Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institution of Science Education and Research, Mohali

Crystallographic Point Groups and Space Groups
Lecture - 09
Understanding of Crystallographic Space Groups

Welcome back to the course of Chemical Crystallography. In the previous lecture we were discussing about the 32 point groups and we have learnt how to draw the stereographic projections of various point groups.

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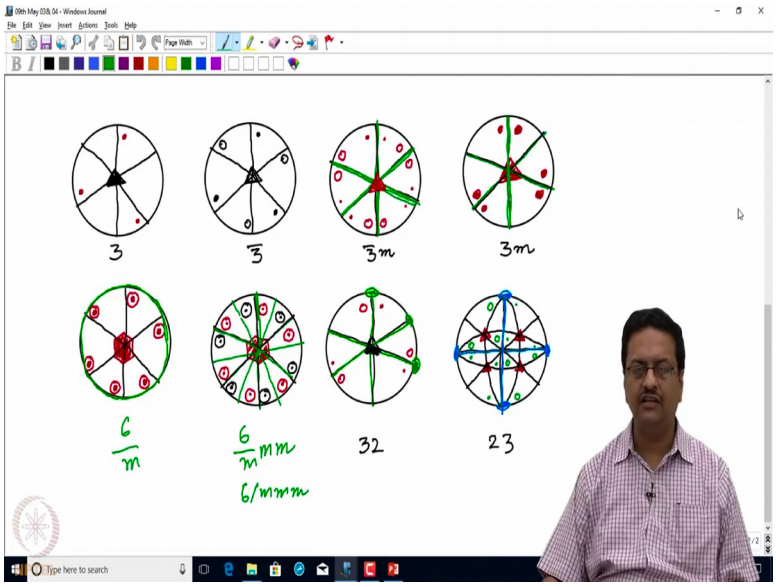

Starting with simple point groups and we ended up drawing the point group 23 as we you can see on the last part of the previous lecture.

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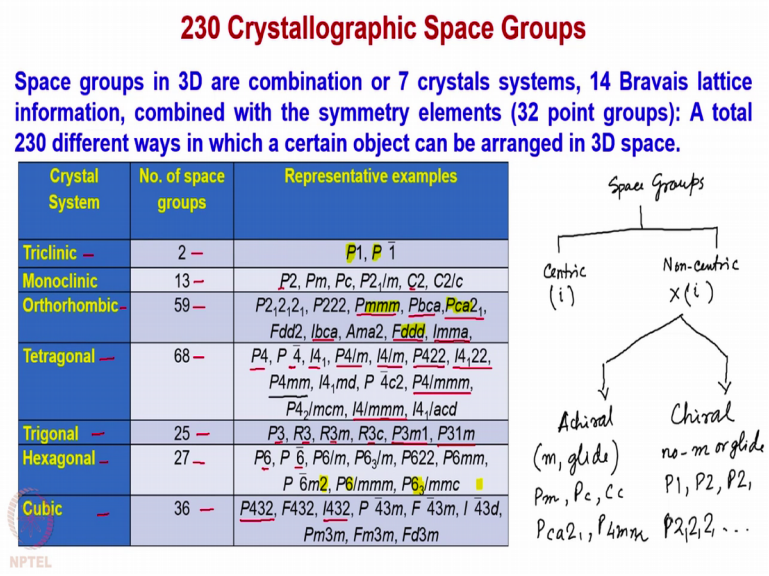

So, today we are going to start talking about the crystallographic space groups, as we have already indicated there are 230 crystallographic space groups and these space groups are the only ways in which the objects can be arranged in 3 dimension following the translational symmetry and all other possible crystallographic symmetry elements.

It incorporates all the 7 crystal systems and utilizes the lattice centering of Bravais lattice and incorporates the special crystallographic symmetry elements like different varieties of screw axis glide planes and so on. So, if you can concentrate here on the new table, we have categorized or classified these crystallographic point group a spaced groups in different types of lattices. Here we have under triclinic 2 space groups which are only P 1 and P 1 bar which means the first letter P stands for primitive and 1 or 1 bar stands for the corresponding symmetry that is present in that. So, 1 means there is no symmetry and 1 bar as we already know means the inversion center.

The next higher symmetry crystal system is monoclinic, under monoclinic there are 13 space groups possible with different lattice settings, I have given some representative examples here P 2, P m, Pc P2 1 by m, C,2 C2 by C these are examples of monoclinic space groups with various symmetry elements present. See there are 2 types of lattices possible in monoclinic primitive and C centered, so I have chosen both primitive and C centered lattices as representative examples in case of monoclinic there can be

centrosymmetric and non centrosymmetric space groups. The non centrosymmetric space groups are P2, Pm, Pc, C2 etc where you do not have center of inversion I.

Whereas in case of P2 1 by m or P2 by m or C2 by C where we have a combination of twofold and a perpendicular mirror it results into a centrosymmetric lattice or centrosymmetric crystal structure the next higher symmetry is orthorhombic. You can see under orthorhombic there are large number of space group possibilities simply because, in case of orthorhombic you have both primitive, body centered, face centered and one of the faces centered lattices possible. So, all 4 types of Bravais lattices are possible for orthorhombic system and then in orthorhombic system you can see the symmetry elements are 3 in number.

The first symmetry element that we see if it is a it is 1 axis whether it is a simple axis or a screw axis that first symmetry element signifies either it is if it is an axis it is parallel to x axis, if it is a mirror plane it is perpendicular to x axis. So, when we say for example a space group Pca2 1 it means it is a primitive lattice having a c glide perpendicular to x and a glide perpendicular to y and A 21 screw parallel to Z.

So, in the same manner if we think about the space group I mma, it indicates that this is a body centered lattice which means I the first m is a mirror plane perpendicular to A or perpendicular to x the second mirror is perpendicular to y and then the third 1 is a glide plane it is A glide perpendicular to C. So, accordingly we should then try to generate the symmetry equivalent points for these space groups.

Once again among these there are some space groups which are non centrosymmetric for example, P2 1 2 1 2 1, P222 Fdd2 these are non centrosymmetric space groups whereas, Pmmm Pbca Ibca Fddd these are Imma these are all centrosymmetric space groups. The next higher symmetry crystal system is tetragonal, as we have seen in the previous lecture the tetragonal system has a large number of possibilities of point groups, as a result it has a largest number of space groups that belong to tetragonal system and once again here you see that it can be P4, P4 bar I4 because, in tetragonal you can have primitive and body centered lattice and you can have point groups either 4 or 4 by m or 4 by mm.

So, there are tetragonal space groups like these as well, so when we see P 4 this means it is primitive and you have a fourfold axis parallel to Z, when we say P4 by m or I4 by m;

it means you have a fourfold axis along z and a mirror perpendicular to that fourfold axis. That means, it is perpendicular to z the P and I as usual signifies primitive and body centered lattices when we look at the space groups like P422, I4 1 22, it means there are other symmetry elements other than just the 4 which is parallel to z.

So, in case of P4222 sorry P422 in that case you have a fourfold parallel to z you have a twofold parallel to x another twofold parallel to Y. Similarly when we talk about I4 1 22 1 it means I have body centered lattice 4 1 is parallel to z and I have a twofold here and the twofold in the y axis, so both x and y are having 2 twofold sorry in this here to the twofold axis right. So, when we go to trigonal system we have 25, in case of hexagonal system we have another 27 the distinction between trigonal and hexagonal you can see that in case of trigonal system the highest symmetry is 3 fold while in case of hexagonal the highest symmetry is 6 fold.

So, by looking at 3 or 6 we should be able to distinguish whether it is a trigonal lattice or a hexagonal lattice and you see in the previous class we tried to distinguish between P3m1 and P31m in 2 dimensional lattice and here in case of trigonal we have similar situations. The final is cubic under which you have 36 point group a space groups and they are designated as P432 I432, remember these are just representative examples I have not listed all the space groups. So, here what we need to do is we need to go to any standard textbook and look at the table which indicates all the possible space groups that are there in crystallography and try to understand why 1 space group belongs to cubic and not the trigonal and hexagonal and so on.

So, at this point what we need to understand how to write these space groups, if you have noticed by now all the letters that I have written all the letters that are written here like P in all the cases mmm ddd ca with p. So, all the letters that we are writing those letters are all written in italics and the numbers that we have are non italics in nature. So, while representing these space groups using any document using word or power point, ones should use these notations the space groups wherever you have letters identifying the lattice centering or any symmetry element like mirror or glide those letters are written in italics and the numbers that is this axis 2 3 4 4 1 2 1 6 6 3 whatever I have written in normal font.

At this point I would like to also indicate that the crystallographic space groups can be subdivided into few ways, these space groups can be divided into 2 major divisions centric or centrosymmetric and non centric or non centrosymmetric space groups. Centric space groups will have inversion center i and it will not have inversion center i, but then there are point groups which do not have i but can have a mirror plane; for example, pm pc cc these are non centrosymmetric. Similarly P2, P2 1 2 1 2 1, P222 there are also non centrosymmetric, but without mirror planes.

So, the non centric space groups can be subdivided into a ring 2 different subclasses Achiral and Chiral Achiral space groups may contain a mirror or a glide in them and Chiral space groups will not contain any mirror or glide. So, the example of non centrosymmetric, but Achiral space groups are Pm, Pc, Cc, Pca2 1, P4 mm that are present here. But then the Chiral space groups are P1, P2, P2 1, P2 1 2 1 2 1 and so on we do not have any mirror plane in them.

The importance of this Chiral space groups are that all Chiral compounds will end up crystallizing in this Chiral space groups, in general this Chiral space groups the finding the number of crystals that we find crystallizing in different space groups the occurrence of Chiral space group is very less. Because, mostly the Chiral compounds adopt these Chiral space groups all other molecules which are not Chiral they can adopt centric or non centrosymmetric space groups which are Achiral in nature.

So, now since we have talked about these crystallographic space groups I would like to now show you how to draw these space groups in 2 dimensional representation the way we were doing it for 32 point groups.

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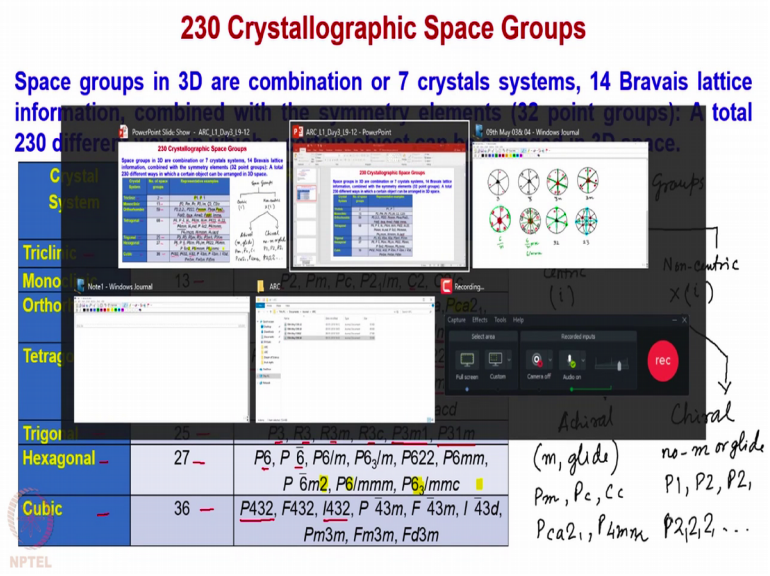

So, I will take some simple examples I will restrict myself mostly towards triclinic monoclinic and we will do 1 or 2 orthorhombic towards the end of the next lecture. So, now we will try to see how these simple space groups can be represented in a 2 dimensional figure.

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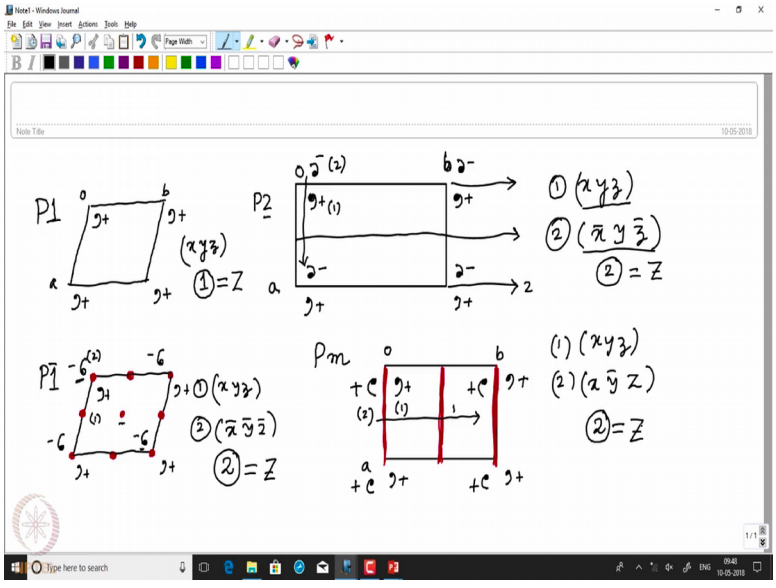

So, the first space group that we know is P1 which is primitive and there is only 1 symmetry that is 1 fold rotational axis of symmetry. So, this appears in case of triclinic lattice and as you know the triclinic lattice is nothing but a not equal to b not equal to C

angles are not equal to 90 degree. So, I have drawn a projection of oblique lattice with the o b and a as a projection plane of projection and now if I put 1 object with a plus sign which indicates that this object is somewhere inside the unit cell and the projection is falling on the 2 dimensional board, plus sign indicates that the object is above the plane of projection.

Since there is no other symmetry element if I just draw the translational symmetry related objects outside this unit cell, it will complete the present representation of P 1 space group. The next higher symmetry is P 1 bar, which means it has a center of inversion. So, once again if I draw oblique lattice I am not going to do anything wrong because, in case of triclinic the angles are not 90 and hence we can draw oblique lattice. So, just like before like P1 I am drawing the symmetry related objects first which is the translational symmetry that is there in P1 and now when we say that it is bar the center of inversion that we have comes at the corners of the unit cell as I have marking it as red.

So, the inversion related object if this was your unit cell, if the object is here and it is inverted against a particular origin it goes to the lower unit cell; that means it goes below the plane of projection, so as soon as something goes below the plane of projection we draw it with a minus sign. So, now we place the inversion related object for all the points that we have drawn with minus sign on it, this represents the P 1 bar. Now you see what has happened because of the symmetry related molecule here, the original molecule which is at the first point and the newly generated object there is a center of inversion at the center of this face there is a inversion center here.

So, these are the inversion centers which got generated at the centers of all those faces and at the center of the body. So, now if we try to write down what are the equivalent points present in these 2 lattices; in case of P1 you have only one object or only one molecule present in the unit cell. So, it has only one equivalent point x y z but in this case if you see there are 2 such there are 2 such atoms and these 2 are numbered as 1 and 2. So, the point number one represents x y z and point number 2 represents x bar y bar z bar.

So, this point number 2 which is here can be translated inside the lattice by doing 1 unit translation along b and then 1 unit translation along a. So, if we add 1 to y bar and 1 to z bar we end up getting the lattice, if the point inside the lattice and it is still x bar y bar z

bar with respect to a difference center of inversion. So, the next lattice that we would like to see is P2 in case of P2 it is primitive and it has a twofold axis of rotation and I am now drawing the a b face as the plane of projection and I am taking my object inside the unit cell as plus.

When I am saying P2 this 2 fold is along the unit axis b which means the 2 fold is here. So, now if we do a 2 fold this is my cube I have object here and the 2 fold is somewhere are there. So, if I do a 2 fold with this object it goes to the lower unit cell, so when it goes to the lower unit cell; that means, it goes to the plane below the plane of projection the 2 symmetry related object should be written as a minus.

Now, I would like to draw these objects with their corresponding translational symmetry, in all the 4 places and what we now see is that a new 2 fold is generated in the middle of the unit cell. So, this is the representation of P2 space group and now we have 2 point,1 and 2 as the equivalent points this point 2 can be moved inside the lattice by adding 1 along a. So, the equivalent points should be x y z and the second point is a twofold about the y axis; that means, it should become x bar y z bar because, y is the unique axis about which it is rotating. So, the coordinates of x and y should say x and z should change the sign and generate the 2 equivalent points.

So, here we have one equivalent point in case of P1, in case of P1 bar we have 2 equivalent points it is centrosymmetric here we have 2 equivalent points, but it is non centrosymmetric, how do we know it is non centrosymmetric? Because, we have 2 coordinates x y z and x bar y bar z bar sorry x bar y z bar they are not related by inversion symmetry. The next point group that we would like to draw is pm P again means primitive and m is a mirror and since it is a monoclinic space group this mirror is by convention perpendicular to 2 fold.

So, once again I will draw a rectangular lattice and it is like represented as origin here b and a. Now I am placing my object at 1 point here and drawing the corresponding symmetry related objects in the adjacent unit cells. Now as I said the mirror is perpendicular to b that means the mirror is along a, this red line is the mirror. So, if you apply mirror symmetry what happens if the object is here your mirror is here it gets reflected like that, but it still stays above the plane of projection. So, I am doing a mirror image but with a plus sign.

So, when we look at this representation what we find is that there is a mirror plane generated in to the midpoint of this unit cell. So, if the first point is 1 the mirror image is 2, the point number 2 is moved inside the lattice by adding 1 unit along b. So, the equivalent points for these are x y z and for the second point it is x y bar z because, the mirror is perpendicular to y and once again we see that there are 2 lattice points in this unit cell. So, whenever we are identifying these number of lattice points these number of lattice points are designated by a number called z.

We will see that this number z is highly significant when we are trying to identify a particular unit cell from x ray diffraction data and we are trying to calculate some parameters to see whether the unit cell that we are getting can fit our molecule or not. So, to do that we need a knowledge of this value z for every possible space groups that we can think of for the data that we are getting.

So, in this today's lecture we have learnt about the space groups, we have understood how the space groups can should be represented, if a space group is written how to understand, what kind of crystal system what kind of symmetry elements that are present in that space group and then we should be able to now identify a centrosymmetric and a non centrosymmetric space group. We should be able to identify a Chiral and Achiral space group and now I have just taught you how to draw these projections of these space groups in 2 dimension.

These drawings are there in international table of crystallography volume a with a similar notations present in that. So, in the following class we will continue learning these projections for other space groups because, some of them are bit complicated just if you see the diagram or drawing you may not be able to draw it yourself and that is why we need to do it during the lecture hours and I would like you to practice it at home.