Chemical Applications of Symmetry and Group Theory
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Lecture – 32

Hello and welcome. We were discussing about how to determine the symmetry of the normal symmetric type of the normal modes.

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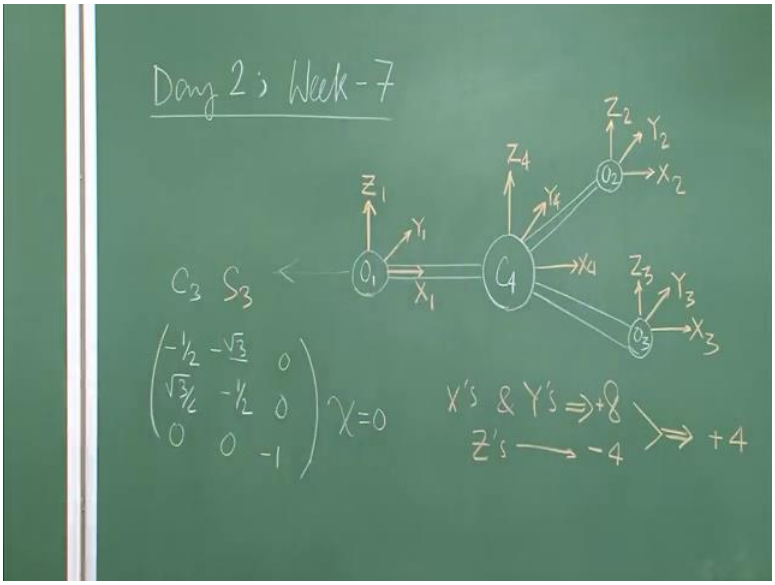

What we are going to do? We are going to take one particular example of this carbonate ion and that we discussed in the previous class itself. What we will do to start with we will take all the X Y Z coordinates on sitting on each and every atom. The atoms of the nuclear to be in the origin and then the corresponding X 1, Y 1, Z 1 or X 2, Y 2, Z 2 and all this Cartesian coordinates, will be there to act as a basis. We have total 12 basis functions in our case.

Now what we have to do? We have to form early presentation based on this. We have already learned that. Now we are going to see what are the characters of the representation technical form using these basis functions now when we will operate the by the way. Here we have differentiated each 1 of these atoms by in a given number. This is 1 2 3 and 4. The carbon atom is given the number 4, now when we operate the

symmetry operations on this basis function what you will do we will operate on the X Y Z. This is vectors, but not on this atoms.

Let us try to figure out, what will be the characters of this representation, identity will give me matrix which is 12 by 12 and it is a unique matrix of 12 by 12.

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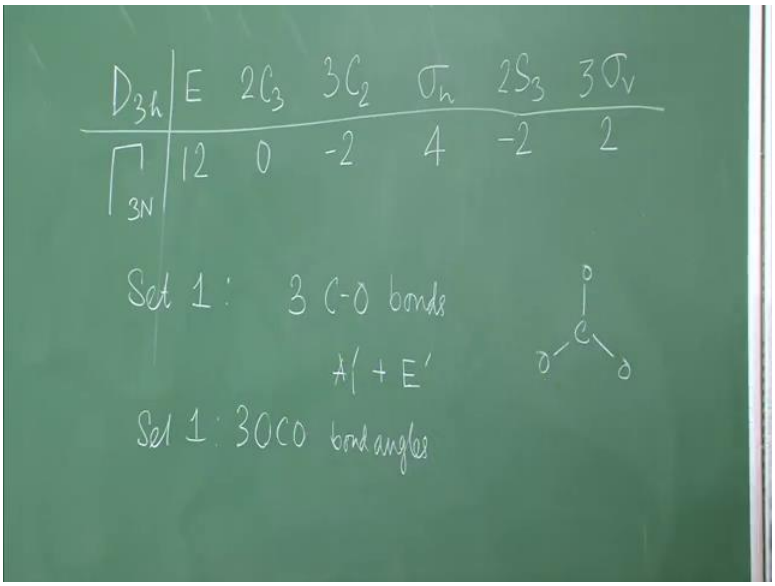

Ultimately on the diagonal element it will give me 1 each and total 12 diagonal element. I will get a character of 12 now, when I operate C, three on C C 3 on this particular structure. What do I get? C, three this is a C 3symmetry. C 3 is right here. When it operates, 1 2 and 3; they shift their position by 1. 1 will go here, 2 will go here, 3 will come here. As we discussed earlier this X 1 Y zone Z 1 or X 2 Y 2 Z 2 X. 3 Y 3 Z 3are not going to contribute anything to the diagonal.

This fourth atom that is the carbon atom and this is functions that are basis vectors here. All of our use and since the C 3 is not changing this atom or it is not shifting this atom. This basis functions will contribute. Let us target 1 by 1. This says I have the axis C 3 axis along z 12 axis along z axis. What will happen? This Z will remain as it is correct. It will contribute 1 to the diagonal now X and X 4 and Y 4 upon C 3 operation what will be the total diagonal contribution from there.

If you look at that geometrically you can easily solve for that. We are not going to do that, but I can tell you that ultimately if you consider only this 3 basis vectors, because

all the other atoms are moving completely shifting. We have to consider only this part. Therefore, this whole thing falls down to a 3 by 3 matrix right; z will remain unchanged. So, that will contribute 1 that is without any doubt I can immediately write down.

What will be the form of X and Y. If you solve it geometrically you will see this will be something like this because if you apply C 3 on X 4, it will give you minus half of X 4 minus half of Y 4. The other part will be root 3 by 2 and here it will be minus half. So, this side, you can figure out yourself. Therefore, if you look at the trace of this you will have 0. The rest of the 3 oxygen are contributing 0 and this 1 also though they contribute to the diagonal, but overall sum will be 0. You will get 0 characters for C 3.

If you look at the C 2, say you choose 1 of the C 2s. If you can solve it for 1 C 3 1 C 2 then you automatically has the characters for other 2 C 2types. If you consider this X C 2axis then what you have this O 1 and C 4. They remaining at their place, but O 3 and O 2 are interchanging. We do not consider this. We had now 6 by 6 matrix. To start with this C 2 is along X axis correct. The X will remain and unchanged. I get a contribution 1 from here and 1 from here. I get already a contribution of plus 2.

Now, this Y 1 will become minus Y 1, if I rotate along this X-axis. So will be path for Y and therefore, this and this will contribute totally minus two. I have minus 2 contributions coming from the Y side and then the Z side. Z will also give me and minus Z one. I have minus 2 contributions from the Z. Out of this 6 basis vectors I get total character to be equals to minus 2. I can simply write minus 2 for all the C 2 primes. Now let us consider the next symmetric element that is sigma N. What is sigma N going to do? Sigma N, which will not change any of the atoms; everything is remaining their case now X and Y constitute the plane of sigma N. There is nothing going to happen to X and Y. There are total 4 such X Y. Total 8, you know this is vectors will be contributing 1 each to the diagonal. I have a contribution coming from the X S and Y S I have a contribution of total plus 8 correct because nothing is changing while this 8 if you look at it will be completely inverted it will be reflected onto the negative Z side. Also we contribute 1 minus 1 each.

Therefore, I have a contribution from Z S to be minus 4. The resultant of this is going to be plus 4, correct. You have this 1 to be plus 4 next is S 3. See when you talk about S 3 here, S 3 has only 1 difference from that of C 3. C 3 gave me this matrix by which is

actually this is the block in the total 12 by 12 matrix. This 3 by 3 block, gave some contribution to the diagonal, but ultimately overall this is going to be 0 for C 3.

What happened here? That is this Z remain unchanged therefore, it contributed plus 1. This plus 1 and then minus of minus of it all together becomes 0 now in case of X 3 everything will be same except for the fact that there be reflection in the X Y plane which will cause this plus 1 to be actually minus 1. In case if I consider this, C 3 then say in if I write in white color this will be C 3 then this is plus 1and if I consider S 3 in this color, then this will be minus 1. When you consider S 3, it will have total character to be minus 2. So, I have minus 2 for this s 3. Now we consider sigma V here also. We can choose from 1 of them. Let us take this particular sigma v alright. This contains X Z plane correct. What will happen to O 2 and O 3 three, they will be shifted completely because they are interchanging. Again I am left with this O 1 and C 4 correct and this is vectors.

So, since we are considering X Z plane then I have no contribution coming from X Z and Z S to the plus 1, each because nothing is going to be change. Then I have 2 X S and 2 Z. Total 4 while the contribution from Y S is carry, S will be minus 1 because this X S plane will reflect this plus Y 1 2 minus Y 1 or plus Y 4 to minus Y 4. There will be contribution of minus 2 from the side of Y S to the overall diagonal. Therefore, I have 4 minus 2 because 2 plus 2. Sigma V S we contribute plus two to the overall character of the reducible presentation. This is my reducible representation that I got using 3 N Cartesian coordinates as my basis Z alright. What is my next job? My next job is to deduce this correct. In order to deduce that, what we have to do you have to use the formula that we have already deduced earlier. If you deduce that, what you are going to get? You are going to get say if I.

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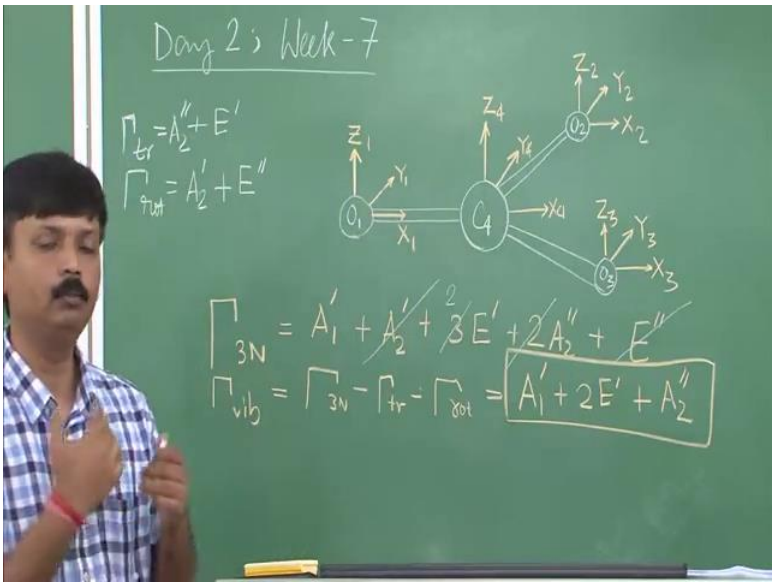

Essentially I have gamma 3 N equals to A 1 prime plus A 2 prime plus 3 E prime and you have 2 A 2 prime, double prime and you have E double prime. This is what you will get ultimately. You solve this meaning that you deduce it and then you are supposed to get this particular expression. Now, I could find out what are the irreducible representations which to which all this my basis vectors X Y and Z transform as. We have used 3 in basis vectors meaning that we have considered all the possible motions translations rotations as well as vibrations and they all to be transfer as this many number of this many number of this thing number of reducible presentation. If you can cross that, here you will see this 2 are 1 dimensional and this E S is 2 dimensional - 1 plus 1, 2 then 6, 8 and then again 2, 10 and then again 2, 12. Total dimensionality is 12 which is matches with this as well as this matches with overall number of this is vector that we have used. Everything is in ordered.

What is our job? We have to find out from this list of irreducible representation we have to find out what are the irreducible representation that actually arefor which the molecular vibration or the normal modes are actually the basis for. How do we do that is very easy? Again you have to take help from the character table of the particular point view. Again we will resort to the character table of this particular table point group (Refer Time: 14:36).

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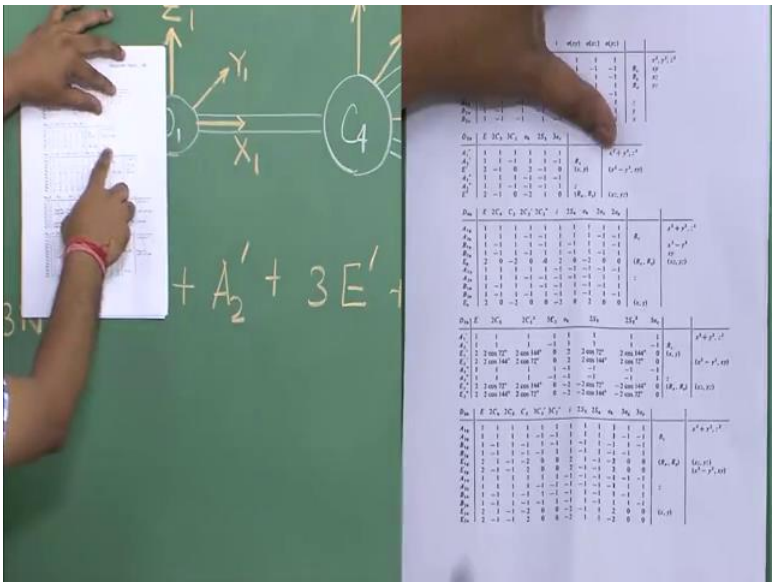

We have got our, list of irreducible presentation correct, now what we have to do? Essentially we have to strike out all the options that are for translation and rotational motion then the residual irreducible presentation that we get will be for molecular violation. If you concentrate on this particular character table here the area 3 and area 4 for (Refer Time: 15:13) you will see that there are different linear functions that you have already discussed.

Now what we have to do? For translation we have to look at the irreducible presentation for which the linear functions that is Cartesian coordinates x y and z them from the basis for. Here if we look at what we see is this representation E prime for representation E prime X and Y from the basis together while Z from the basis for a 2 prime correct. This X Y and Z, this forms the basis of translational motion. Therefore, what we can write that out of this if I go for say for example, gamma for translation. Gamma T R if it I then what we have? We have E prime plus we have a 2 double prime. I will again till this part. So, in order to find out which irreducible presentation will correspond to the translational motion if you have to find that all you have to do you have to look at the character table and particularly area 3 because area 3 gives you the linear basis functions X Y and Z.

Now in, area 3 this X or Y or Z, they will be written besides one particular irreversible presentation or another particular irreducible presentation and you have to find out which representations they are and what we saw that this X and Y to get that from the basis for

E prime, irreducible presentation while the Z function transform as a 2 double prime. If I take out this two part I know that this to irreducible representation they actually belongs to this there is possible for the translational motion in other word actually this translational motion for this particular molecule it transforms as a 2 prime and e prime in irreducible presentation.

Now, similarly I have to find out what is the irreducible presentation for rotational motion. Again if I look at the character table and we look for the functions this R X R Y and R Z. We have to find out which irreducible presentation you have this R X or R Y or R Z, find out those irreducible presentation and you have got the irreducible presentations for rotational motion. If I look at again we will see that R Z, that is rotation about the Z axis, it form basis for E 2 prime alright. If I write gamma rotation to be A 2 prime and R X and R Y; they transform together at the basis of E double prime. So, therefore, how many rotational degrees of freedom are there? 3. How many transmission degrees of freedom there, 3. If you check here that you have total dimension of this is 3 and here also 3 so that is again tells see that everything is in order. I have found out the irreducible presentation which corresponds to translational and rotational motion.

Now, if the altogether translation to rotational I have A 2 prime A 2 double prime E prime and E double prime if I take out this 4 irreducible presentation then from this list, I have got the irreducible presentation which gives me the symmetries of the molecular vibration. In order to do that, I have to get gamma. So, I can write gamma vibration equals to comma 3 N minus gamma translation minus gamma rotation. What do I have here? A 2 prime I have 1 A 2 prime here correct. If I remove a 2 prime from this list, let me strikeout this and then a 2 double prime I have 2 a 2 double prime. I will strike 1 of them; I still have 1 A 2 double prime and then 1 E prime and 1 E 2 E double prime from this list. E double prime is gone and then I have now left I am now left with 2 E primes.

If I write that ultimately, what do I have? I have a 1 prime plus 2 E prime. Alright and I have 1 A 2 prime how many number of vibrations means normal modes we have, I have total 6. The dimensionality wise I should have a match. 1 plus 1 plus 4 total six everything is in order. So, these are the normal modes and these are the symmetries of the possible normal mode of vibration or C O 3 2.

Now, if you just go back to those structures that I showed and I showed you that symmetries also there I just wrote down, but how did I get this 1 is this way now if we have to suppose I do not know what are the normal modes, right? No one has drawn those structures modes with atoms particularly then how do I know which modes which particular which are correspond to.

Now, what we need to do there? If we look at the characters here again, I have to look at the character corresponding to A 1 prime. A 1 prime has all the characters to be plus 1. This is totally symmetric higher. If I have to assume something completely symmetric about this molecular vibration, what can I think of? I can think of just a structure where this all this atoms are straights in equal amount in the same direction as the direct bonds, that means, is that symmetric stretching. I can accordingly draw the normal mode of that and then I have the characters for E prime.

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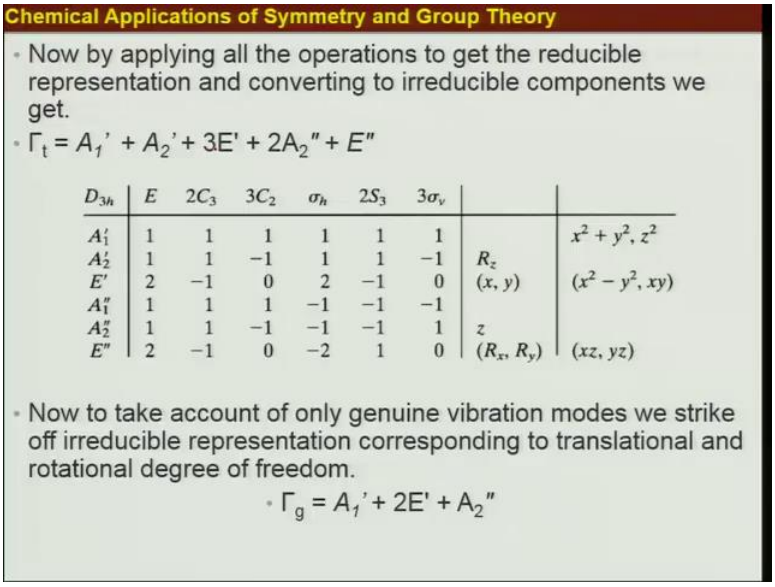

E prime, what it has? It has 2 for identity and minus 1 for C 3, right. You have minus 1 for S 3 also and sigma V S is 0. In this case I cannot comment on the extract stretching bond stretching or movement of a particular angle, but it is not it cannot be expressed in superior form, but I can say some combination of bond stretch are combination of 1 angle movement will give rise to this e type of symmetry.

And this a 2 prime that has character of negative 1 with respect to sigma each which means that is not symmetry. This motion is not symmetric with respect to the molecular

plane that initially tells you that this must be something related to the out of plane motion then only you will have a negative character for this sigma S. Now, having said all these things, next question is like could we come to these normal modes and their symmetries without dealing with all this coordinate systems X Y Z and all these things. The answer is yes. How can you do that? You can do it by taking the internal coordinates into account. How to do that? You have to consider either certain bonds or the bond angles to be your internal coordinates. Here we can consider this C O bonds as my basis function or this O C O bond angle as my basis function or any diagonal angle as my basis function.

Now, which 1 you consider first or which 1 you consider late and there is no last and first rule. You can start with any 1 of them. For example, if I start with this co bonds then what we have, we can form a formal representation where by number of basis functions are 3. So I consider as set 1 which has 3 C O bonds, they act as my basis function. Then on this 3 C O bonds, I operate all the symmetry operations of the (Refer Time: 26:27) point group and I form the representation, alright and then I deduce that, if formal representation, where you are considering this only this.

So, these three bonds can either straight in the same amount at the same time which will very much symmetric. Definitely that will be giving me totally symmetric universal presentation A 1. Here it is A 1 prime and the rest 2 it can be like 1 is stretching in this direction, 1 is contracting. There will be a combination of 2 motions. I can intuitively we can say that will belong to 1 of the E representations. So, call it E prime. So, I can say that intuitively.

And I can similarly form another state of basic functions. Then let us call it as set 2 while I consider this C 3 O C O bond angles. Now, unlike this C O bonds I cannot have all the 3 angles being expanded in a same way that is not possible. So, therefore two angles will changes in a same way, but other one will be in a different way. Again in that way I can intuitively say that I will have a 3 dimensional representation that I can deduce it to say 1 dimensional, and to have 2 dimensional presentation and that is how we can form we can say or comment about the normal mode of vibration from the symmetry angles.

This particular part we will elaborate in our next class where will show that how using the internal coordinate we can exactly deduce the symmetries of the normal modes. So,

that is what we will deal in the following class. And then, next after that we will go and find out how to get the selection rule of Vibrational transition.

Thank you for your attention. See you in the next class.