Chemical Applications of Symmetry and Group Theory
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Lecture – 22

Hello and welcome back, today 2 of week 5. So, we will have been discussing about D4 point book and we are trying to find its character table, form its character table completely.

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So, why we left we have studied this and this particular place. So, we took we form this one dimensional representation. We saw that it has 4 one dimensional irreducible representation and taking the Orthogonality into consideration which found the 4 irreducible representations starting from gamma 1 to gamma 4 and knowing that the fifth one is the two dimensional representation we took x, y axis as matrices and operated all the symmetry operations and we found the matrix form of those you know symmetry operations using x, y as a basis set and thereby, we got the characters of those particular symmetry particular representations.

So, this was our results. So, for identity we can character 2. Now we already knew that right there is nothing surprising about that we already wrote that and for C 4, the class for C 4 it gives the character as 0. So, let us put that and C 2 z gives minus 2 and C 2 x as well as C 2 prime x y both give character as 0 seemingly, we have got our character table completely for area 1 and area 2, but we have to yet check that. So, first let see if that square of the characters of this particular irreducible representation which is two dimensional whether it is equal to or they are group or not. So, very easily we can see that it is 8th the square of 2 plus square of 2 equals to 8, so that is satisfied. Last thing we are left with is to verify whether Orthogonality holds or not.

So, similarly, similar to the previous example where we checked up between I think gamma three and gamma 4 here we will check the Orthogonality between, gamma 5 and say you know gamma 4 as one of the IR's. So, if I do that then what we have 2 into 1 equals to 2 plus 0 into minus 1 into 2 equals to 0 then 1 into minus 2, equals to minus 2 and then 2 into minus 1 into 0 equals to 0 and again 2 into 1 into 0 equals to 0. So, ultimately we have 0. So, this gamma 5 is orthogonal to gamma 4 and I will leave it with you, yet you verify, if this one is orthogonal to any one of them. Actually you will find that yes it is orthogonal gamma 5 is orthogonal 2 any of the other 4 IR's and all the IR's are orthogonal to each other and they are normalized to the order of the group.

So, we have successfully found the irreducible representation for this point group D4 now at this point, let us complete both area one and area 2. So, here we are supposed to keep them the Mulliken symbol. So, if I look at this is total symmetry irreducible presentation of course, it will be E type. Now there is other E type you know representations there also we can see their B types. So, I am not going to talk in detail about this one because, we have already discussed about Mulliken symbols for irreducible representations in detail earlier.

So, here with respect to principal axis of symmetry these 2 are symmetric. So, without worrying about anything this two will be given that notices A we will worry above subscript or supers scripts. Later and this 2, one dimensional representations are; if I look at the characters correspond to this principal access of rotation I find that as symmetry. Therefore, this two belong to B type of symbol and this one being two dimension representation, we have E as the symbol for the IR and since there are no center of inversion we do not have to worry about whether there are g or u you know subscript for this one, neither we have another you know two dimensional representations.

So, we not have to in a separate 2 different e type of representation. So, he will remain as such only we have to worry about A and B. So, here what is our notion? Our notion is to look at the symmetries of the character with respect to the perpendicular C 2 right. So, when we want to differentiate between these 2 IR's we look at this C 2 primes. So, we that this one is symmetric while this is anti symmetric, this one will be A 1 and this one will be A 2 similarly, if we want to differentiate between B these 2 B's then, I look at again here. So, irrespective to this one and this one I have this one is anti symmetric this one is symmetric. So, I can write this is as B 1 and this is as B 2 and this inverse E. So, I got the Mulliken symbols as well.

Now, what we are supposed to do here is to find out what will happen to the other 2 areas of the character tables. So, I have area 3 and area 4. So, we may not able to complete the whole thing, but we will start and rest of the things, you should you know complete as and assign now. So, this is area three where we have the Cartesian coordinates and you know rotational symmetric coordinates as this is functions. So, we need know say x this contains x, y, z. R x, R y and R z this 6 functions you know you will find in this region.

Now, our job is to ascribe this x, y, z or R x, R y, R z to particular IR's which transform as one of this you know coordinates or the in a rotational coordinates. So, first if we look at the z, just the z axis if you look at and you operate on operate all this switch operations what you will find that with respect to E C 4 and C 2 z the characters will be 1 because, this will give you one dimensional you know matrix because this is only 1 single function right that we act as basis function. So, I will get factor 1, 1 and 1 for this, now for C 2 x suppose what will C 2 x to C 2 x will change you know z to minus z correct. So, we will we done by C 2 y. So, that will give you minus 1 as character. So, this is minus 1 and C 2 prime what we will do that will also do the same thing. So, because all C 2's are perpendicular to this z axis correct. So, all these C 2 prime or C 2s will terms you know convert z plus it to minus z. So, this one as well we will get as minus 1.

So, now these are the characters that you get when you use z as the basis you know vector. Therefore, you just compare this one with this 4; one dimensional irreducible representation and you see that this matrix exactly with this one correct; that means, this A 2 irreducible representation you know it contains z axis basis function. So, we ascribed z here what we say that you know this z transform as a 2. Now x, y and x, y you have just done right because, x, y, if you remember those you know matrices that we form one think probably I missed out that is those. Today you know 2 by 2 matrices that we found for when we took x, y as a basis functions then those matrices they are you know not reducible because they are not block factor in the same way.

So, you have like a 1 0 0 1and then you had 0 you know 1 1 0. So, they are definitely not block factor in the same way so; that means, this 2 by 2 matrices they themselves are the blocks which cannot be reduced in further and that is why we could use that as irreducible representation. So, there we found that x, y together form the basis excuse me for this two dimensional irreducible representation E. So, you can write x, y. So, whenever you see this one then you will realize that x and y are not you know separable and the together they form the basis. So, individual x or y cannot form a basis for any of the irreducible representation for this particular point group for any other point group particular any other point group it may formed, but in this particular case they are not capable of forming what as basis function individually they transform together as E all right.

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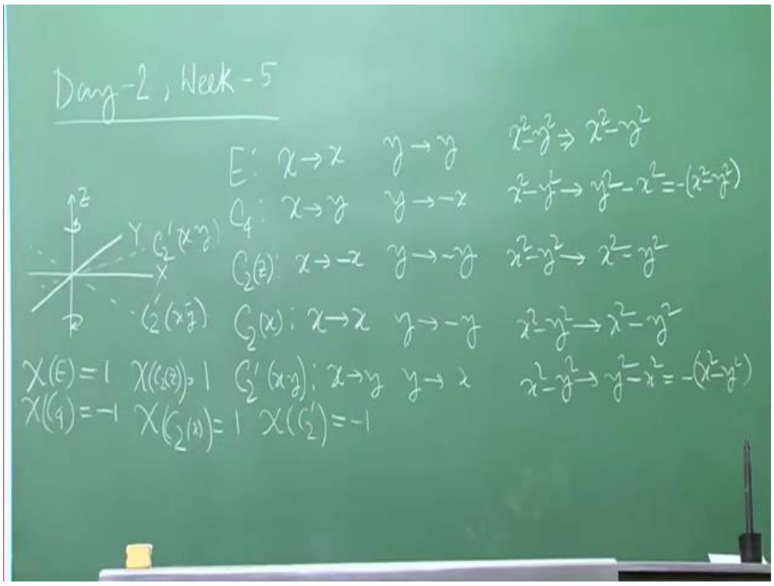

So, what about the R x, R y, R z, what is R z? R z is the rotation about the z axis. So, suppose I have this is my coordinate system again while this x, y and z axis. So, this wills v by R z. So, this is the rotation about z axis in the particular direction suppose, I have this direction exactly light what I showed here. Now when I operate E nothing happens to this you know particular directionality of the arrow C 4, C 2 z also retain the same you know direction of this arrow while we have we apply C 2 x. So, C 2 x is along this axis what will happen this will come down here. So, if it comes down here it will be like this which is just opposes it. So, if this one I call symmetric then this one anti symmetric.

So, what does that mean that will keep me you know a one dimensional representation which gives a character of minus 1. So, if I look at here for C 2 y that also will be giving the same character. So, what I will get just like for z when, I am looking at R z I got you know symmetric one dimensional characters for E C 4 and C 2 while for C 2 I am getting minus 1 and if I apply the C 2 x y. So, this one or C 2, this 1 is C 2 prime x y and this, 1 is C 2 prime x y bar both of them will act in the same way. So, I will get minus 1 here because this 2 will also you know change the irrationality of this arrow here which signifies the rotation about z axis a particular direction. So, this 1 also you know is the same as a 2. So, I have R z of character this particular now, you can find out about R x and R y. So, that is left as a home tasks, you can try this out.

Now, this is the area 3 and this is area 4 areas, 4 you will find you have either square functions or some you know binary functions. For example, like you know z square or x square plus y square x square minus y square or xz, xy, yz these. So, you can you can you can probably easily see that these function are related to the weight function of d (Refer Time: 15:47). So, this part which contains something like or this kind of function square functions or like you know binary function like this particular functions are chosen because they contain the symmetries of matrix differently of matrix and this is used in case of you know different, you know type of bonding and when we will use like you know combination of different like to form symmetry linear combinations. We will see how useful they can be and particularly like you know ergonomic chemistry. Why we the talk about the metal bonding. Where the d orbitals have really vital and there you need to know about the dependence of the irreducible representation on this particular type of functions where functions in order to have a proper idea, about this metal bonding and in the next step, you know about that in aesthetics.

So, now suppose we want to find out to which IR this particular function x square minus y square transform class. So, this is not very difficult how. So, what we can do we can individually work on this x, y and z and then, we can see how this x square minus y square. For example, changes when we apply one of this symmetry operation all the symmetry operations. So, here in this picture if you look at and if you try to see you know how x and y gets in a change we have already seen that. So, we can just quickly recap that. So, upon E x remains x and y remains y.

So, this is for E. So, for C 4 what happens? C 4 x becomes y and y becomes minus x right. So, C 4 x becomes y and y becomes minus x all right and C 2 z x becomes minus x y becomes minus y. So, C 2 z x becomes minus x y becomes minus y then C 2 plus x C 2. So, C 2 x will not change x, but it will change. So, y 2 minus y, C 2 x it will change x to x; that means, it will remain unchanged and y will become minus y and then C 2 prime x y say for example, then what will happened x will become y and y will become x right. So, C 2 prime x y for this x will become y and y will become x.

Now, if I know this one so I can easily find out what will happen to x square minus y square. So, nothing is changing. So, I will have x square minus y square. When I operate E on that, now in case of C 4 if I apply C 4 on x square minus y square what is going to happen x is becoming y. So, this is becoming y square and y is becoming minus x. So, it is minus x square which is nothing, but minus of x square minus y square right. So, here for example, we operate C 2 z then what is happening is x square minus y square is getting transformed into. So, x is becoming minus x. So, there is no change here and this one is also remaining unchanged and for C 2 x here your x is remaining x. So, therefore, and y is becoming minus y, alright.

So, and in the lastly C 2 prime x is becoming y. Therefore, it is y square and y is becoming x. So, minus x square which is equals to minus x square minus y square all right? So, whether this is you know symmetric this transformation that is x square minus y square to something is symmetric with respect to E symmetric with respect to these or not depending on that you can get either plus 1 or minus 1 and you can see here for E it is suppose I write here as chi of E is equals to 1 and then chi of C 4 equals to minus 1 and then chi of C 2 z equals to 1 and chi of C 2 x is equals to 1 and chi of C 2 prime equals to minus 1.

Now, if I look at that and compare this chi, so chi of E is only 1 chi of C 2 z equals to 1 and chi of C 4 equals to minus 1. So, this definitely belongs to b symmetry and then you have chi of C 2 prime as minus 1. So, if you look at that you have this symmetry. So, then x square minus y square belongs to this particular symmetry. So, in the same way what you can, do you can try out different other function say. For example, z square or x z or x, y, so only what you have to do you have to just see how that individual x or y or z gets transformed upon the operations of this symmetry operations and then taking those you see what is happening to the total over all function what about that you have and then we find out the corresponding change.

So, you get the characters and then you match with this irreducible representation that, we have already formed and then you ascribed that particular function to one of the IR's with which you know you get the max. That means, that particular function will correspond as that particular IR that you are getting. So, this is how you can form the total character table the reason be we dealt with this one is, that in an later stage we will go in a different way like knowing from this one. Suppose we are given a particular type of orbital and you know say suppose that is d x square minus y square.

So, I know that this particular orbital has a symmetry which gives me one particular irreducible representation for a particular point group. Whatever molecule we take we are considering suppose, we have to look at the character table of that particular point group and then we can you know find out that this particular ligand has this particular if transform as this particular irreducible representation and that information. We will utilize later on that with which particular other you know like and it will you know combined with or which particular wave function it will combined with because every orbital is characterized by it is own weight function right.

So, those things we will start looking at from the next class onwards. So, what we will do, we will have very brief introduction about the relation of truth theory and quantum mechanics and then, we will start looking at how one can form the symmetry combination, linear combinations and to look at their energetic and then, in the next step we will look at the you know symmetries of molecular vibrations and see how to and find out different normal modes and then, try to figure out how to find the selection rule of different transitions vibrations and electronics. So, with that I will leave you today and we will see you on the date 3 of with 5, till then.

Thank you.