Chemical Applications of Symmetry and Group Theory
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Lecture – 06

Hello and welcome to this course. Today is the day of first of second week. In the last week, we looked at the symmetry elements of a given structure and we also look at the basic mathematical frame work, what called group theory. We learnt how to form a group, what are the requirements and we tried out a few a simple problems and also we learnt how to find out the symmetry elements of any given molecule.

The main idea of this week's lecture and to some extent for the following week also, is to classify the molecules and their symmetric elements in terms of particular, you know mathematical frame work called group.

What we would learn in this particular week is how to, you know find a point group, so called symmetry point group for any given molecular structure or in that way any given structure so that we can, you know classify different molecules under different type of this groups and utilize that to find out different other properties. Let us get started. First we will look at today, how to find out the symmetry operations from the symmetry element for any given molecule?

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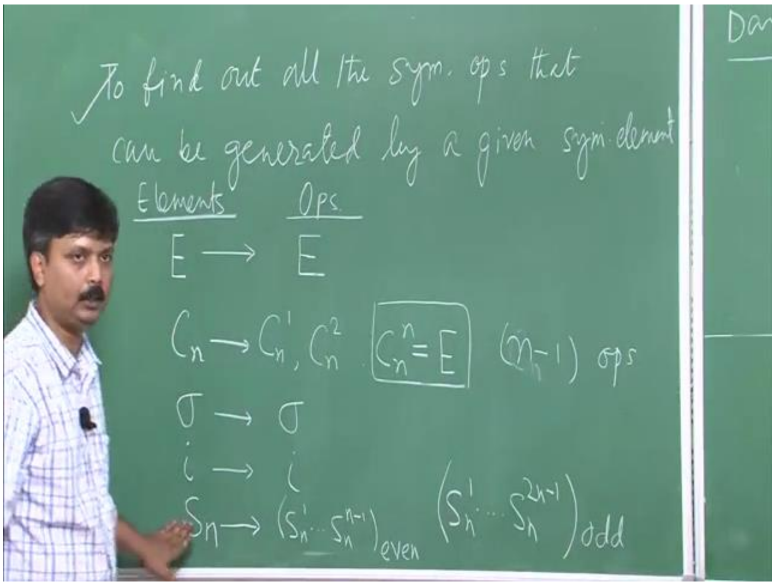

Our aim is to find out all the symmetry operations that is generated by a given symmetry element. We have 5 different symmetry elements that we found out last week identity. We have a proper axis of symmetry, we have center of inversion, we have an improper axis of symmetry and we have a plane of symmetry or reflexion symmetry. Let us do 1 by 1.

The identity operation E if I operate E on any molecule, it will give me back the same molecular structure and if I operate it once more, it is not going to make any difference. You operate E on any molecule n number of time, infinite number of time, every time it is going to give you back its original structure. 1 identity element E will generate only 1 symmetry operation that is also E. If these are my elements and these are my symmetry operations. These are symmetry elements and this part will be symmetry operations.

So, E element will generate only 1 symmetry operation that is identity operation. now next will be proper axis of rotation. Any given proper axis of rotation is denoted as C n, n is the order of rotation now. We mention about it when I showed you example of the methane molecule that once I found out, which 1 is my C 3 axis in that particular C n was C 3. Once I look at that principal axis of symmetry, then you know for every 360 by n degree rotation, I get an this, in this stimulation structure so; that means I can keep on operating C n till the point I get back my original structure. For example, in case of methane I had the C 3 axis and you start rotating, you know 120 degree, 120 degree, 120 degree and ultimately you will end of the getting the original structure. You keep rotating the molecule above C n. The first rotation will give you C n 1 second rotation will give you C n 2 and so on.

And when you reach C n n; that means, you operate the, you know 360 by n degree rotation for n n-th time, you will get back the original structure. For any given C n, you can generate n number of operation now; out of this n number of, you know rotational symmetry operation. This n-th rotation will actually give you back the original structure. Operating C n n on any molecule will mean that you are as if operating identity operation. C n n is nothing, but identity so that already we have 1. In that sense, what we mean is for A C n symmetry element, I can generate C n n minus 1. The total number is C n operations; you can generate n minus 1 operation. Starting from C n 1, which is normally written as C n to C n n minus you do not have to go to C n n because it gives you identity operation.

Next, it is worry about sigma plane. So, sigma plane is a symmetric element in a given molecule sigma is what it does. It does, it reflects in molecular structure across that plane. If you operate sigma you get an indistinguishable structure. If you again operate sigma on that what you get? You get the original structure black, is it? It is as good as, like you are standing in front of a mirror, your left and right hand will be interchanged. Now if you have another mirror on your back the reflection of the first mirror will go there and you will see your right hand is on the right side only. So, you get original structure back. So, if you operate sigma twice, it acts just like an identity operation. In that sense sigma will generate only 1 operation and that is also called sigma. Now what about center of inversion I. Center of inversion I, when we operate the symmetry we called you know, it is an inversion symmetry operation. That is also written by I.

All the symmetry elements and symmetry operations, they have the same symbols in case of operations. You keep on doing the operation as many times as you can until and unless you reach identity. For inversion operations, what you have? You just invert the, you know any particular given point in a body. That means, if you have 1, you know molecule which has center view of inversion, which is actually you know called as center of symmetry molecule because is this center of symmetry also.

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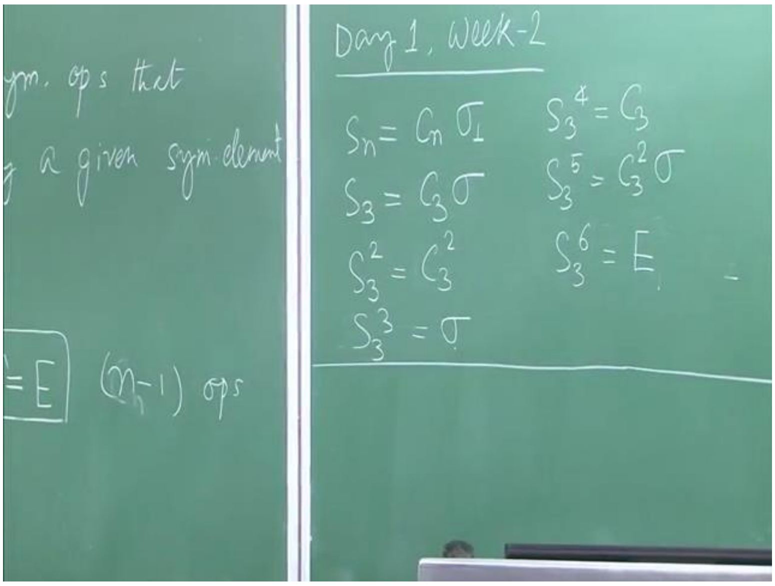

If you have a molecule which is center of symmetry meaning having I then any given point at in any particular coordinate will be exactly inverted.

If you have coordinate X Y and Z, then passing through this center of inversion you will get minus X minus Y minus Z. now you see after doing inversion operation, you come from X Y Z to minus X minus Y minus Z. If you again operate i on this 1, what will happen? This will all move here. First i, it takes it here, second I, takes it back in to the original place so; that means, if you apply i twice, it is as good as an identity operation. I also we can see, generate, only 1 operation that is just 1 inversion now we are left with the last 1 that is improper axis of symmetry and you know symmetry operations generated by this symmetry elements. Now here the things are little bit different. This number of operation that you can generate is very much dependent on whether it is n, is even or n is odd.

Now, what we will do? We will find out how many operations this S n can generate when S n is even. So S n is nothing, but A C n followed by a reflection on perpendicular plane, that we call as sigma perpendicular. Now, when n is even, let us take a particular example. So, I will take S 4 that is equals to C 4; that means, rotation by 90 degree followed by sigma, I am omitting, I am not using this perpendicular anymore because you know this is perpendicular plane. For simplicity I am not writing this perpendicular anymore I am just writing sigma, but remember this is a perpendicular plane, a plane perpendicular to this C 4.

Now I, you know I operate S 4 once that is, this if I want to operate S 4 second time then it is S 4 2 which is nothing, but C 4 sigma 2, which I can write simply here C4 2 sigma 2. Now we have already seen the sigma if it is applied twice, it generates identity. Identity means I do not have to write anything here. This identity operation will end up; you know giving the same structure the identical structure. This means equals to C 4 2.

Now, think about this C 4 when it is operated twice; that means, 90 plus 90 100 and 80 degree, I can actually have you know axis which is C 2, here C 2 will transfer the, or rotate the molecule by 180 degree. So, C 4 2 is nothing, but C 2. I have generated this 1 this is a symmetry operation by itself and this 1 S 4 2 generates another operation C 2, similarly if I go to S 4 3 without doing all these things, I can now, you know write I can jumps the steps. It will be C 4 3 and sigma 3 means sigma followed by sigma followed by another sigma. 2 sigma, will give you E. You have E followed by a sigma means sigma. I have this; this is also a unique operation.

Now, if I can just rub this word then I can go to S 4 4; that means, C 4 4 C 4 4 means what C n n meaning identity. That is not going to give me anything and sigma to the power 4 is also identity. S 4 4 is identity, alright now we have said that for any given symmetry elements, we start generating symmetry operations until and unless we reach, you know A the identity operation and we have reached that. Here this S 4 generates 4 operations out of which 1 is identity and 3 others are you know symmetry operation by themselves, so here S n will generate S n 1 to S n n minus 1 operations, also there is E for S n n. Well this is even this is for even.

Essentially they are generating n number of operation and out of this n, 1 is identity and then rest n minus 1 are other operations. This is pretty much like the C n C n also does the similar thing. Now let us see what happens in case of when n is odd, let us take a simple a case of S 3 3 is an odd number. S 3 number, I have a C 3 followed by a sigma. This is S 3 means S 3 1 and I operate it twice; I get C 3 square and sigma square means identity. This is C 3 square. This C 3 square, we have also generated for proper axis of symmetry if C n is C 3. S 3 3 is nothing, but C 3 square then I go for S 3 3. This is C 3 3 meaning identity and sigma 3 means sigma. S 3 3 generates a sigma. This is true for any odd order of improper axis of symmetry when I operate it in a way like A when S n n I generate a sigma when n is odd, this is true irrespective of any order. If I take S 5 then S 5 5 is sigma. It is easy to find out because S 5 5 means C 5 5 sigma 5 Sigma 5. We will generate sigma and C 5 5 will generate E. You end up with only sigma. Alright move on to S 3 4 because we have not reached identity Eth. We will see what it is. C 3 4 means C 3 3, if I expand this 1 C 3 4 sigma 4, sigma 4 is a identity

So you have essentially sigma 3 3 and sigma 3 which is this is identity. We have left it only C 3. I can write here that S 3 4 is nothing, but sigma is A C 3 alright. S 3 5 is C 3 5 meaning C 3 3 and C 3 2 C 3 3 is E. I am left with C 3 2 and sigma 5 odd number. So, it will end up giving sigma. This is also a new operation that is not present here and if I go to S 3 6, I have C 3 6 means C 3 3 followed by C 3 3. 2 identities I am getting and sigma 6 even numbers, it will generate only E.S 3 6 is E. What I get here for an odd you know number of n S n will generate total 2 n number of operations out of this 2 n 1 is identity as ever. Here I get S n 1 to S n 1 2 n minus 1. These are independent symmetry operations and the 2 nth numbers is nothing, but identity.

Now, also you see here there are you know, of important thing that I 1 I already mentioned that you know S n n equals to sigma for n equals to odd alright, and in this particular case you see this S for 1 n is odd S n will definitely have and C n. This is an important consequence if you remember what I did for S n when n is even that S n n when is even. S n will make sure that you have a C n by 2. If you go back to the previous case of S n when n is even you can verify that 1. This is the case of S n when n is odd. S n even will generate A n number of version out of which n minus 1 number of are independent and nth 1 is identity where as S n when n is odd, you get generate 2 n number of operation right 1 is identity.

We will need these things very soon. We found out, how to get the symmetry operations or how to generate the symmetry operates operations from a given symmetry element for all identity proper axis symmetry, reflection symmetry, inversion symmetry and improper axis of symmetry. Alright now next thing we should learn is how to combine the symmetry operation or in another word if I operate like I, you know generate different symmetry operations by successively applying the symmetry operations on a particular molecular C n 1 more C n 1 more C n in that way or S n 1 more S n in that way now what I did here is, we are going to learn about combination of symmetry operations. You know in the last case what we did? We operated C n and then again we operated C n.

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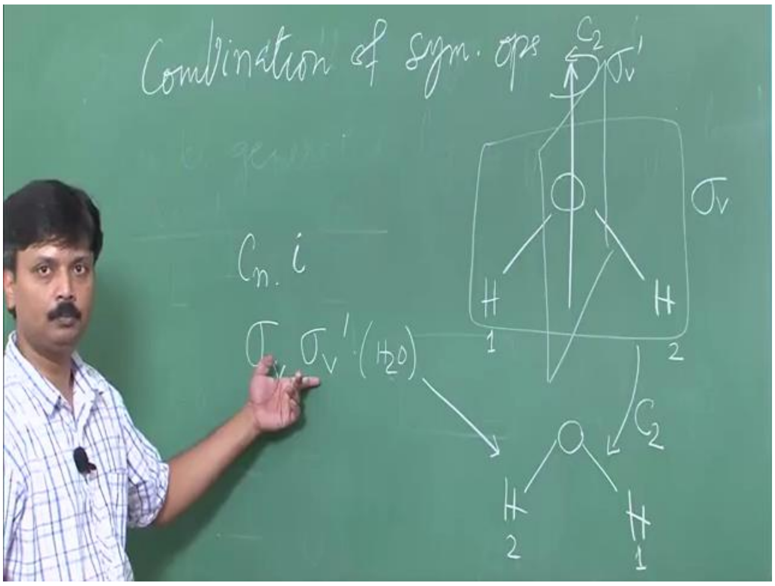

Now, what happened if I operate say C n followed by I what will happen if I have sigma we have seen that if I operate same sigma plane twice, then I get back the identity. Now if I have a case, where I have 2 different sigma. For example, I take this molecule water. Here I have 2 different plane 1 is containing this molecule, the as a whole all the atoms. This plane of this board will constitute 1 sigma. Let us call this 1 as sigma and then another 1 which will be perpendicular to this plane cutting these molecules into half. Let us call this as sigma V prime. Now my question is, what will happen if operate sigma V and then Sigma V prime? What is that result? I should know that. Essentially what I am asking is what will be the result of binary, you know combination of 2 different symmetry operations, I have seen already what happens in case of the combination of the same symmetry operations with itself.

Now we are going to see, what happens in case of 2 different symmetry operations. Let us take these examples, this is the simplest example. So, let us start with this particular friction itself. now in order to solve this, what we will do? We first mark this hydrogen by 1 and 2. This is 1 and this is 2. I am going to do is what I am going to do is I am going to apply this 1 on this molecular structure correct. What I will do - I will first operate sigma V prime on this and then what about the result that I get, that is result in structure. I will operate sigma V on that, let us do that.

In an operate sigma V prime that is this plane which is cutting half then, what will happen? 1 will come to this place, 2 will go here, nothing will happen to O. So, I get a structure right like this. This is 1 and 2. Now if I operate sigma V on that, what is going to happen? Sigma V is in this plane. Sigma V is not going to do anything to this molecule. That will remain same. Ultimately operating sigma V and sigma V prime on this molecular structure will give me this 1. Now can you tell me, you know could I get the same structure from this starting molecular structure by operating any other symmetry operation? A close look will tell you the answer is yes. What is that? I have a rotational axis of symmetry right along this direction, which is A C 2; if I rotate this 1 then I get equivalent or indistinguishable structure.

Now if I operate C 2 on this structure, what will happen? This will just rotate it 180 degree. 1 will go over to the place of 2 and 2 will come here, which is nothing, but this. I can bring, you know this structure to this by simply operating A C 2 and I can create the same effect by combining these 2. This is an example, how to combine this. What you should do is you take any molecule, find out the symmetry elements and then you find out the symmetry operations generate all the symmetry operations. You find that you know exhaust list of the symmetry operations, that can be generated for a particular given molecular structure and then you start combining you know any 2 symmetry operations.

How will you do that? Just like this, you take the molecular structure, operate 1 then what be the resultant, operate the other 1 on that and you get your results. You can combine like you know 5, you know 1 after another and you can end up of getting that the derived result fine. You have learnt how to combine these symmetry operations. Now we are pretty much ready to check if we can use these symmetry operations that 1 molecular structure can generate, whether they can form something like a group. If it is, you know capable of forming a group, that is the symmetry operations of a given molecule structure, can form group that will be wonderful because we can utilize all the properties of a group to define the symmetry of a molecules.

When I say the define that the symmetry define the symmetry of molecules means, we can you know classify several molecule you know into a particular group then we can utilize the you know characters of those group note this particular word character here I just meant a characters like a characteristic thing, but it has you know the another meaning also which will be clear in a week or so, so we have to check with this symmetry operations can forma group or not and you know that will be very help us in a finding out, how the molecular symmetries dictates you know the observation of several properties chemical or you know physical properties.

We will stop here today and in the following class we will be looking to this possibility of the formation of a group using these symmetry operations as the element of the group.

Thank you very much.