Chemical Applications of Symmetry and Group Theory
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Lecture - 20

Welcome back today is the day 5 of week 4. So, in the last class we learnt about the theorem called the great orthogonality theorem and we also learnt about 5 you know important rules that come out as you know consequence of that great orthogonality theorem.

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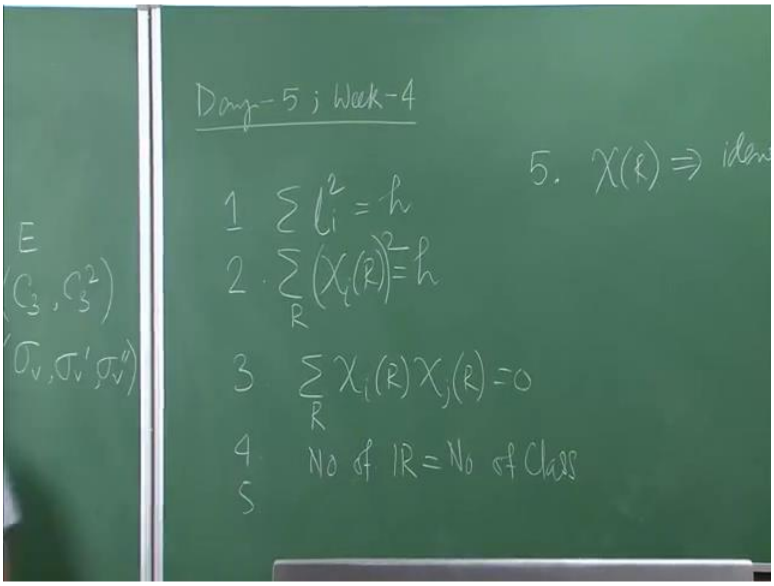

So, the rules were the first rule were the sum of dimension square is equal to the order of the group and second we found that sum of the characters square for any given irreducible representation is also equals to the order of the group.

So, also we learnt that any two irreducible representations are orthogonal. So, is equals to 0 and we also learnt another two rules fourth and fifth which says that the number of irreducible representation equals to the number of class present in the point group. So, the fifth rule is that the characters corresponding to the symmetry operations belonging to the same class are identical. So, the characters for any given r, so if there are 1, 2, 3, 4 different number of symmetry operations belonging to one particular class, then they all will be identical. So after getting these 5 rules we took an example of the point group C 2 v to illustrate these 5 rules.

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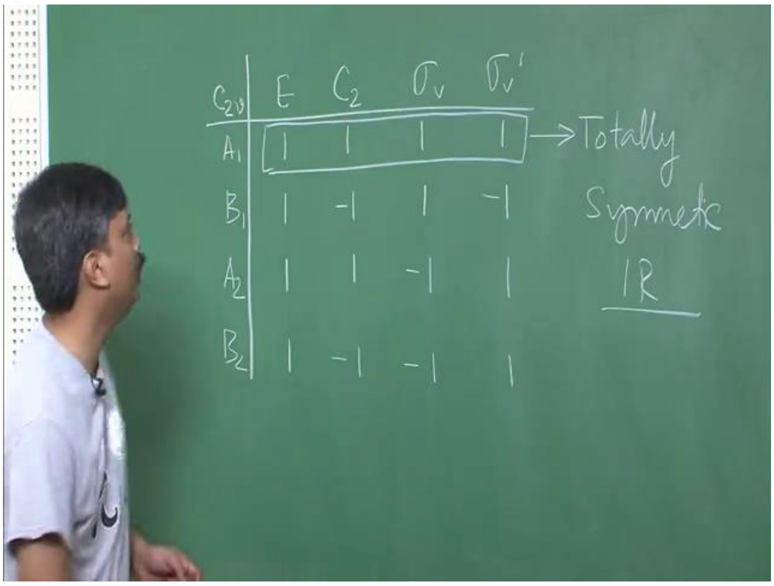

So, what we got in that case is the character table, so using those 5 rules we could form the character table for the point group C 2 v and this character table contains all the irreducible representations that are possible for the point group C 2 v.

Now, one thing we should notice here that we also mentioned during introducing the character table. I will re correct again here, so now you see in this character table there is one particular irreducible representation which has all of its characters as positive one. So, what does that mean; that the characters of this irreducible representation are symmetric with respect to all the symmetry operations of the group correct because plus one means it is symmetric the character is symmetric with respect to that particular representation. So, you will find that all the character tables for all the point groups, one irreducible representation will be such that characters of corresponding to all the symmetry operations are plus 1 and this particular irreducible representation is called totally symmetric irreducible representation. So, for any given character table if you have to form then you know for sure that one totally symmetric IR will be there. So, this knowledge will even will help you even more when you would like to form the character table.

So, as a second illustrative example where we can show that we can form the character table utilizing those five rules which are consequences of the great orthogonality theorem and we will take the example of the point group C 3 v in this case. So, a molecule which has a point group of C 3 v is like ammonia. Now we will try to form the (Refer Rime: 05:00) character table of C 3 v.

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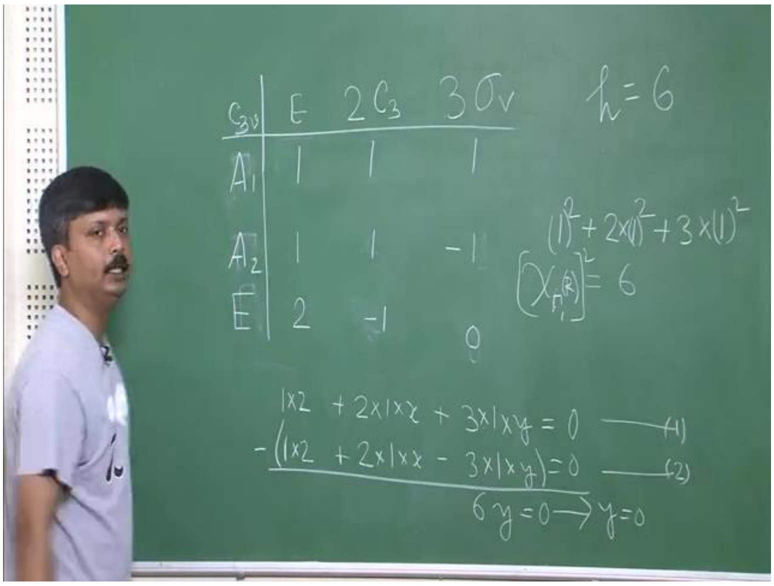

So, what are the symmetry operations that point group C 3 v has, so C 3 v has identity, it has C 3 as the principle axis of symmetry. So, therefore, the operation directly from there that will be C 3 and C 3 square and there are three sigma v's, so sigma v, sigma v prime and sigma v double prime and this sigma v's are along the any spots, if I take ammonia as the example for C 3 v.

Now, we also know that C 3 and C 3 square, they form a class and sigma v's all three sigma v's, they form a class. So, our rules says that like what is written for rule 5 here on this board it says that character corresponding to you know sigma v, sigma v prime and sigma double prime are same. Similarly characters of C 3, C 3 square will be same because this forms the class. So, therefore, while writing the character table I do not have to write explicitly C 3, C 3 square, sigma v, sigma v prime, sigma v double prime instead what I can write is this; like instead I can write 2 C 3 because C 3, C 3 square will have the same character, so without repeating all this characters, we can club them together.

So, similarly I will have 3 sigma v's and now with this we have to form the character table of C 3. So, what we do what we learnt in the last class is that first we have to determine how many irreducible representations are possible. So, the number of irreducible representation is equal to the number of class, so we have total three class e forms a class by itself and these two classes. So, there will be three irreducible representations so I will have gamma 1, gamma 2 and gamma 3, now I have to find out what will be the nature of the characters.

So, we have to use in this case rule one correct, so the square of the dimensions of the irreducible representation, if I sum them I should get the order of the group. So, the order of the group here h is equals to 6 because I have 6 operations fine. So, this should be 6 now, so means l 1 square plus l 2 square plus l 3 square equals to 6, knowing that all the l's are greater than 0 an integer. We can solve this equation only in one possible way that is two of this irreducible representation will be one dimensional and the third one will be a two dimensional meaning that it will be 1 square plus 1 square plus 2 square that will give me 6.

So, here let us say gamma 1 is one dimensional and gamma 2 is one dimensional then in that case gamma 3 will be two dimensional representation fine. So, here what we can start with is the following, in the previous example today itself we talked about the presence of a totally symmetric irreducible representation in any given character table right and this totally symmetric irreducible representation is always one dimensional correct. So, without worry about anything, I can fill out at least one row corresponding to one irreducible representation which is supposed to be one dimensional.

So, let us write down the totally symmetric irreducible representation and I know immediately that this corresponds to a type of irreducible representation if we look at the Mulliken symbol. We can also verify here the rule 2, which is over here is satisfied that is summation of the square of the characters for any ith irreducible representation over all the symmetry operations should be equal to the order of the group. So, here if we look at that 1 square plus again 1 square, but I have to remember there are two operations here that is why this 2 is written here. So, I have 2 multiplied by 1 square and similarly here I have 3 into 1 square correct, so this is equals to 6. So, we have verified that and we can verify for each one of this i rs. Now we have to find out the other numbers here, so I have total there should be 6 more characters that I have to fill in here.

Now, we have already seen from this clause that this and this should be one dimensional and this should be two dimensional and dimensionality comes from the character of the identity operation and they are always positive. So, without worrying about anything I can fill this one, so then I have to fill other four. Now let us first worry about gamma 2; gamma 2 is another one dimensional irreducible representation so; that means, all the characters of the representation also will be 1. In that case if I have to satisfy the condition 3 here, so any two irreducible representation of the point group will be orthogonal to each other, that is true for any two irreducible representation.

So, gamma 1 and gamma 2 should be orthogonal, meaning if say this character is x and this character is y then 1 into 1, 2 into 1 into x plus 3 into 1 into y should be equal to 0. So, therefore I can very easily find what is the value of x and y, because there are total 6 elements in this group correct. So, total you know sum of the square of these characters here is also 6; that is what I showed here this is nothing, but the chi gamma i of all the r square right. So, I have 1 plus 1 plus 1 plus 1 plus 1. Now here if I have to satisfy the orthogonality, I have to have 3 plus 1 and 3 minus 1, how can I get that because here I have two characters, so I can put this one as; plus 1 and y to be minus 1 then what I have 1 plus 1 plus 1 here then here 3 minus 1. So, if I multiply gamma 1 and gamma 2, I am getting 0. So you know clause of orthogonality of two irreducible representations is satisfied in this condition.

So, now I am left with the third irreducible representation which is two dimensional, so here also we will use the clause of orthogonolity of two irreducible representation and we have to satisfy that you know this gamma 3 is orthogonal to any of the irreducible representation of this character table. So, in that case what I can do, suppose I write this one as say again if I take this one as x and this one as y, while x is the character of the class C 3, y is the character for class sigma v. Then I get two sets of equations, so when I combine gamma 2 and gamma 3 and I combine gamma 1 and gamma 3. So, first take gamma 1 and gamma 3, so what I get; I get 1 into 2 plus 2 into 1 into x plus 3 into, this 2 and 3 they are coming from the total number of elements present within a class correct, so 3 into 1 into y and this should be 0 due to orthogonality.

Similarly, I combine this two so I get 1 into 2 plus 2 into 1 into x minus 3 into 1 into y equals to 0. Now if I subtract, so this is my equation 1 and this is my 2 and if I subtract 2 from 1 then what do I get, if I take the whole minus of this one then what I get is. So, these two get cancelled and this one also gets cancelled, so this one I have 6 y equals to 0. So, here I get y equals to 0, so let me write this here, now I can again you know add this two and then I can get the values of x so, but without doing that also I can easily figure out because thus you know if I look at rule 2, the sum of this; square of this characters of any IR is equals to the order of the group then 2 square plus 2 into x square plus 3 into 0 should be equals to 6. So, if I do that then I should get the value of x and if I do that, I will easily get x equals to minus 1.

So, also you can verify by adding these two because here what you will get is, if I add these two equations in a second step. So, forget about this minus sign, so you get 4 x equals to 0; sorry 4 x equals to minus 4, so x equals to minus 1 correct. So, here we can put minus 1 here and thereby I get the total all three irreducible representations. Now if we come to the naming so this were one dimensional so either a or b; so if I look at the character corresponding to the principle axis of rotation then I see both of them are symmetric with respect to C 3 therefore, both of them belong to a category. So how to differentiate that, so if I look at the characters corresponding to sigma v then I see this one is symmetric, while this one is anti-symmetric. So, this one will be A 1 and this one will be A 2, so let us do that A 1 and A 2 and two dimensional representations are denoted by the term E. So, this is E and this point group does not have any inversion symmetry, so I do not have to worry about adding something like (Refer Time: 18:46) or (Refer Time: 18:48) terms.

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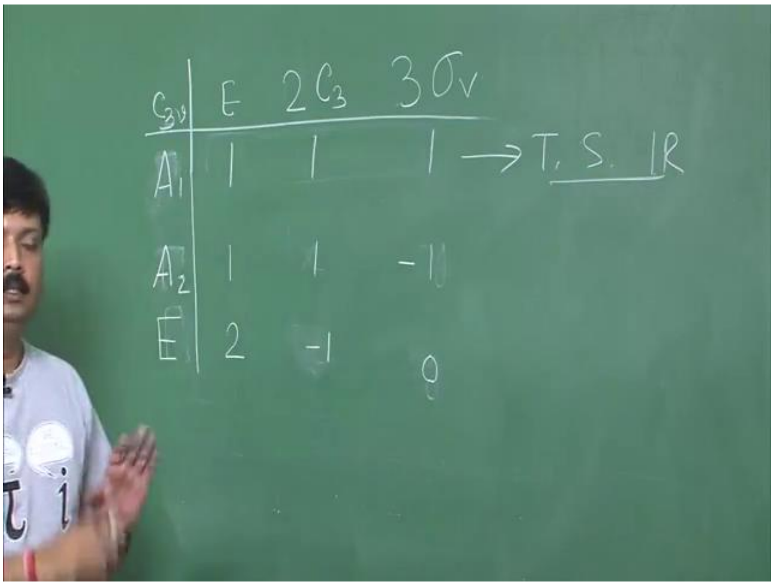

So, this is again you can see the totally symmetric IR that is what we started with. So, this is how you can formulate the character table of any given point group and you should try out various different point group and try to formulate their character tables. You should start from you know a smaller point group meaning a you know point groups with number of elements which are smaller and then go to more rigorous.

Now suppose the way of following directly this character table of irreducible representation, now earlier we showed that you can form any representation which can be reducible fine. So, what you can do, you can formulate matrix representation of that point group and based on the basis functions that you choose you know matrix representation can be smaller or very large and many of the cases they may be reducible. So, earlier we mention that, you can reduce the representation; matrix representation by doing a similarity transformation, if you find a suitable matrix to do that and upon doing the similarity transformation you can block factorize the matrix and then you can you know get to serve you know blocks which are not further reducible, so they represent your irreducible representation.

Now, if you really want to do that sometime it may be cumbersome because you may have a fairly large matrix representation and finding that matrix may be quite difficult. So, are there any ways to reduce any representation, so the answer is; obviously, yes and that also you know follows from the consequence of this great orthogonality theorem and we will see that next. Now one important thing about this you know reduction of a representation to yield irreducible representation is as follows.

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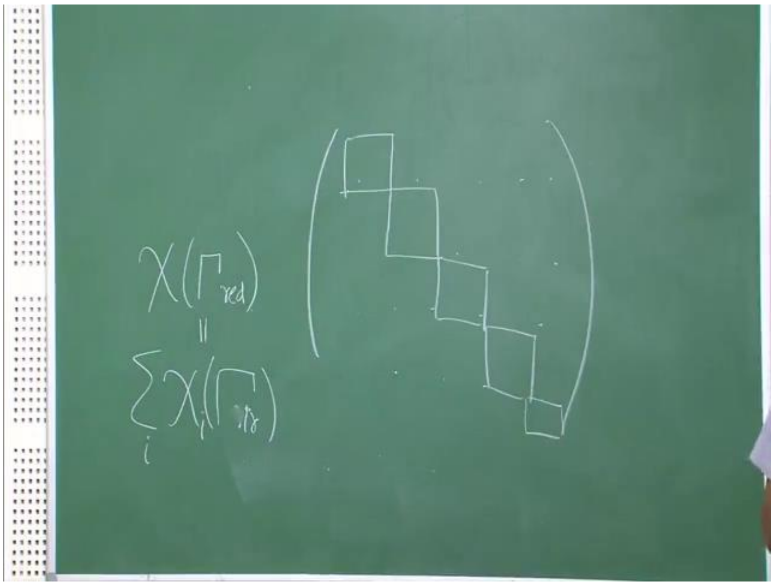

So, suppose you have a representation having a big matrix and having several you know elements in it, so you form this square matrix of any order. Now when you do the similarity transformation what you have, you form these blocks along the diagonal, so different number of blocks that you can form.

Now when you start with representation before block factoring that, you get the trace of the matrix fine. So, suppose before doing this block factor you have a character for a representation, suppose I call that as a gamma reducible because you can reduce it, so this is before block factoring and after block factoring when you get these blocks which themselves what you know behave like a representation then and if they are reduce you know they are irreducible, that is you cannot find a matrix which can perform similarity transformation on this blocks again and reduce it further, so therefore you get the irreducible representation.

Now, a good thing is that, if you take the characters of this individual blocks which are the irreducible representation and sum them up and suppose I call it gamma sorry chi of gamma irreducible and if I summit over the total number of blocks that I can get. So, suppose this is my i and I summit over I, so i is the number of such blocks then this and this are equal, that is the char; you know nature of this matrix representation. So, after reducing the character does not change, so that is very good thing for us because that will help us you know having a way out to reduce any given representation. So, suppose I form a representation of the C 3 v; C 3 v point group, so for example, I write the representation of C 3 v, here again, so C 3 v, so what I can do? I can form the matrix and then I can find the character.

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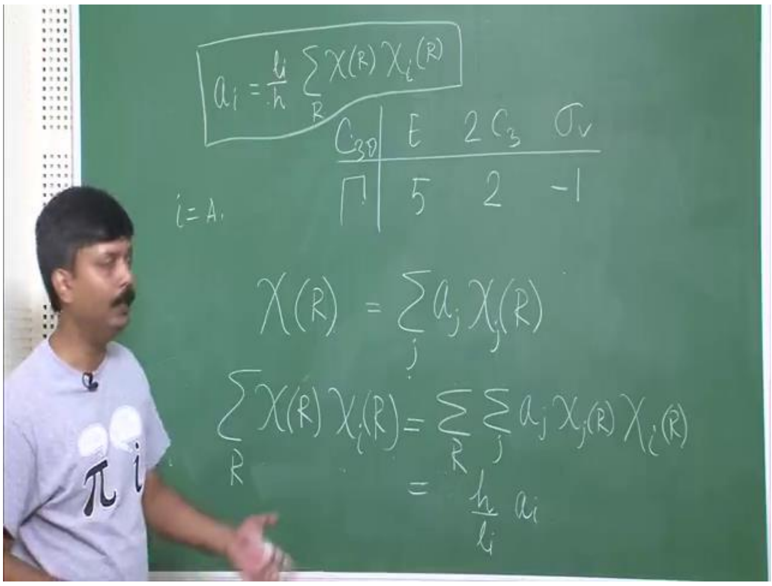

So, suppose I get character of my representation as this, suppose this is my character and this is reducible, how do we know this is reducible because for any given irreducible representation this rule 2 should be valid, so chi square and if I sum it for any given i r should be order of the group.

If it is greater than order of the group then definitely it is reducible here you can very easily figure out; 5 square 25 and when you square it all becomes positive. So, therefore, you can easily figure out this is much higher than order of the group which is 6. Now how do I reduce it, I am not dealing with any matrix anymore; I am just directly dealing with the character. So, the way we can do it, we can utilize this property that is the character of the matrix does not change upon similarity transformation. Therefore, suppose that you know I am talking about this reducible representation and the character of the reducible representation is chi of r for any given operation.

Now, for any given operation what I can do is, I can reduce this representation and ultimately what will happen, it will give me those irreducible representation that are possible for C 3 v like what we got A 1, A 2 and E. So, depending on what type of a basis function I choose at the beginning and the size of the representation. I may have a situation where there will be in n 1 number of A 1, n 2 number of a 2, n 3 number of e irreducible representation will be you know present if I reduce this large representation, so I want to know what are the n 1, n 2 and n 3 that is my aim correct.

So, I can write any of this character for any given symmetry operations for a reducible representation as the sum of the character of the same symmetry operation belonging to any particular jth irreducible representation. Suppose I am worried about any jth irreducible representation then I may have some particular number. So, suppose I call it a j, so a j number of jth i r will appear in my reducible representation when I reduce it and so there will be several irreducible representation, so j can be 1, 2, 3 whatever. So, I can have this relation because the character of the matrix does not change on the similarity transformation correct.

So, now let us see if we can find you know a mathematical relation by which I exactly determine the value of this a; that is the coefficient in this equation, so in order to do that what I can do is; I multiply both the sides by chi of r corresponding to an ith irreducible representation and then I sum it over all the symmetry operations. So, I can do that same thing here also, so I can sum it over r multiplied by chi of i chi of r for ith irreducible representation. So, now the order of you know so what we can see here; suppose I rewrite this one before we when rewriting. So, now, if I look at this particular part which is the multiplication of chi j and chi i, now from relation 3 what we know is that if they are you know different irreducible representations then they will yield 0.

So, this term can survive only when i equals to j fine, so if I put j equals to i then only this term can survive. So, therefore, what I can write is, so not only that will survive and that will yield a particular value which is h over the dimension l i into a i right. So, because when j equals to i then only I can; this part can survive and can give this value h by l I; l i is the dimension for one dimensional l i is equals to 1.

This comes from that term in the great orthogonlaity theorem that h by root over l i, l j when i equals to j then it is l i square, so root over l i square I am getting this l i. So, now, if I look at this a i then a i equals to, if I can write here a i equals to l i by h order of the group into this into chi of r into chi of r for the ith irreducible representation and summed over all the symmetry operations. So, this is a very useful relation for us this will tell me if I form any representation such as this and try to reduce it. So, this will help me doing that job, it will exactly tell me that how many times suppose if a I; if i is equals to a 1, then it will tell me that how many time A 1 will occur in this representation. In other word if I reduce this then A 1 you know a number of times A 1 will occur.

Similarly, I can find what is the number of occurrence of A 2 or E for this particular point group, so this relation we you know should try to remember, so you can follow this method, you can derive yourself again and try to remember this one because this will be used very often. So, now just to illustrate this particular relation, you can apply this one on this particular representation, so whenever you are given a representation you have (Refer Time: 33:06) first see if it is reducible or not, you can check by following the equation 2 whether it is reducible or not. So, we have already stated that it is reducible because the square of this you know characters if I add then it is greater than h; h is equals to 6 here.

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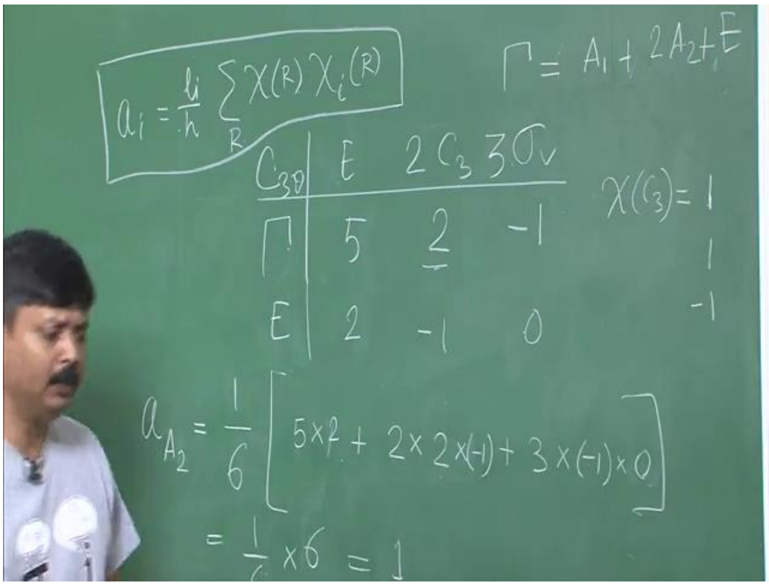

So, now if I remember what was a 1, A 1 was all 1, so suppose for example, I write A 1 here, so A 1 was this correct totally symmetric i r. Now I would like to find out how many times A 1 will occur if I reduce this one. So, let us look at that a A 1, so l i is 1 so I do not care about that. So, it is 1 by h; that means; 6 and then I have to sum this combination. So, I will combine this one and then keep summing and you have to remember this number, so here we missed 3.

So, I have 5 into 1 plus 2 into 1 into 1 plus 3 into minus 1 into 1, so this gives me 1 upon 6, this is 5 plus 4, 9 minus 3, so equals to 6 meaning 1. So, this means that if I reduce this one, I will get A 1 only once. I can quickly find out what will be the fate of a 2, so what was a 2; A 2 was 1, 1 minus 1. So, now, if I try to find out a 2, I will utilize the same platform so only thing I have to do here instead of plus 1, I will have minus 1 again.

So, now what I have? I have 5 plus 4 minus, minus plus, so I have plus 3 so I have 12. So, for A 2 I have 12 correct and therefore, number of times A 2 will represent if I reduce this particular representation is 2, so I got for A 2. So, I got say gamma, I can start writing, so I found A 1 which will be occurring once and A 2 will be occurring two times, next find out what about the E, the representation E. So let me write it here, so this will be 2, this is minus 1 and this one is 0. So similarly if I do this, so instead of 5 into 1, this will be now 5 into 2 and here it will be 2 into 2 into minus 1 and here it will be 3 into minus 1 into 0 alright. So, let see what is the result, so I have here is 10; 10 minus 4 plus 0 means 6. So, I get equals to 1, so I get the E representation, E irreducible representation only once, so what I can write now is gamma which was reducible equals to A 1 plus 2 A 2 plus E. So, you can see here that though A 1 and A 2 are appearing only once, A 2 is appearing two times.

Now, you can also figure out that the characters remain the same, a simple example if you take the character for identity; so A 1 gives me character 1 for identity, A 2 also 1, e is 2. So, A 2 is appearing 2, so 1, plus 2, plus 2 equals to 5; that is what we have. If you check for C 3, what you can have for a 1, it is 1; for A 2 also it is 1 and for e it was minus 1. So, what you have is 1; you can find that out, so corresponding to C 3, so character for C 3 equals to 1 for A 1 and for a 2, it is again 1 and for e it is minus 1.

So, if I add this that is 1 plus 2 into 1 that is 3 and then e gives me minus 1, so 3 minus 1 is 2 and if I check here yes, so this is verified. So, in this way you can reduce any representation that you can form and find out what are the irreducible representations are present here. So, this is of tremendous importance because very soon, we will try to find out different normal modes that one molecule can exhibit and we will also try to find out which mode is active toward Raman, scattering which is active toward just infrared spectroscopy and several other things.

So there what you will need to do, we need to choose a best set and then form a representation and find out the characters, find out whether it is reducible or not and then reduce it and then we have to find this irreducible representation that borne out of that reducible representation that we formed and utilize those irreducible representation that you finally get to do the further analysis be it normal mode analysis or anything and so far we have been talking about forming the matrix, but you know actually without forming any matrix you can still find out the character of the representation and ultimately this is the character which you want to matrix. If you even do not form, if you get the character then your job is done.

So, in the following week we will take a very illustrative example and we will try to show, how you can form a presentation without forming the matrix for this one very easily and then you know reduce this thing and then you know go to the next level of our you know analysis.

So, till then I thank you for your attention and see you next week.