Symmetry and Group Theory
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Lecture No.1
Symmetry point group: Introduction

On this course as I hope you know because it was in the course after is all about symmetry in chemistry right. So, everybody knows qualitatively what symmetry is what we learn here is symmetry is one way of using mathematics. Symmetry is a beautiful subject, symmetry is all about beauty and we will all about numbers where something is beautiful are not depends on whether it as the correct propositions. So, that is what you are going to learn here in this course. We are going to learn how to use numbers to figure out many things about molecules as I say beautiful subject.

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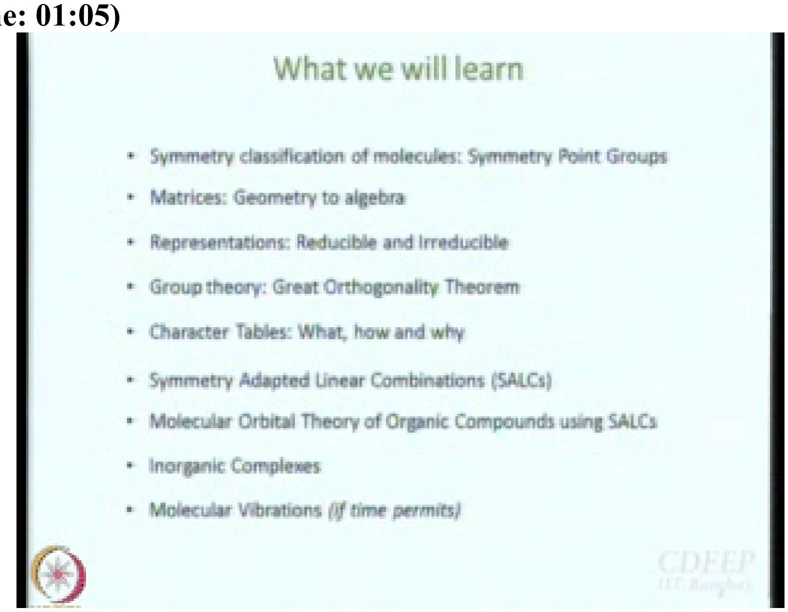

So, this is what you are going to learn roughly to start with today we will start itself will perform a symmetry classification of molecule and learn what are symmetry points groups. So symmetry points groups are basically system in systematic nomenclature of molecules right. I had teacher with whom I studied something at one point of time his name is Bupinthranath Banerjee he use to stay in Bupinthar Avenue a state in Calcutta and his father's name was Ram Banerjee.

So, his friends systematic nomenclature of the of this person they just started calling Bupenpalli Ram Bupen, Bupenpalli stays in Bupen avenue and Ram is his father name and own name his Bupen there is systematic nomenclature. All chemist or student of chemistry are familiar with

IDST nomenclature. So, you are going to learn similar kind of nomenclature and you see many disarray molecule which do not really think that they are close to each other in terms of chemical properties.

They actually belong to same family as far as symmetry is concerned and these families will be called symmetry point groups. I think some of you might already know how to work out symmetry point group for them it will be revision for those do not know we learn how to do this today. Next what will do is this you talk about symmetry you talk about turning things and reflecting things and doing inversion and all that is geometry right.

Symmetry is not good enough for our purpose because we cannot go on for drawing pictures all the time. So what we need to do is that we need to translate this geometrical understanding into the language of algebra. And as we see, here we are going to do this translation is by using matrices. What will age matrices what we will do is we write a matrix for every symmetry operation and this is going to translate from geometrical operation to algebraic quantities.

And there is something which will make our job really very simple. So, as you will see first of all we determine the family of the molecule and then we will work out the kun view of the molecule. Depending on how they behave in terms of symmetry operations. I think everybody has seen some kunley at some point of time or the other that is not easily to write right. It has very strange symbols.

Part of this perhaps to communicate to be very difficult to say only out will be going to very mysterious. But then as you see it is not very difficult to arrive at those kunley's we are going to call them character tables right. Before we get to character tables we have to learn what are representations? Basically once you like the Bupenpalli Ram Bupen if you want to best over a person you have to oscillate the state of properties and it defined it properties for that persons.

And there is deformed molecule as well and when we do that we will see that many different kind of representations will come out. Representation is essentially is a collection of matrices or else we will see point out to a collection of numbers right. And then there can be big representation broken down to smaller ones and there will be representation that cannot be broken down any further. Representation that can be broken down will be called reducers representation.

And the representation that cannot be broken further the fundamental ones they will be called irreducible representations. And when we go there you are going to learn these irreducible representation behave like unique vectors in orthonormal space. They behave like set of orthonormal unit vectors right and that is where you are going to use this Big theory and this theory particularly we are going use this big theorem this is called grate Orthogonality theorem.

Great orthogonality theorem is really great because we have not gone any further we would not have that character table, so would not have this particular branch of chemistry at all ok. Using this orthogonaltiy theorem we see how we can work out what are called character tables. How you will do it? What they are and of use these character tables are? I have told you character tables are like kunlays of the molecules.

So, if you are believer in astrology say that kunley can tell you all out yourselves right. How much marks you will get in this particular courses how tall you will be, how long you will you live so and so forth. So, you see all character tables where been illustrious, all character tables can actually tell us about many properties of the molecules. Which one will give you idea and which one will not give there what will be the properties and what will be the spectrum look like.

We have to consider at least one spectrum and so and so forth. So, before we go there we learn to do something else. This is a very useful technique we will learn to generate what are called symmetry adopted linear combinations. Physical chemistry class linear combinations here what we will do is linear combinations of things that have the similar kind of symmetry.

And once we learn how to generate symmetry adopted linear combinations then the scope becomes really large. So, what we will do after that is that you can venture into something as general as molecular orbital theory. When you say bonding we generally think of quantum mechanics right. We think of equations and then brackets and all that. What we will do is that we are going to take a different approach to a corresponding of course all the quantum mechanics still will be there.

But we will try to develop more pictorial representation of bonding with the help of the SLC’s and we will see that will be combined and what we will learn in courses like 4 to 5 which for those who are new to the system is really the chemical bonding course of our department is to be studied in the fourth year or first year depending on which course you are in. Then we are not going into the content in organic chemistry only we will like to venture into further into more complicated systems we talk also inorganic complexes.

And essentially we are going revisit many things you already know. Today we took entire distortion to know about crystal fill theory, you know about Tendique right; you know perhaps we know about molecule orbital theory of inorganic complexes is it not. What we will do is just take little more informed approach of the same problem. I think everybody knows an octahedral field, the orbital splits into the T2G and EGX's, so, here we are going to learn why it is called T2G and why it is called EGX and how symmetry as a role to play here.

And the whole premise of this is that symmetry and degeneration are hand to hand. I will seal a particle in a box, two dimensional particles in the box right. Think of two dimensional particles in the box. Let us start with a square box and let us think of the 1 2 and 2 1 level. Square box this side is A that side is B quantum mechanics for this side is 1 and that side is 2. This is one case and the other case is quantum number of that side is 1 and this side is 2.

We have same energy or different energy when it is a square box. So, I do not even remember the what I remember is n square by n square dependence right, n square by n square , so A on this side is equal L on the other side what will happen 1 by L square will be common will come outside the bracket and you will be left out n1 square + n2 square. Now it does not matter all come outside the bracket and you are left with n1 square + n2 square.

But does not matter whether it is n1 square + n2 square or whether it is n2 square + n1square one and the same ok. Now think of rectangular box, rectangular box is either symmetric than square box now what happen l1 is not equal to l2. Now see n1 by l1 square + n2 by l2 square and n2 by l2 square + n1 by l2 square are not the one and the same you believe me on that right. Which one will be more and which one will be less depends on what on l1 and l2 right which is longer l1 or l2 ok. So, see this is very simple example where more symmetric system is degenerated.

And less symmetry system is non degenerated symmetry and degeneration goes hand in hand. Now if I come to the simple example to talk about may while one step simpler than that think of a free Machaline. A free Machaline as infinite number of element of symmetry, infinite number of symmetry operation right because it is a sphere a perfect shape right what happen there is orbital’s are degenerated. Now when I place this spherical machaline in even in octahedral filed which is actually highly symmetric.

It is still in very less symmetric environment compare to what it was in absence of field right. So, what happens it is picking of the orbital’s why does it happen because you have gone down on symmetry. Even the perfect octahedral complex forget about the anti-lateral complex , also talked about octahedral complex is less symmetry than the bear metal ion that is why not all the orbital as the same symmetry they are spitted into two sets T2G and EG ok right.

And then if time permits and if students permit then we are going to talk about molecular vibrations and I am not very inclined to giving to this because molecular vibrations I believe that I have covered in significant details in stage 442 in molecular spectroscope course right. So, if you discuss it here you can see some redundancy. So, we definitely go up to here in organic complexes but molecular vibrations if time and clientele permits then we can go into that alright.

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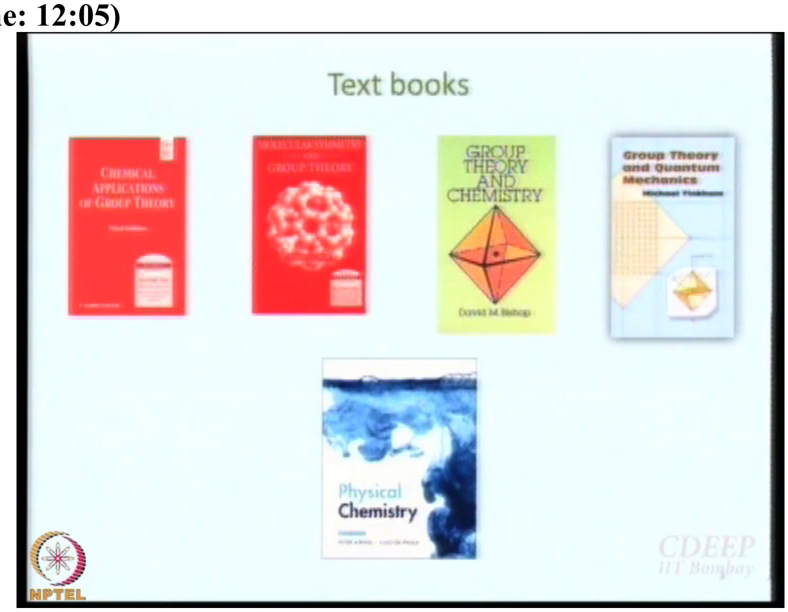

These are the text books we are mainly going to depend on these two, can you read the authors name, yes FA Carlton, F Albert Carlton and this actually the cover of this book one that I have does not have this structure any way this is Carlton, Carlton’s text book. And any way I am going to share this with you on Moodle ok. And then we are going to use Bishop’s book as well and review with Tinchem not too much. Tinchem is a significantly high level notional mathematical book. And in any physical chemistry course so matter what you study. We always follow Atkinson for something or the other. So, from time to time we also fall back on Atkins. Atkins has some good examples.

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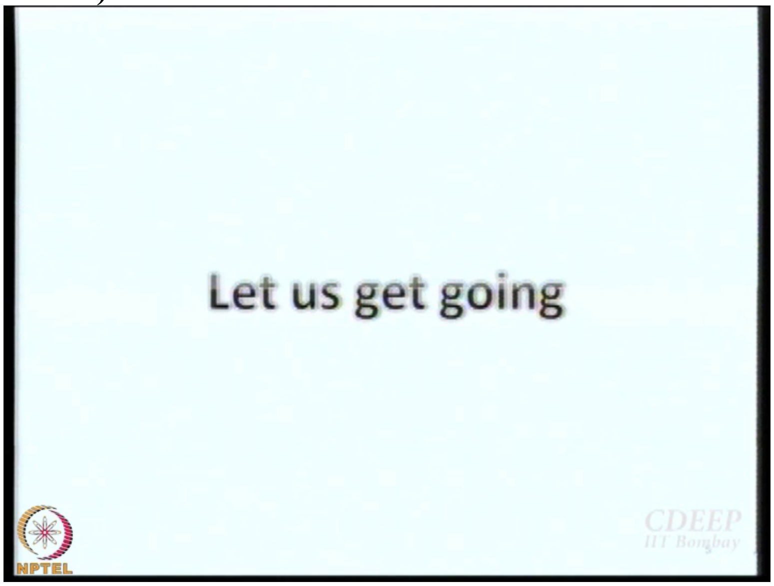

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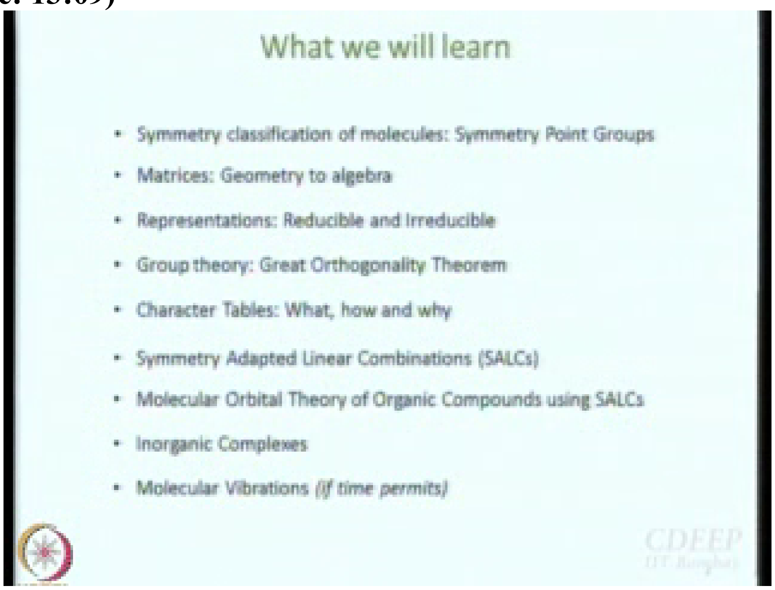

Before we get going to start with let me ask a question that everybody knows that what is a symmetry element and what is the symmetry operation. Operation is something you do that is very good right. Now tell me what would be the symmetry operation right to do something to the molecule and then it looks the same and indistinguishable you cannot make out the difference right and word that we use is configuration right. Indistinguishable configuration something that we do to the molecule that leaves you in indistinguishable configuration or what I have written is equivalent configuration indistinguishable is actually a better word alright.

Now if you perform what is a symmetry element if you say there is an operation, what is an element yeah a point, a line or a plane with respect to which you bring about a change ok?

Geometric entity geometric is the word with respect to which the operation is performed. Geometric entity is of course a point, a line or a plane and as you perhaps know already the symmetry operation as you performed with respect to a point is called an inversion.

Let us say I have a molecule very easy example I will take my time drawing this waiting for the changeover to happen ok. Whereas think of a very simple example drawn very badly right benzene.

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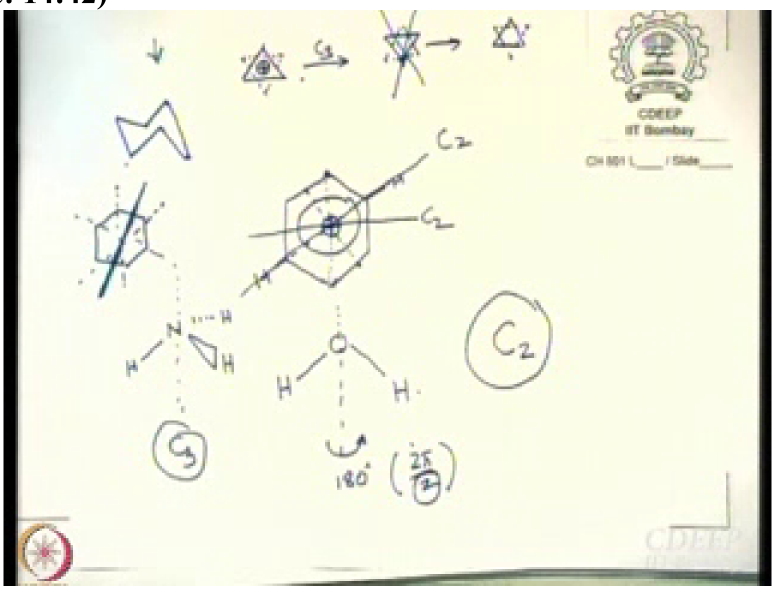

You start from any point on benzene start from a carbon atom go to the centre right and produce this line to an equal distance on the other side you reached carbon atoms right. Instead of carbon atom if I start from a hydrogen atom then what happen start from here go to the centre produce a line when equal distance of the other side you still get hydrogen atom right.

When you start from the middle of a carbon-carbon bond go to the center produce a line of equal distance on the other side you reach the middle of a carbon-carbon bond. So, start for any point in the molecule draw line to the centre and the produce the line to an equal distance from the other side you should get the same thing there this is called inversion symmetry ok. The next thing of course is the line what can you do with respect to a line.

New line what do you do with the line you can rotate right. So, a line the operation associated with the line is rotation and as I think all of us would know it can be either simple rotation or it can be not so simple rotation depending on eventualities you call it either a simple axis of symmetry or alternative there is another word improper axis of symmetry. Proper axis of symmetry and improper axis of symmetry and automatic axis of symmetry, simple variation is very simple as named would suggest. Let us take as simple as water.

Since you want to develop simple axis of symmetry right, now if you think of this line rotate it by how much by what angle 180 degrees or 2 Pi by 2 then water will looks same once again. what happens if I rotate by 90 degrees what are the ways in plane, we are out of plane so that is not indisputable right alright. So, this is simple axis of symmetry and we call it a C2 axis of symmetry where did the two come from, from this 2 right not this 2, the two in the bottom.

So, if I divide it by 2 Pi by 3 it will called Se3 axis, can you think of a molecule which as a C3 axis, ammonia draw it like this one bond coming out of the plane one bond going behind the plane where is a C3 axis? This is a C3 axis right you rotate by 120 degrees this 2 by Pi by 3fine. Now or you can have a complex rotation right what does it mean. You rotate by 2 Pi by n and then you reflect with respect to plane that is perpendicular to the axis any example, Cyclohexane it is chair form or a boat form.

Yeah what happens let us try to draw Cyclohexane in a different way ok because when you talk about symmetry it is very important to develop a 3 dimension visualization in fact I use models for it but I forget to bring it unfortunately models have lot of fun. So, let us look down upon the molecule not in the figure in this sense in the actual sense ok. What would you see, you see forget the hydrogen atoms; you see 3 carbon atoms right.

And then far away you see these three carbon atoms right if you then join them all these lines, these is what they look like right, is it right star of David, it is called star of David right in the current political scenario everybody know the star of David. It is correct or not can you draw Cyclohexane like this, of course this are not the bonds. These are just the three carbons atoms on the top, I just join them by some line and these are 3 carbon atoms at the bottom I join them by dotted line ok. Now it is easy to figure out now think of this axis it is very difficult to figure out from that.

Think of this axis ok perpendicular and the way which we have tried is I will draw plus sign I hope you are familiar with this convention plus means it is jumping out or minus means it is going down from the paper. So now with respect to this axis, if I perform a C3 rotation is big enough for you, the letter is big enough for you ok good. If I perform a C3 rotation then what we will I get, I will get something like this bad artistic skills that is C6.

So if I perform another C3 what will I get, I get identical or indistinguishable right. So, what is when, what we draw now this is C3 axis fine will you be S6 as axis if I am right here then if I reflected to with respect to the plane of the paper, whenever I get indistinguishable configuration right. So, C3 axis doubles up as an S6 axis and why do you bother about alternative axis of symmetry you have studied already in the chemistry perhaps for priority is it associated with presence or the absence of presence or the absence? If alternative symmetry axis is not there orbital or not orbital ok so that is all about axis.

So, now we have talked about point and talked about line I am really I am going very slow here and I am sure that I am going very slow for some of you but then you know as a famous songs says it always good to start at the very beginning, really good way to start.

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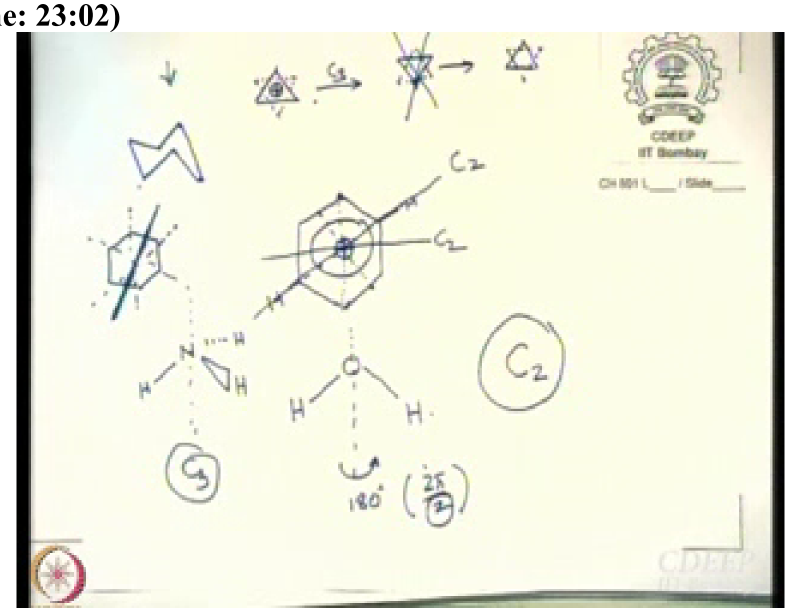

Now what do you do with respect to plane we performed reflection. A reflection is something that we do not have to define. Everybody knows that what reflection is right yeah that is why it is. Now some other definition with respect to axis are reminds are principle axis of symmetry, in a molecule it is possible that we can have several axis of symmetry. Principle axis of symmetry is the one with largest value of n, Cn with the largest value of n is called the principle axis of symmetry. So, if I go back to the example of benzene, what I am doing what are the axis that we can see? I think everybody can see this is a C6 axis of symmetry.

In addition to that do you see other axis of symmetry C2 where is C2 yes how many such C2 will be there, 3 will be there anything else very good, this is another kind of C2, how many total axis of symmetry are there 3+3+1 7 out which C6 is the principle axis of symmetry right keep forgetting when it is 1 and when it is 2, yeah. Now when you have principle axis symmetry where you can actually classify the planes of symmetry if they are there, horizontal plane of symmetry is a plane to which principle axis is perpendicular.

Once again it is easy to understand with the example of benzene molecular plane of benzene is a horizontal axis right. So, this is the molecular plane this is your principle axis of symmetry. Principle axis is perpendicular to the molecular plane so this plane is called horizontal. So, essentially what you have actually is that principle axis is always held vertical ok. Now what is the plane that would contain the principle axis something this?

Is there is a plane like this, it is called the vertical plane does benzene has vertical planes similarly through the carbon atoms 3 of those and through the midpoint of the bonds 3 of those right. In case of benzene we do not call them vertical planes there is a special name for the vertical plane they are called dihedral planes. Dihedral planes are vertical which bisects the angle between the C2 angles.

What is the C2 axis earlier plane that we are talking about, they bisect the angle between two C2 axis right. So, we draw it fresh, this is one C2 axis this is another C2 axis this is third C2 axis ok. Now think of this plane like this right perpendicular to the plane of the molecule does not this plane bisect the angle between this C2 axis and this C2 axis it does right so in this case is called dihedral plane ok.

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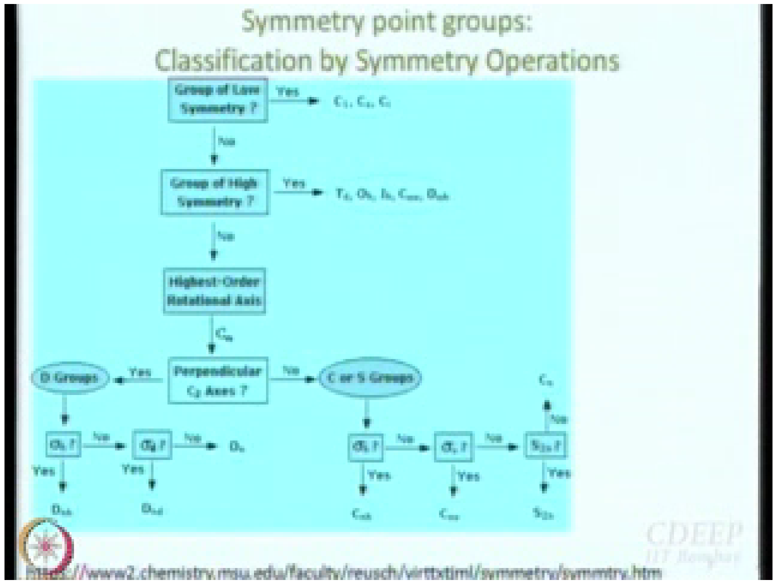

If you know which symmetry elements and operations are there in a molecule then what you could do you could develop a systematic nomenclature for that class of molecular using the symmetry operations that are there. This is something that we should be expressing I will show you a molecule without actually going through all this algorithm you should be able to tell me which point of tables it is.

So, this is the very popular table but nobody uses you really do not needs this table ok. It is nice systematic way of showing it when it says that; here are different ways of defining the algorithm I derived from this website is mentioned here we find it any standard book of physical chemistry right. So, it says that first of all see whether symmetry dealing very low what is C1, C1 means you rotate by 2 Pi right. So, you rotate anything by 2 Pi you reach not only indistinguishable but identical configuration right.

You take concubine and rotate it, concubine would have C1 symmetry so this is nothing else you have to give some name you cannot leave the poor chap unnamed so then we call it C1. Because C1 accessible for everything not only molecule, molecule, chair, table planet, anything and everything would have this C1 axis ok. Next thing to ask you it is other end of the spectrum. If it is not close to the symmetry, it is group of close to very high symmetry.

We are going to discuss these groups tetrahedron, octahedron icosahedra C infinity and D infinity we will see out there they are all special groups. Tetrahedron, icosahedra, octahedron these are multiple principle axis of symmetry ok. And C infinity and D infinity are essentially linear molecules, linear molecule with or without inversion symmetry. If not then what we do is we see for highest order rotational axis what is the principle axis of symmetry ok.

Then perpendicular C2 axis are there then the name will be D, if there is no perpendicular C2 axis name will be C or may be S ok. So, here it is little bit easier first question we ask is in addition to the principle axis symmetry we arrive a horizontal plane sigma H, if you have a horizontal plane then what you do you take Cn from the principle axis and you take H for horizontal and you called CnH it is not very difficult to figure out actually.

If there is not horizontal plane of symmetry you ask at least is there some vertical plane of symmetry so you horizontal will have higher preference then vertical right. We have sleep or else stand, so, horizontal as higher preference than vertical. So, if there is no horizontal plane of symmetry then look for vertical planes of symmetry. And if vertical plane of symmetry I think guess what it can going to be Cn whatever the value of 2, 3 , 4, 5, 25 Cnv and even then that is not there then you ask so what is it, is there a alternative axis of symmetry.

If there is no alternative of symmetry then you have not option that to call it Cn. See this is only part you can actually need the algorithm this is little bit confused otherwise you cannot do it. Here this is actually you have remember if there is no horizontal plane of symmetry and no vertical plane of symmetry then you ask is there S2n, Cn is there S2n there . For benzene for example what is the principle axis symmetry C6 benzene is not good example actually.

Whatever the chair form of Cyclohexine what is principle axis of symmetry C3, we have S6, S6 we just showed, S6 is there that is kind of question you ask here. No other plane is there say that is not true for Cyclohexine, some you know plane of symmetry is nothing then you ask is there S2n. If S2n is there then you actually call it as S2n. If S2n is not there then only you call it very reluctantly Cn.

Cn is the last option if a poor molecule noting other than the principle axis of symmetry then only you can call it Cn. However we try to find some more glamorous name for you ok. I will try very hard look for alternative axis of symmetry. Now if you answer this question if a perpendicular C2 axis is S then you do not call it Cn anymore because in addition to principle axis symmetry it has some more axis C2 axis. So, even in the name we have some more D = C+1, D is more than C, so instead of C you call it D alright.

I am also asking the same question that ask here, you ask is there sigma H, if sigma H is there so do not worry you just name it D and H and sigma H is not there then you look for sigma D remember it is not going to be sigma D any more right perpendicular C2 axis is there. So, if vertical plane are there bisect the angle between the perpendicular C2 axis and then you call them dihedral plane not a vertical plane any more. So, if sigma D is there then you call it D and D and if sigma D is not there and then once again with heavy heart you call it Dn alright