Chemical Crystallography
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Crystallographic Point Groups and Space Groups
Lecture - 07
Crystallographic Point Groups

Welcome back to this course of Chemical Crystallography. In the previous class we were discussing about the 2 D lattices with symmetry elements and 2 D space groups. So, we will continue our discussion in this direction, but now we will try to draw these 2 D lattices with the symmetry elements only without placing any object or any compound in that; the way I was doing in the previous lecture where I was incorporating, a letter p which signifies the presence of a particular compound or a molecule or a chemical entity. So, we will try to draw these space lattices with symmetry elements only mentioned.

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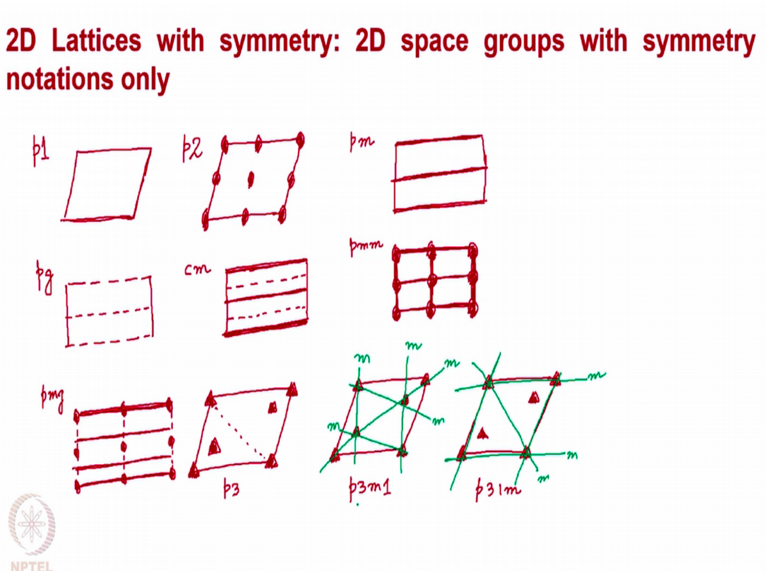

So, the first symmetry element that we have in 2 D lattice is just as we indicated p 1 and since there is no symmetry in this which means it has only a 360 degree rotational symmetry and nothing else. So, the oblique lattice we draw for p 1 lattice does not have any symmetry element indicated in that; but when we go to p 2 as we know 2 means it has a twofold axis of rotation and that twofold has to be identified by it is appropriate symbol.

So, we should draw the oblique lattice and then identify the twofold axis first at the 4 corners and because of the presence of 2 parallel 2 folds, the midpoint of these edges become twofold as well in addition the center of the unit cell a twofold is generated in the same manner. So, when we do the third one which is p m this p m indicates that it has a mirror plane a transverse mirror plane along the edge. So, now I am drawing a rectangular lattice with the bold line on 2 sides up and down and 2 vertical sides are non-bold. So, these 2 are mirror planes and as we have seen in the previous lecture because of these 2 mirrors 2 parallel mirrors a third mirror is generated in the middle portion at the middle of this unit cell.

In the same way let us try to draw pg; what is g, g is a glide plane and this glide plane is going to run in horizontal direction in a rectangular lattice the vertical lines are just lines and they are not mirrors. So, I am not making them bold I am just drawing them to join and make it a rectangular lattice, so the up and down edge indicates the glide again the glide plane is further generated in the middle of this unit cell and this is the notation for pg. Now, as we had done earlier cm where we have a centered lattice and then which it means that the lattice has one lattice point at the center of the unit cell, so this is the unit cell the mirror that we are talking about is located here that is at the in 2 sides and also in the middle as you have a lattice point in the middle of this unit cell.

Now, the presence of these 2 parallel mirrors would give rise to a glide in between, this was shown in the previous class with the letter p; see above we have p m. Now if we want to do p m m; that means, we have 2 mirror planes which are perpendicular to each other, which means all the 4 sides of the of this rectangular lattice correspond to a mirror plane.

So, if I want to highlight all the 4 sides all the 4 sides are bold, so these are the mirrors 2 parallel mirrors from up and down generates a mirror in the middle in the horizontal direction and the mirror which are perpendicular the middle point of that is also a transverse mirror. What is the result of this here we have 2 mirror planes intersecting like that, so when 2 mirrors intersect like this the point of intersection becomes a twofold axis. So, we have twofold at every point of intersection of these mirror planes.

So, this represents the 2 dimensional space group p m m with the symmetry elements only, now we will try to do 2 more which we did not do in the previous lecture 1 is p m g other ones are p 3 m 1 and p 3 1 m. So, let us first see how the pg p m g would look like, this involves 1 mirror and one glide. The mirror is a longitudinal mirror along the length and the glide is a transverse glide which is like this, so this dashed line indicates the glide.

So, as soon as we draw 2 parallel mirrors and the corresponding glide here, what happens is in the middle point a glide is generated and 2 mirror planes are generated at 1 forth and 3 forth. So, now at these points of corners and the glide and the mirror intersection points we generate a twofold and this is also there in the center of the unit cell. So, these are the 2 folds that are generated in this particular 2 dimensional space lattice.

In the previous lecture we saw that in case of a threefold lattice that is p 3, we have threefold axis at 4 corners and 2 more threefold axis in these 2 locations as if it forms a triangle and this threefold alternates these 33 folds to each other when it is rotated by 120 degree. Now, we will see 2 very similar but highly different 2 dimensional lattices one is designated as p 3 m 1, in this case as just like p 3 we have threefold axis at all the 4 corners and exactly same way 3 folds at 2 D places in the middle of the lattice and then what we have is per mirrors and in this particular case the mirrors that are there are through all the threefold axis in concern.

So, these are all mirror planes so what we have here is that the 3 folds all of them contain a mirror plane in different direction, the corresponding other 2 dimensional space group that we can construct which is p 3 1 m has threefold axis at same places. But the locations of the mirrors are such that not all the threefold axis contain a mirror plane, so how is it visualized let us take a different colour and show it in the same manner. So, the edges are the mirror planes and the diagonal which does not contain the threefold is another mirror plane.

But the 3 folds which are inside the unit cell do not contain any mirror plane along them, so these 2 p 3 m 1 and p 3 1 m are very similar, but significantly different 2 dimensional space groups that one can construct. Why do we need to know all these because, in 3 dimension also we have space groups of this kind. So, the location of mirror plane changes the 3 dimensional orientation or arrangement of molecules in those lattices and gives rise to 2 different crystal structures.

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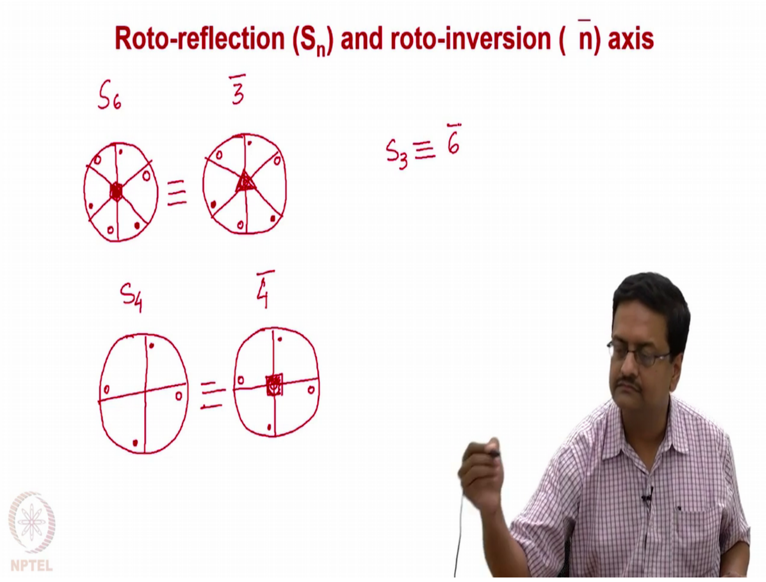

At some point of time in the previous lecture we discussed about the Sn and n bar axis Sn is a roto reflection axis in molecular symmetry while in crystallography, similar axis is called roto inversion which is written as n bar. So, let us see how these two different notations are going to result into similar diagrams which indicate that some of these Sn are same as n bars. Let us see, what happens if we try to draw S 6 what is S 6 S 6 means it is 60 degree rotation followed by a reflection perpendicular to a mirror perpendicular to a mirror which is perpendicular to your S 6 axis.

So, if this is a S 6 axis the mirror is here. So, now if I have any object at this point and I am rotating this object by 60 degree and then reflecting it goes below the plane. So, as soon as some object is rotated and reflected it goes below the plane, so the object which is above the plane is written as a closed circle, the object which is in the below the plane is written as open circle. So, like this let us construct a diagram first I divide this circle into 6 parts.

Now, if I start from here I rotate it by 60 degree and reflect. So, my angle of rotation is perpendicular to this plane of projection so this is my 6 fold axis, which is perpendicular to the plane of projection. So, as a result if I rotate and reflect the plane of reflection is my plane of projection, so when I am reflecting this point should go below the plane and become open circle we do the operation once again rotate that open circle do a reflection it comes above the plane, because it was here rotation reflection rotation reflection rotation reflection. So, every time I reflect it changes the plane.

So, again rotation and reflection makes it close circle rotation and reflection makes it open circle, let us see what happens if we do the it for 3 bar what is 3 bar 3 bar indicates that 120 degree rotation followed by inversion. So, if I have this axis here I rotate the object from here like this 120 degree and then if we invert across the center of inversion the object comes in the lower hemisphere. So, once again it becomes open circle, but you see it is not a reflection which brings the molecule here it is rotation and inversion, so it goes somewhere else exactly on the opposite corner.

So, 1 thing in we draw a circle divide it into 6 parts and this is my 3 bar axis so I should draw it accordingly. So, when I start from this closed circle I should rotate it and bring it here that is 120 degree rotation followed by inversion across the center of inversion it goes there and becomes an open circle; then again you rotate that open circle by 120 degree it should come here as open circle. And then, when I am reflecting it should go and get reflected as across circle again I do 120 degree rotation followed by inversion the open circle becomes a closed circle, then again this open circle is rotated by 120 degree to this point and inverted it comes here.

Again I rotate it by 120 degree and do an inversion it comes here, so what we can see here in these 2 figures is that they are one and the same; that means, the molecular symmetry S 6 is equivalent to crystallographic symmetry 3 bar, let us do the same exercise for S 4. What is S 4? It is nothing but 90 degree rotation followed by reflection, so when I am doing 90 degree rotation I divide this circle by in 4 parts.

I start with a point here and rotate it by 90 degree and then take a reflection. So, by taking a point here rotating it by 90 degree and taking a reflection it goes to the lower hemisphere, so it changes the plane. So, it becomes an open circle then again we do the same we rotated by 90 degree and take a reflection it comes to the upper plane or above the plane. So, it becomes flow circle do it once again another 90 degree rotation followed by reflection takes it there as open circle.

Let us see what happens if we do the same operations in terms of 4 bar, what is 4 bar again fourfold rotation followed by inversion. So, we should draw the symbol for 4 bar and now we start with a closed circle what we do is we rotate this closed circle by 90 degree and do inversion. So, by inversion it goes across the center of inversion goes to the other side and becomes open circle then again we rotate it by 90 degree do an inversion it becomes closed circle.

Then again we do it another 90 degree and invert it becomes open circle, so this left hand side drawing indicates S 4 the right hand side drawing indicates 4 bar. So, this these 2 drawings are again same which means S 4 is equivalent to 4 bar molecular symmetry S 4 is equivalent to crystallographic symmetry 4 bar. I hope you understood the logic behind these drawings, so I would like you to try and draw the same form S 3 and see that whether it is equivalent to 6 bar or not.

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32 Crystallographic Point Groups

Sl. No	Crystal System	Crystallographic Point Group	Equivalent Molecular point group
1	Triclinic	1	C_1
2		$\bar{1}$	C_i
3	Monoclinic	m	C_s
4		2	C_2
5		2/m	C_{2h}
6	Orthorhombic	mm	C_{2v}
7		222	D_2
8		mmm	D_{2h}
9	Tetragonal	4	C_4
10		$\bar{4}$	S_4
11		4/m	C_{4h}
12		4mm	C_{4v}
13		$\bar{4}2m$	D_{2d}
14		422	D_4
15		4/mmm	D_{4h}
16	Trigonal	3	C_3
17		$\bar{3}$	S_6
18		3m	C_{3v}
19		32	D_3
20		$\bar{3}m$	D_{3d}
21	Hexagonal	6	C_6
22		$\bar{6}$	S_3
23		6/m	C_{6h}
24		$\bar{6}m2$	D_{3h}
25		6mm	C_{6v}
26		622	D_6
27		6/mmm	D_{6h}
28	Cubic	23	T
29		$m\bar{3}$	T_h
30		$\bar{4}3m$	T_d
31		432	O
32		$m\bar{3}m$	O_h

Laue groups

Now, in this particular slide I have incorporated all the 32 space point groups that we encountered in crystallography and along with that we have the corresponding equivalent molecular point group symbol for all these 32 point groups in crystallography. And you see, that these point groups are denoted with the corresponding denoted with the corresponding crystal systems.

So, under triclinic we have 1 and 1 bar and the corresponding point molecular point groups are C 1 and C I which means in case of one there is no symmetry other than n fold rotation which is 360 degree rotation, onefold rotation and in case of 1 bar you have only inversion symmetry and nothing else under monoclinic. There are 3 different point groups m 2 and 2 by m, whenever we say m it is only a mirror when we say 2 it is just a twofold and when we say 2 by m it means it is a combination of twofold along b and the mirror is perpendicular 2 b by convention.

The corresponding molecular point groups are cs C 2 and C 2 h then when we move to orthorhombic once again we have 3 point groups mm 2 2 2 and mmm. So, when we say mm; that means, we have 2 mirror planes which are perpendicular to each other when we say 2 2 2 you have 3 2 folds perpendicular to each other and when we say mmm then that means, you have 3 mirror planes perpendicular to each other 1 2 and third one is like this.

So, the corresponding molecular point groups are written here as C 2 v D 2 and D 2 h, now in tetragonal you can see there are larger number of point groups because, there are different possibilities we can have 4 4 bar 4 by m 4 mm 4 bar 2 m 4 2 2 4 by mmm and the corresponding molecular point groups are listed here. In case of tetragonal lattice the unique axis is C because your A and B axis are same and C is the unique axis along which your fourfold lines.

So, when we say 4 or 4 bar that 4 or 4 bar is parallel to C, so as soon as we say 4 by m as here it means you have a fourfold axis along C and the mirror perpendicular to C. In contrast to monoclinic where the twofold is unique axis is parallel to B and the mirror is perpendicular to B, in case of tetragonal the axis C or Z axis is the unique axis. So, 4 is along Z or along C and the mirror is perpendicular to that when we say 4 mm it means we have 1 fourfold axis along C, but then there are 2 other mirrors which contains that fourfold axis 1 is like this the plane I am showing like this and then the other plane which is perpendicular to that.

But there is no mirror perpendicular to this fourfold, so these 2 mirrors which are written here as 4 mm these 2 4 mms these 2 mirrors are parallel to your fourfold axis, then we have 4 bar 2 m again 4 bar is are on C 2 is along 1 of those A or B which are same and neither is 1 mirror which contains the 4 bar axis then you have 4 2 2 which means you have a fourfold axis and 4 2 folds perpendicular to that fourfold axis. So, we just write 2 of them and then the last 1 is 4 by mmm where you have a fourfold you have a perpendicular mirror and then you have 2 parallel mirrors containing the fourfold axis.

So, this gives you total 15 crystallographic point groups on the left hand side of the table, the right hand side of the table has the point groups for higher symmetry systems crystal systems like trigonal hexagonal and cubic and these are again cell flex explanatory 3 3 bar 3 m 3 2 3 bar m and so on and the 6 6 bar and all that what is interesting here is that I have identified some of these space groups with yellow highlight. These yellow highlighted point groups 1 2 3 4 5 6 7 8 9 10 11 those 11 highlighted point groups are called as Laue groups.

Which identify the symmetry of that particular type of lattice and these Laue groups can be identified, if we take a rotation photograph of a crystal. So, what do we mean by rotation photograph a rotation photograph is the diffraction pattern of a crystal, when the crystal is placed in front of the x ray beam and the crystal is rotated by 360 degree at a given speed maybe in 1 minute you rotate the crystal by 360 degree and shine x ray on that.

The diffraction pattern that comes out of that will have a symmetry which corresponds to the corresponding Laue symmetry of that particular crystal lattice. So, here what we see 2 point groups which are highlighted in sum 3 2 and 2 3 they look similar in the way we write, but they are entirely different one is 3 2 belonging to a trigonal system; while the other one is 2 3 which belongs to a cubic system. .

In case of a cubic system the threefold axis is the one which passes through the body diagonal, in case of trigonal also this threefold axis is one which passes through the diagonal. But the systems are different because the angles are not 90 degree, the angles are not 90 degree and that is why these 2 are different and we will see how to draw these 2 diagrams using a crystallographic projection that a stereographic projection of these point groups in the next class.

So, today we have discussed about the 2 dimensional lattices, how to draw those 2 dimensional lattices on a plain of paper identifying their symmetries then we discussed about roto inversion and roto reflection axis and we have shown some cases where the roto inversion and roto reflection identified. So, that they are identical and then we discussed about the 32 point groups that are found in these crystal structures. I think one has to really go through this using a textbook, so that the orientation of different symmetry elements and the mirror planes twofold axis threefold axis will be clear if you go through a textbook.

So, we will study in the next class the stereographic projections of some of these point groups and we will learn how to present this 32 point groups in a plain sheet of paper.