Chemical Applications of Symmetry and Group Theory

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Lecture – 21

Hello and welcome. Now today is day first of fifth week of this course. So, in the last week we learnt about the great Orthogonality theorem and it is consequences and we also tried to use those consequences of the great Orthogonality theorem, to find out the character table 2 simple point groups; namely C 2 v and C 3 v. So, what we will start with today is? To take most comprehensive example of, how we can use the great Orthogonality theorem and the rules that come out as consequences of that theorem to form the character table, the complete character table. What I mean because in the previous class we learnt about the how to find out the (Refer Time: 01:20) representations and terminal the their molecule symbols, but today you we will try to derive the whole character table; that means, including the area 3 and area 4, if you remember a character table has 4 different a segments area 1, 2, 3 and 4.

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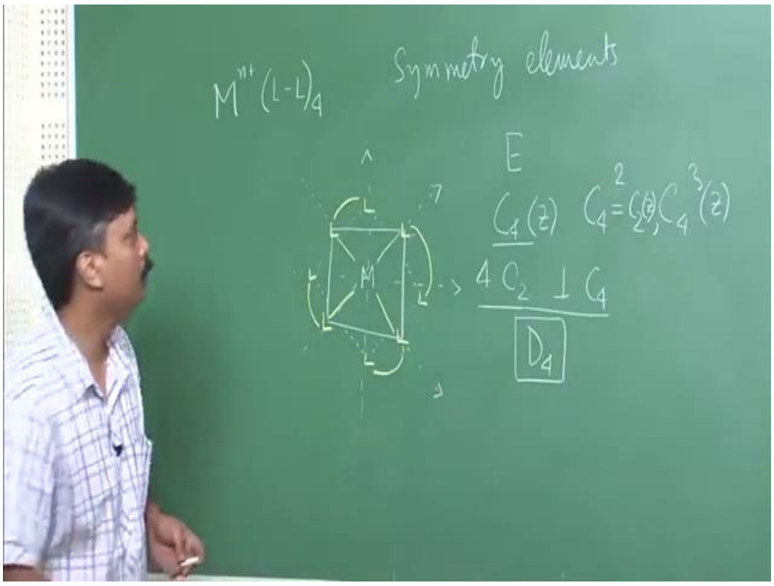

So, we will start with a molecule which is like M stands for metal having its (Refer Time: 01:56) and you have 4 Bidentate Ligands of type this; for example, Ethylenediamine. So, while solving this problem we will use all the knowledge's that we have so far acquired throughout this course. So, this example is going to give you an overall idea that how to use the symmetry and the theories of group theorems of group theory help you finding out the character table and the total character table of any given molecule. So, first question that we have to ask, what is the point group of this particular type of molecule? And in order to do that we need to find out that what are the symmetry operations? Now first symmetry elements and therefore, the symmetry operation stated from that.

So, what are the (Refer Time: 03:19) elements that are present here. So, in order to find that out we need to know the structure of the molecule. So, if I draw in a proper way that will help me finding out the symmetry elements that this particular molecular structure can have. So, let me do that in a quick. So, this is going to be pretty similar to the case of that Co en whole 3. So, let me put the Ligands here and maybe I will use a different color. So, we have to remember these are the Bidentate Ligands and here we are ignoring the (Refer Time: 04:15). So, so this is how we can represent this molecule. So, here you can easily figure out that there is a C 4 axis, which is the principle axis of symmetry. So, this is the C 4 axis. So, I have one C 4 axis of symmetry and if I take this as Z axis, I can also say that this is C 4 Z. So, I can even specify this one and we will figure out what are the symmetry operations that can be generated and by now you should be able to do that real quick.

So, what are the other elements that are possible here? So, you can imagine an axis which is perpendicular to this C Z, which will flip this molecule if I rotate by 180 degree about this axis. So, this will be a perpendicular C 2. Similarly I can find another perpendicular C 2 in this direction. So, we have got 2 perpendicular C 2s. Now it is also possible to find the perpendicular C 2s along the diagonal of this first square you can see. So, this is another C 2. So, we have got four C 2s which are perpendicular to the principle axis that is C 4 here alright. So, I have got total four C 2s which are perpendicular to C 4. Are there any other symmetry element? There is nothing else apart from the identity which is implied always it will be there.

So, now identity will generate only one operations identity and this C 4 will generate C 4 2 C 4 3 and C 4 4 is identity. Now C 4 2 is nothing, but rotate this same Z axis by 180 degree. So, this one I can write as C 2 along to Z axis. So, this is also along Z. Now therefore, C 2 which are perpendicular to C 4 they are along this 4 axis. So, if C 2 will generate only one operation because C 2 operates twice will generate identity, these are the all symmetry operations that are possible for this point, for this particular molecule. So, then what is the point group of this molecule? So, we know how to find out the point group of any given molecular structure, if we know the symmetry operations. We now know the symmetry operations. So, this molecule if I look at this symmetry operations, it clearly tells that it does not belong to any of the special groups neither it has multiple principle axis of rotation symmetry, neither it belongs to linear molecule, neither it has only inverse or only sigma as the elements that are present.

And therefore, we directly go if you remember to step 4 and step 5, which we use to classify the molecules into point groups. So, therefore, I have a principle axis of symmetry which is single principle axis of symmetry and not mere consequence of the improper axis of symmetry. So, next question will be, are there N number of perpendicular C 2s to this C N. So, we have yes this is C 4 and we have four C 2 perpendicular to that C 4. So, therefore, it belongs to D type of point group not only that it is specifically D 4 type and next question that we ask are there any sigma h? Answer is no. Next question we ask are there any sigma v’s? That is also no. So, therefore, this is the point group. So, I have got my point group for this particular molecule which is D 4.

So now knowing that, we will try to find out, the character table of this particular point group D 4. So, let us do that now. So, in order to find the character table first we have to find out the classes right. So, what are the classes that are present here? That let us have a look at that first.

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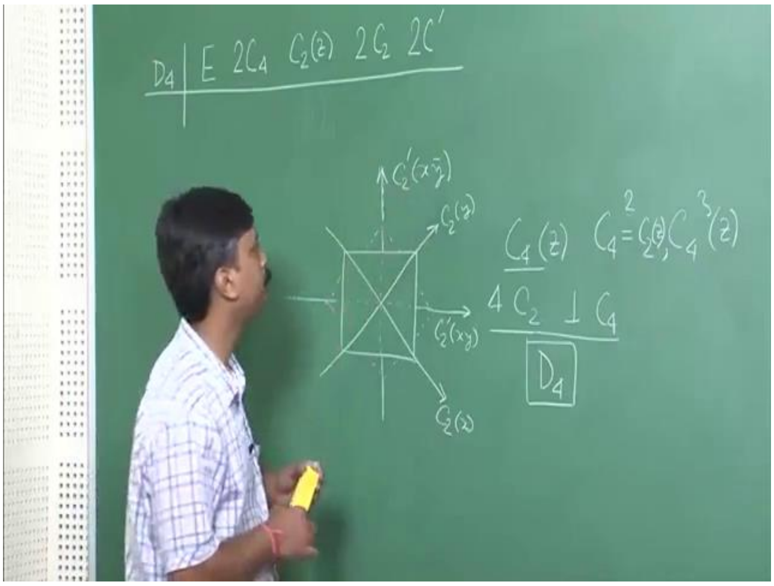

So, identity will form a class by itself. Now if you do a simulated transformation on this each of this symmetry operations of this point group, you will find out what are the difference symmetry operations belonging to particular class or the which particular symmetry operations form class together or class by itself? So, now, C 4 and C 4 3 they form a class, in some previous examples we have seen that. While C 4 2 forms a class by itself because if you intuitively you can easily figure this out this C 4 2 is nothing, but C 2 and C 2 when you operate twice it will give identity. Now this particular C 2 is a unique type of C 2 for this particular molecule, they are other C 2s, but those C 2s are completely different from this one. So, this particular C 2 which is C 2 Z is not going to be club together with any other C 2s. Therefore, this C 4 2 or C 2 Z will form a class by itself.

So, next I have class for C 4 which combines C 4 and C 4 3. So, I have 2 elements in that particular class and we also said about C 2 Z right. Now we are left with 4 other C 2 which are perpendicular to C 4. Now if you remember when I drew the C 2s there are two different types of C 2s here also. So, two of the C 2s they were along the diagonal of the font square that I drew while, the other 2 C 2 they were along the diagonal of the square that I drew which was behind the plane of the first square. So, 2 C 2s will form a class and another 2 C 2s will form another class. So, therefore, I can differentiate them. So, for example, if I just quickly redraw this structure, something like that and right. So, we had C 2s which was along this as well as this. Now you can use C 4 2s take this particular axis over here. So, therefore, this C 2 if I call this is as C 2; suppose this is my C 2 x then this will be my C 2 y right. So, C 2 x can be converted into or transform into C 2 y.

Therefore C 2 x and C 2 y are equivalent and we also know that equivalent operations form class. So, therefore, C 2 x and C 2 y will form a class which I can write as 2 C 2. Similarly the other 2 axis which are along this diagonal and this diagonal they will also form a class right. So, if I call this as x this as y then I will call this 1 as C 2 x y may be I can separate them C 2 prime and this one let me call as C 2 x, C 2 prime x y bar to differentiate. Now in that case this 2 C 2 primes will form a class because similarly similar to this C 2 x and C 2 y this C 2 primes they are also equivalent. So, let me write this as 2 C 2 primes and since the characters of the symmetry operations, character of the representation for a symmetry operation belonging to a one class will be identical to another element also belonging to the same class. So, if I find the character of the representation for one of them, I automatically have for the other one. So, we will also look for only one of this either C 2 x or C 2 y right. So, similarly here we will only look for C 2 prime x y or C 2 prime x y bar.

So, having this idea let us try to form the character table, so what is the order of the group here? We have the order of a group here as h equals to 8.

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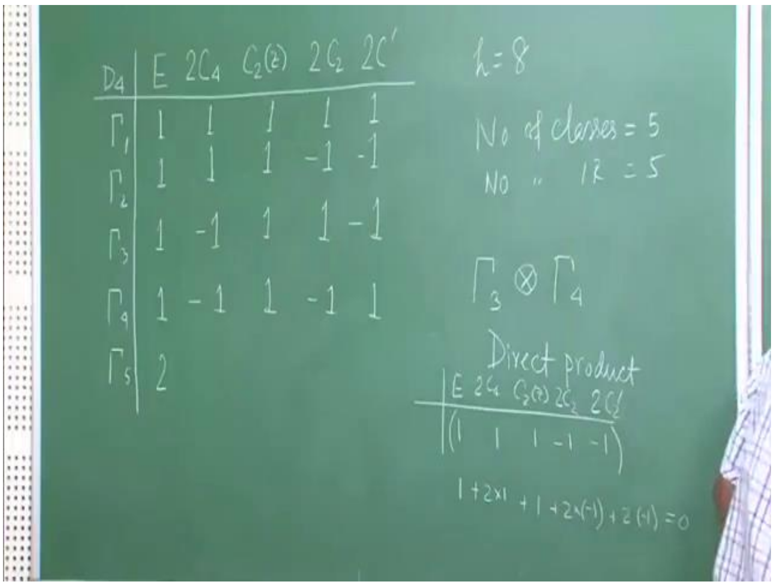

Now, how many irreducible representation it can have? It will be equal to the number of classes that are possible that, we got from the consequence of the great Orthogonality theorem. So, we have 1, 2, 3, 4, 5 classes. So, number of classes equals to 5. Therefore, the number of irreducible representation is also 5. So, I can write there will be Gamma 1, Gamma 2, Gamma 3, Gamma 4 and Gamma 5. So, far we do not have any idea, what is the nature of the irreducible representation? Therefore, we are just giving them a general name in terms of Gammas.

Now, what about the dimensionalities of this irreducible representation? So, then if we go back to those rules that we got out of the great Orthogonality theorem then, we can say that summation over i l i square equals to the order of the group right. So, in our case what we have? We have 5 different irreducible representations, l 1, l 2, l 3, l 4, l 5 equals to 8 that is our equation. So, what are the different ways I can form? Remember l has to be positive and should be greater than 0 for sure. So, l cannot be 0 and l has to be positive. So, if I assign all of them as 1 then I have 5, which is less than 8. So, that is not a solution in case I make one of them as 2, then I have got 4 plus 4 equals to 8 and that seems to be the unique solutions because if I make two of them as 2 then, already I have got total 8 and then rest of them will be minimum 1. So, total sum will cross 8. So, our unique solution is that that l 1 equals to 1, l 2 equals to 1, l 3 equals to 1, l 4 equals to 1 and l 5 equals to 8 which makes this equation satisfied.

Therefore this four are 1 dimensional irreducible representation and this fifth one is a 2 dimensional irreducible representation all right. Now we also know that for a given character table of any point group there will be one totally symmetric irreducible representation right. For which all the characters are plus 1 and we can write down that for Gamma 1. So, let us fill this row all right quickly let us check that if a square of the characters corresponding to each symmetry operations for 1 IR is equal to the order of the group or not. So, if you do that. So, 1 plus 2 into 1 plus 1 plus 2 into 1 plus 2 into 1 yes that is equals to 8. So, this is satisfied.

Now, what else we know so far? That there are 4 one dimensional irreducible representation and 1 two dimensional representations, dimensionality is given by that character and dimensionality of any representation reducible or irreducible is given by the character of corresponding to the identity operation. So, this much we can write. Now we have to fill out the rest of the places. So, regarding the one dimensional irreducible representation we can very easily do that because what we have to consider is that any 2 irreducible representation will be orthogonal until and unless we are considering the same irreducible representation. So, Gamma 1 and Gamma 2 will be orthogonal, Gamma 2 Gamma 3 will be orthogonal. So, any two of them if you pick they will be orthogonal to each other. So, if we keep that in mind then we can easily fill this place at least up to Gamma 4.

So, let us do that. So, so total we have 8 operations and these are all one dimensional IRs. So, what I have to do? If I have to make them orthogonal say we already have this total symmetric irreducible representation. So, if I want to form another irreducible representation which is orthogonal to this what I have to do, I have to make 4 of the operations having character plus 1 while the other 4 we have minus 1 as character. So, if I do that very simply I can get it. So, here I have 4 operations I will ascribe plus 1 to it and there we have another 4 which I ascribe minus 1 to this. So, this will again satisfy the clause of sum of the dimension square of the IR will give you sorry some of the characters of the IR will give you the order of the group because square of the any negative quantity will give you a positive quantity.

So, I got 1 and then I can keep filling. So, let me do this one. So, I have 2 plus 2 4 negative 1s and other 4 are positive. So, let me just interchange this 2, now if you quickly verify, if they are orthogonal or not? You can find that out. So, let us say I am looking for Gamma 3 and Gamma 4. So, if I make a product between the characters of Gamma 3 and Gamma 4 on 1 to 1 basis. So, what I am going to do is Gamma 3 and Gamma 4. This type of product which I already have this used in my last class, this kind of product is known as direct product. A few important things about this direct product will be discussed in the following class or the next to next class; however, so in this particular type of product which is direct product we have 1 to 1 multiplication. So, what we have here? We have if I write in terms of a direct product; we do it very similar to the character table. So, we have 2 C 4, C 2 Z, C 2 x or C 2 y and then C 2 primes. So, if we multiply 1 into 1, I have 1 minus 1 and minus 1, I have plus 1 then 1 and 1 it gives me plus 1, then 1 and minus 1 it gives me minus 1 and this 1 gives me minus 1 .

So, if I have a sum of all these quantities at the end. So, I will have 1 plus 2 into 1 plus 1 plus 2 into minus 1 plus 2 into minus 1 which is equals to 0. This proves the Orthogonality you can take any two irreducible representations and you can verify this

Orthogonality relation between the irreducible representations, which is also telling you that so far whatever you have got for Gamma 1 to Gamma 4, they are correct. So, each of them are normalized to the order of the group and any to IRs are orthogonal to each other. So, they are forming an orthogonal cell. Now the next thing that we are left with is to find out about this two dimensional irreducible representation. So, one way to do this is to try out. So, like doing a trial in error method if you find some number which will be orthogonal to each of this. Otherwise there is a very very easy solution where, you can take generalized point and take its co (Refer Time: 26:57) and then you apply all the symmetry operations and to get the representation.

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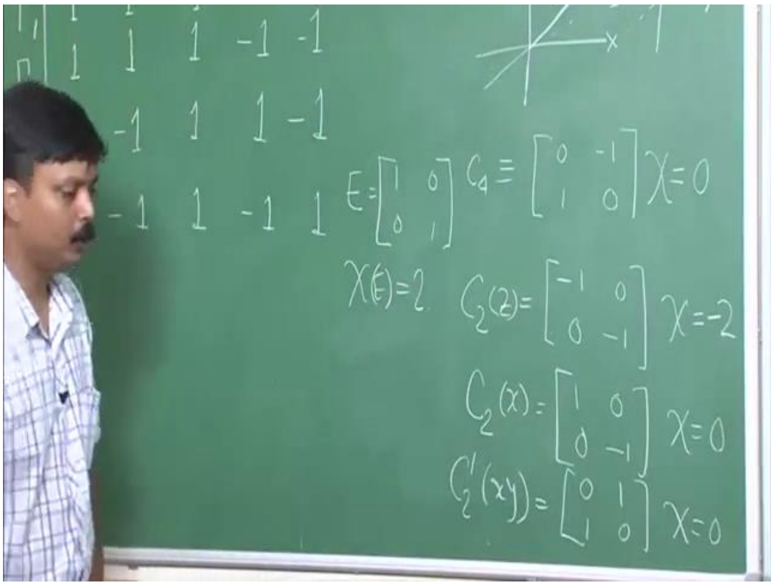

So, for example, if I take a quadrant system as X, Y and Z and then minus X, minus Y minus Z. You can suppose, this is my general point whose quadrants are given by X, Y, Z. So, if I apply all these operations. So, by C 4 is along the Z axis.

Now, one important thing is that the Z axis remains unchanged. So, under most of this operations and under certain, but what will be the case Z axis can independently form an irreducible representation and therefore, this will give you and one dimensional representation. So, one dimensional representation for this particular group we have already found and we are looking for the two dimensional representation. So, we have already seen in certain cases that X and Y, they transform together and you can separate out Z and X, Y. So, here also we will do the same thing. So, we will omit Z and we will perform our work on X and Y all right. So, my C 4 is along this direction and if I perform C 4 on my X and Y basis, what I am going to get? So, here suppose I rotate then X will go to place of Y and Y will go to the place of minus X right.

So, if you form a matrix for this C 4, you can do that very easily because (Refer Time: 29:15) in operation of C 4 on X, X is becoming Y right. So, this will be Y, Y is becoming minus X fine. So, this will be coming. So, this is my matrix for C 4 right.

And then we can have the matrix. So, this will give you the character of the (Refer Time: 29:53) representation which is 0. Now if we look at the representation for C 2 Z what we are going to get? We are going to get X getting transformed into minus X, Y getting transformed into minus Y. So, what we have is this right. So, if I look at the character for this one, this is equals to minus 2. Next we have C 2, that is C 2 x or C 2 y. So, let us take this is as C 2 x, if I find C 2 x or character for C 2 y will be also the same because they belong to the same class. So, what the C 2 x do? So, C 2 x is along X axis right. So, it will do nothing to X axis, but it will transform Y to minus Y correct. So, you can find out that X is remaining same while Y is becoming minus 1.

So, therefore, the (Refer Time: 31:16) equals to 0 right and for C 2 prime, if I take C 2 prime as C 2 x y. So, if I call this one as X Y. So, if I can re draw this one without this Z. So, if I have X and Y, then this if I call C 2 prime x y and what it will do? It will transform X into Y and Y into X correct. So, C 2 prime x y it will transform X into Y and Y into X correct. So; that means, I have this. So, you have got for this 4 operations and identity, we know it is always going to be a unique matrix. So, we are talking about two basics functions. So, the dimensionality will be 2, so I have a unique matrix of plan 2.

So, these are the matrixes and the corresponding characters here. So, character of E is equals to 2. So, we will stop here today and the next class we will start from right here and complete the character table.

Thank you so much.