beta equal to gamma equal to ninety degree this a, b, c mean the edge lengths of a cube and this angles alpha, beta, gamma are the angles between x and y, x, y and z, z and x.

And this should be understood in this way if you write a, b and c and then opposite to a you write alpha opposite to b you write beta opposite to c you write gamma. So, the angle between a and c is called beta angle between a and b is called gamma and the angle between b and c is called alpha. So, now this in case of cubic all these 3 angles are same and a equal to b equal to c. Next lower symmetric crystal system is the rhombohedral it is also called trigonal.

Here, it is a equal to b equal to c alpha is equal to beta is equal to gamma. But, not equal to 90 degree you may be wondering how this is possible? This is possible if you apply a certain amount of force along the body diagonal of a cube and the cube gets distorted. So, when the cube gets distorted the edge lengths do not change. But, the internal angles will change get distorted and they will be deviated from 90 degree.

So, that particular shape is called the rhombohedral or trigonal unit cell, then next symmetric is called the hexagonal in this hexagonal lattice you can have a equal to b not equal to c. So, now one kind of difference in the cell dimension is incorporated here alpha equal to beta equal to 90 degree and gamma is equal to 120 degree. So, you see that now a symmetry is broken the symmetry of edge length is broken symmetry of the angle is also broken the next symmetric unit cell is called tetragonal.

So in case of tetragonal lattice a equal to b not equal to c alpha equals to beta equals to gamma equal to ninety degree the next less symmetric is orthorhombic where a is not equal to b is not equal to c alpha is equal to beta is equal to gamma is equal to 90 degree. Next less symmetric is monoclinic where a is not equal to b is not equal to c alpha is equal to gamma is equal to 90 degree and beta is not equal to 90 degree.

The lowest symmetric crystal system is triclinic where a equal to b equal to c sorry a not equal to b not equal to c alpha not equal to beta not equal to gamma and not equal to 90 degree as well. So, this is the lowest symmetric crystal system. So, these are the 7 crystal systems that are possible to be formed using the concept of translational symmetry elements being present in the crystal structure.

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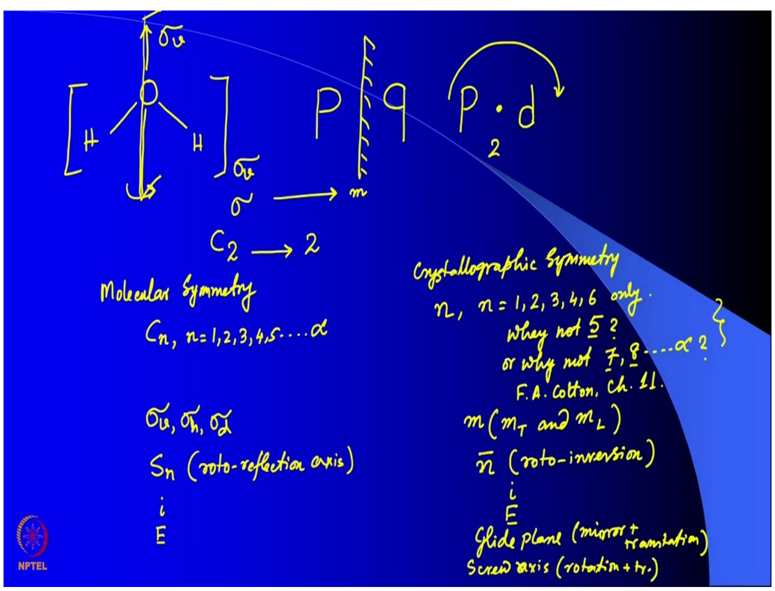

Now in addition to the translational symmetry elements there are other symmetry elements as well. One important aspect about the molecular symmetry versus crystallographic symmetry is that in case of molecular symmetry the symmetry elements fall on the object that means if you are talking about the symmetry elements of water molecule then the 2 fold axis that you have is passing through oxygen.

The mirror plane that we talk about contains the plane of the water molecule and also the perpendicular one which passes through that oxygen. But, in crystallographic symmetry the symmetry elements are either containing the object provided the object has that particular symmetry or the symmetry element is present somewhere in space to generate a symmetry related object. Suppose you have a letter P in space and you have a mirror plane somewhere here it generates an object P as a mirror image of P and this is the crystallographic symmetry mirror plane m.

So, in case of molecular symmetry whatever we write as sigma is represented as m. Similarly a 2 fold axis will be represented in case of molecular symmetry as C2. But, in case of crystallography we just write it as 2. So, suppose if you have an object here and a 2 fold axis which is perpendicular to the plane of projection like this. So, if you rotate the object by about this 2 fold axis you will end up getting this object right.

So, these 2 were related by a 2 fold axis. So, now as we knew that in case of molecular symmetry we had Cn axis with n equal to 1, 2, 3, 4, 5 dot dot up to infinity because we have C infinity axis. In case of crystallographic symmetry this principal axis Cn or the rotational axis of symmetry Cn is simply written as n and the value for n is restricted to 1 2 3 4 and 6 only why not 5 or why not 7, 8 up to infinity.

This I leave it to you for your understanding I can give you a reference where this problem is discussed is the book by F. A. Cotton, chapter 11 where a small simple geometric proof is given to show that y in case of crystallographic symmetry you do not have a 5 fold axis you cannot have a 5 fold axis or you cannot have anything higher than 6. This restriction of not having 5 or anything higher than 6 straight away comes from the requirement of 3 dimensional periodicity of the objects.

In molecular symmetry we had sigma v sigma h and sigma d. In case of corresponding crystallographic symmetry we have mirror which can be mirror transverse and mirror longitudinal or L m T or m L. So, we will discuss about this in detail when we talk about the symmetry elements of one dimensional lattice in molecular symmetry. If you remember we had Sn which is roto reflection axis.

In case of crystallographic symmetry we have n bar which is roto inversion axis in molecular symmetry we had i in crystallographic symmetry also we can have i. In molecular symmetry we had identity element E. So, here also we will have identity element E. So, in addition to these symmetry elements that we are similar or related to the molecular symmetry we have 2 different types of symmetry elements only specific for crystallographic symmetry one is called the glide plane which is a mirror with translational component and screw axis which is also rotation plus translation. So, we will slowly discuss about these symmetry elements in the next page.

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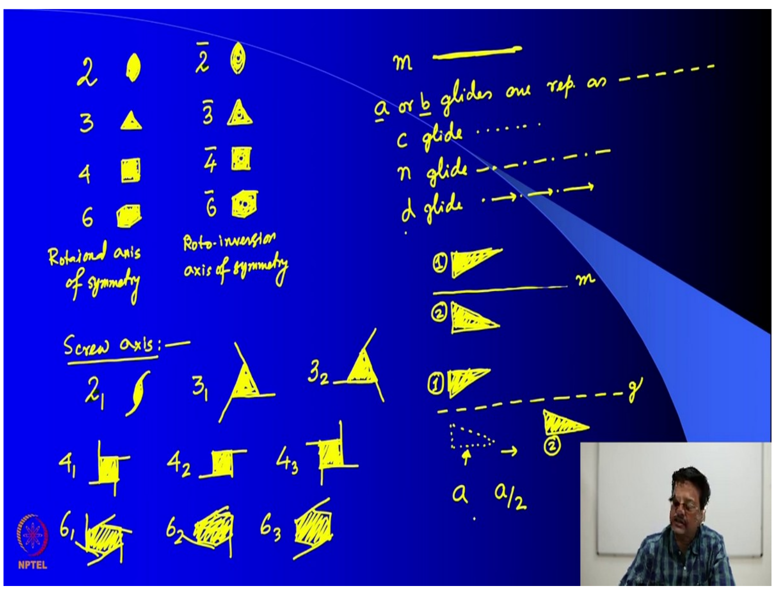

So, in the case of crystallographic symmetry we have certain notations that one need to learn first a 2 fold axis is represented as this, a corresponding 2 bar which is roto inversion is represented like this. Similarly a 3-fold axis is represented as a triangle and 3 bar is represented at this as a triangle with a center circle. So, you can now easily understand 4 fold should be represented as a square and the corresponding 4 bar is supposed to be represented as a square with a circular hole in the middle.

And the next symmetry element is 6 it is drawn as a hexagon like benzene and the corresponding 6 bar is a hexagon with a center circle as open circle. So, as I said these are rotational axis of symmetry and these are roto inversion axis of symmetry which means rotation is followed by an inversion that is done on the object. Then the next type of symmetry that we just discussed is the screw axis.

Screw axis is something like a screw which is simultaneously rotating and moving when you try to tighten a screw you are rotating the screw and in the process the screw moves forward. So, that means a screw axis is something where the rotation is associated with a certain amount of translation. So the 2_1 is the representation of a 2 fold screw which means 180 degree rotation and half the unit cell translation along the direction of motion.

So, this 2_1 is drawn like this which is similar to 2 fold. But, the 2 sides are extended 3_1 is drawn just like a 3 fold. But, the sides are extended like that the corresponding 3_2 is drawn as a triangle as usual. But, the direction of rotation is different which means 3_1 means one twenty degree rotation and one third translation 3_2 means 240 degree rotation and 2 third translation. Similarly 4_1 screw is represented by a square with the indication of a motion and a translation 4_2 is also represented as a square and with 2 sides extended indicating that the translation is half 4_3 is opposite to 4_1.

So, the direction of motion is shown opposite. So, when I am writing like this, this, this. So, it means the rotation is about the clockwise direction when I write the other side then it is anticlockwise direction rotation. So, you can understand what can happen for 6_1, 6_2, 6_3 and 6_4 will be opposite to 6_2 and 6_5 will be opposite to 6_1 a mirror plane is represented as a bolt line there are different types of glide planes a or b glides are represented as dashed lines.

C glide is represented as dotted line, n glide is represented as dot dash dot dash dot dash kind of notation and a d glide or diamond glide is represented as dot arrow dot arrow dot arrow etcetera. So, these different glides are based on direction in which the motion is associated. And in case of a glide the motion is along a in case of b glide the motion is along b in case of c glide the motion is along c for n glide the motion can be along any 2 directions like a and b or b and c or a and c.

In case of d glide the motion is along all the 3 axis in one 4th amount. So, to understand this glide let us try to draw some asymmetric object, suppose I draw a triangle like this if I have a mirror plane the triangle will be reflected here. So, this is a mirror plane. But, if we have a triangle and suppose we have a glide plane like this it essentially means that the triangle is first reflected and then translated along this direction halfway and the object is there.

So, here this 2 objects one and 2 are related by mirror here the object one and 2 are related by a glide plane g there is no object here it is just I have drawn it to show that the initially it formed a reflection and then it has got translated. So, this is the difference between the mirror plane and a glide plane glide plane is a mirror associated with a certain amount of translation and that translation is translation along the direction of motion and if the edge length is a the translation is a by 2.

So, if the translation is along the direction of a then the translation is of length a by 2 along the direction of a.

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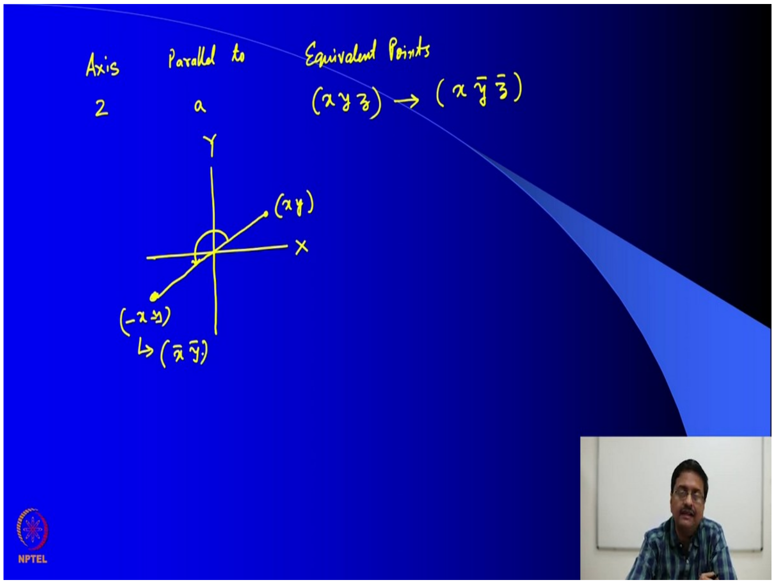

So when we see these different systems that we have and different symmetry elements that we can think of you understand that these symmetries are between the 2 objects. And when we try to apply the symmetry between 2 objects we generate a new object and that new object is having a different coordinate. So, just to give you an overview of how these coordinates get transformed let us take a simple a few simple example of some axis.

Suppose we have a 2 fold axis and it is parallel to a particular axis suppose you have parallel to a then the equivalent points if you have 2 object if you have the object at x, y, z and you apply a 2 fold axis about parallel to a then the 2 points will be x, y bar z bar which essentially means that in a coordinate system if you have suppose x here y there and z perpendicular to the plane of projection. You have one object here which is at a coordinate x y you rotate it by 180 degree that means 2 fold rotation the coordinate comes here and becomes minus x minus y.

So, in crystallography this minus x minus y is written as x bar and y bar. So, I will continue this from in the next lecture from here, thank you.