Symmetry, Stereochemistry And Application
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture No-56
3D crystallographic Point Groups and Space Groups

Welcome back to the course entitled symmetry stereochemistry and applications. In the last lecture we have discussed about the possibilities of different 2 dimensional space lattices and before going to the next topic I would like to quickly discuss about a problem which I gave you in the first lecture. I asked you to find out why tetragonal face centered lattice is not a different lattice rather it is something else. And maybe some of you have found out and some of you have not found it out.

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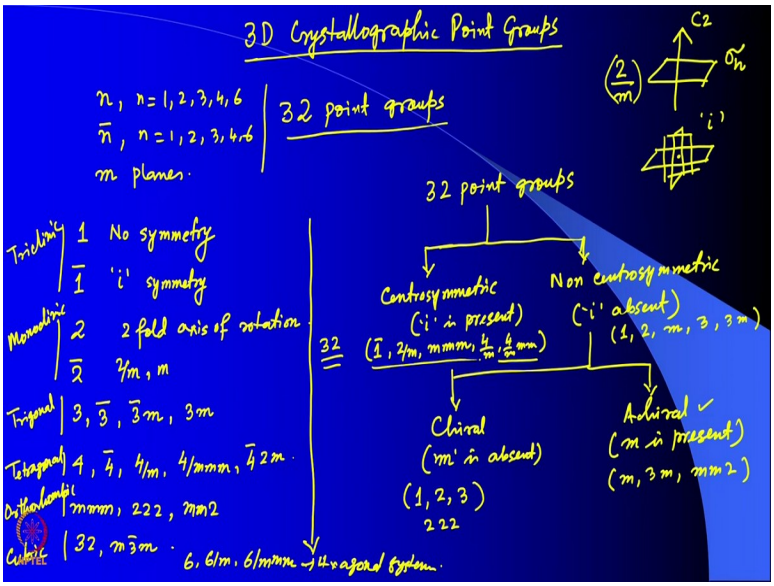

So, for all the students I would like to drop the tetragonal F lattice and discuss why tetragonal F lattice is not one of the bravais lattices. So to demonstrate that I first need to draw nicely a tetragonal lattice and then convert it into a tetragonal face centered lattice and from there we can start. So, this is a tetragonal lattice and when I say it is face centered it essentially means I have objects at all the faces all the corners and center of all the faces.

So, this is the Face center tetragonal lattice just one address the problem that a face center tetragonal lattice does not exist we extend this tetragonal face centered lattice in the next unit cell. So, what I am trying to draw is I am trying to draw 2 tetragonal face centered lattices side by side these are 2 tetragonal face centered lattices drawn side by side. Now if I try to redraw this unit cell using green colour slightly differently.

Now if I ask you what is the volume of the original tetragonal lattice? You would say that it is a into a into c is a square c that is the volume of the original tetragonal unit cell. What is the volume of the modified tetragonal unit cell with green colour? The edge length is nothing but root 2a. So, it should be root 2a square into c that means this sorry it will be root 2a by 2 that is a by root 2. So, the volume of that unit cell should be a by root 2 square into c that means half a square c.

So, the green tetragonal lattice has a smaller volume compared to the yellow lattice that means we should consider the smaller volume for as a repeating unit not at the bigger volume and then when we look at the smaller volume tetragonal lattice which is green one you have atoms at 8 corners. And the face center atom which was there is now the body centered atom of this tetragonal unit cell.

So, this is a tetragonal I lattice not a tetragonal F lattice. The F lattice has a double volume compared to the I lattice and therefore we should consider this as I lattice and not as an F lattice. So, this is why we do not have a tetragonal face centered lattice as one of the bravais lattices. Now let us try to see what are 3 dimensional crystallographic point groups. These point groups that are there in 3 dimension are formed by the n fold axis where n is equal to 1, 2, 3, 4 and 6 with the n bar axis where again n equal to 1, 2, 3, 4 and 6 and in combination with those you will have mirror planes.

So, these symmetry elements will give rise to 32 point groups, a full list of point groups can be found in any textbook for example F. A. Cotton's book that I have been referring to in chapter 11. So, the most unsymmetrical point group is 1 that means no symmetry. There is no symmetry

in the unit cell other than a 360 degree rotational symmetry, the second symmetric point group should be one bar which means it has inversion symmetry.

So, a molecule and its inverted object is present in the unit cell, the next possible higher symmetry could be 2 is written as 2 that is it has only 2 fold axis of rotation the next point group can be 2 bar then you can have 3 and 3 bar then one can have 3 bar associated with m there can be 3 associated with m and so on with 3 fold symmetry. And the higher point rules can be like 4 4 bar 4 by m 4 by mm 4 bar 2m belonging to tetragonal systems and then you can have mmm 222 or mm2 for orthorhombic systems.

And some space with the point groups like 32 m3 barm etcetera for cubic systems. So, like that there will be total 32 different point groups identifying different crystal systems say for example these are for triclinic, 2 2 bar 2 by m only m. These are for monoclinic. These are for trigonal or rhombohedral this for tetragonal these for orthorhombic and some for cubic and of course if you have 6, 6 by m 6 by mm for hexagonal systems.

So, these 32 point groups can be divided among in terms of center of inversion. So if you have inversion symmetry then we call it as centrosymmetric, I is present. And the other one is non-centrosymmetric that means inversion symmetry absent and then in this non-centrosymmetric point groups there can be 2 different types chiral and achiral. Chiral means mirror is absent and achiral means mirror is present.

So, when we try to identify these point groups in terms of center of inversion for centrosymmetric point groups we can write as 1 bar 2 by mmm 4 by m 4 by mmm these things are centerosymmetric because these point groups contain an inversion center. So, what you will see that if you do the higher level crystallography course there you will get to see that when you apply 3 mirrors it will immediately give rise to the inversion center when you have a 2 fold axis and a mirror perpendicular to that 2 fold axis that gives rise to a center of inversion.

So, when we write this 2 by m means you have a 2 fold axis and the mirror plane is perpendicular to that 2 fold axis which is equivalent to suppose in molecular symmetry C2 and a

plane which is perpendicular to your C2 is written as h. So, it is equivalent to have a C2 h point group in molecular symmetry. So, this is 2 by m in crystallography when you say mmm that means you have one mirror like this you have one mirror like that and you have a third mirror like this 3 meters when they intersect at one point that point becomes the inversion center.

So, these point groups which I have written here are centrosymmetric because they have inversion centered the point groups which I am writing here for example I 2 m 3, 3m all these they belong to non centrosymmetric space groups because they do not have center of inversion. So, here these point groups that you have which are non-centrosymmetric among them some of them which do not have a mirror is called the chiral point groups.

And that chiral point group can be 1, 2, 3 these things on the other hand the one groups which are containing mirror like m 3m mm2 etcetera these are called the achiral point rules but non centrosymmetric and they are called the achiral point groups and in case of chiral one can also write 2 2 etcetera. So, the point groups can have chirality and a chiral compound will always try to go and crystallize in chiral point group and eventually they will be crystallized in chiral space groups. So, now one may be asking what do, we mean by space group.

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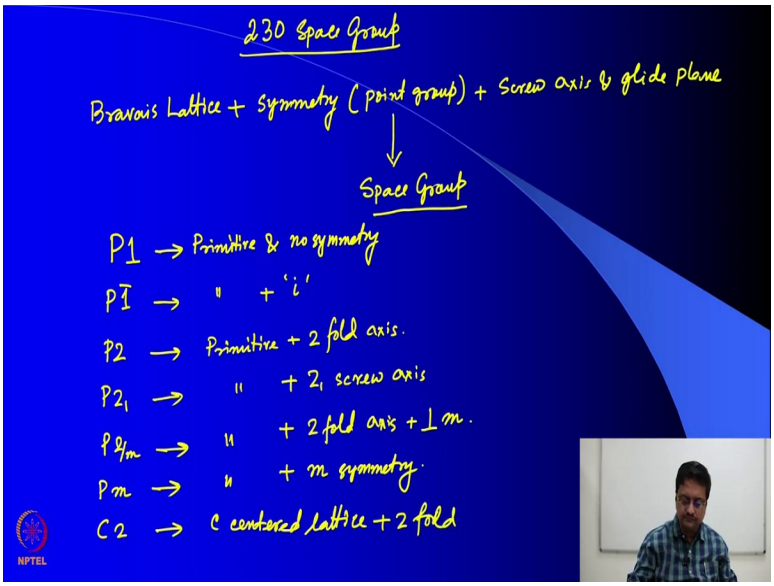

As I indicated in one of my earlier classes that when you combine the bravais lattice information with the symmetry of the lattice that means the point group. And the additional symmetries that

may be present like screw axis and glide planes then what we get is a representation called the space group. This space group is again restricted in number as you can see there are 230 space groups and these space groups represent all the seven different crystal systems and have different chiral lattice information.

So, these space groups are written like this simplest one is P1 which means it is primitive and no symmetry that means there is no symmetry element and it belongs to point group one, P1 bar means primitive plus i the next point group the space group one can think of is P2. So, it is primitive plus have a 2 fold axis. One can have $P2_1$ which means primitive plus 2_1 screw axis. Similarly P2 by m means primitive plus 2 fold plus perpendicular mirror.

Similarly Pm would mean primitive plus m symmetry mirror symmetry. So, if you write C2 now it means a C centered lattice and a 2 fold axis of symmetry. So, like this one can continue and write 230 different possibilities for space groups.

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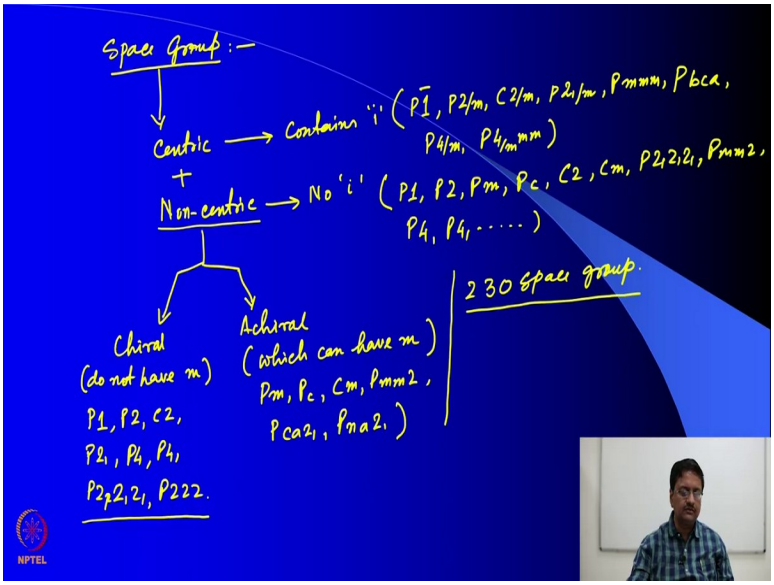

So, in this case we now have gone beyond the concept of point group because the point group is related to the molecular symmetry and then the point group is related to the symmetry elements that are present in the unit cell without considering the translational symmetry elements like the glide planes and the screw axis. So, this space groups can also be centric and non centric symmetric.

Centrosymmetric means contains inversion symmetry contains i in it non centric means no i that is there is no inversion symmetry present in the lattice. This non-cyclosymmetric once again can be subdivided as chiral and achiral. So, when we say that centrosymmetric it contains i one can identify some point groups here P1 bar P2 by m C2 by m $P2_1$ by m Pmm Pbca P4 by m P4 by mmm in all these which has the inversion symmetry are called the centrosymmetric point groups.

Non centrosymmetric point groups can be P1 P2 Pm Pc C2 Cm P211 Pmm2 P4 $P4_1$ many such combinations. So, now when we talk about the chiral point group the space groups. Chiral space groups are those non centrosymmetric space groups which do not have a mirror symmetry and achiral space groups are those non centrosymmetric which can have mirror symmetry. So, achiral is belongs to non centric but can have mirror and chiral do not have a mirror plane. So, examples are P1, P2, C2, $P2_1$, P4, $P4_1$, $P2_12_12_1$, P222 these are different chiral space groups.

Whereas Pm, Pc, Cm, Pmm2, $Pca2_1$, $Pna2_1$ these are non centrosymmetric but achiral space groups. So, when we try to crystallize a compound and then we know that the compound is a chiral molecule then we will end up getting one of these space groups which belong to chiral I am just giving you some examples of chiral space groups it is not only limited to these space groups which I have indicated here.

Rather it has a large number of space groups which belong to chiral a large number belongs to achiral and a certain number belongs to a centric space group all together there are 230 space groups that are possible. So with this I would like to conclude this course saying that the symmetry elements that we have learnt in the beginning of this course for molecular symmetry can also be extended.

And then the knowledge can be used to understand the crystallographic symmetry and one thing that one should always remember that the molecular symmetry that you have learnt contain elements contain the object. That means the symmetry elements always pass through the object whereas in case of crystallographic symmetry the symmetry elements are in general outside the object.

And those symmetry elements relate the 2 objects located in space and in certain cases where the symmetry element of the object is matching with the symmetry of the lattice and they are coincident then you get the molecule only represented as half or one third or one 4th whatever the case may be. So, I hope you have enjoyed the course and I do not want to extend this discussion on crystallographic symmetry because it is the beyond the scope of this course.

And those who may be interested to learn more about crystallographic symmetry and X-ray diffraction I have offered a different course dedicated for X-ray crystallography. So, those may attend that particular course called the chemical crystallography and that is generally offered in the August semester. So, I hope you have enjoyed the course if you have any problems you have doubts and questions please drop email to me I will be happy to answer. And I wish all of you a very happy year ahead and I wish you all the best for your final exam, thank you.