Symmetry and Group Theory
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Lecture -51
Ascent and Descent in Symmetry - I

So, in the last few lectures when we were discussing valence bond and molecular orbital theory, we saw that we needed to reduce our representation, reducible representation under d infinity h point group. So, that is not a very favourable situation because in the reduction formula we have h which is the order of the group in denominator and if h is infinity, for example in d infinity h point group, the calculations are non-trivial.

So, you cannot use reduction formula if something in denominator is infinity, so what to do in those cases? So, let us discuss a topic which is called as ascent and descent in symmetry, so that is increase and decrease in symmetry.

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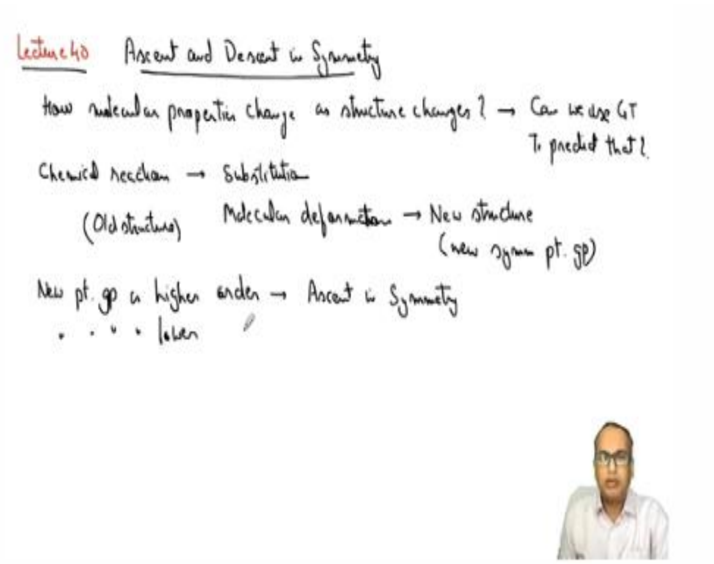

So, let us start with that discussion, so why do we need to discuss ascent and descent in symmetry? So, the idea is that how molecular properties change, so we will say how molecular properties change as structure of the molecule changes, can we use group theory to predict that. So, what do you mean by structure changes? So, for example under any chemical reaction we see that substitution may happen or deletion of an atom may happen leading to molecular deformation or structural deformation.

Structural deformation can also happen due to other reasons and not just chemical reaction, change in conformation, all of this leads to a new structure with new point group. New symmetry point group. So, now this new symmetry point group and, let us say if I am saying that old structure here, so old symmetry point group the order of the groups might be different. This might have higher order; this might have higher order depending on whether you are increasing in symmetry or decreasing in symmetry.

So, if new point group is of higher order, then we call it ascent in symmetry because we are actually increasing the symmetry. If new point group is of lower order, we call it as descent in symmetry, we are decreasing in symmetry.

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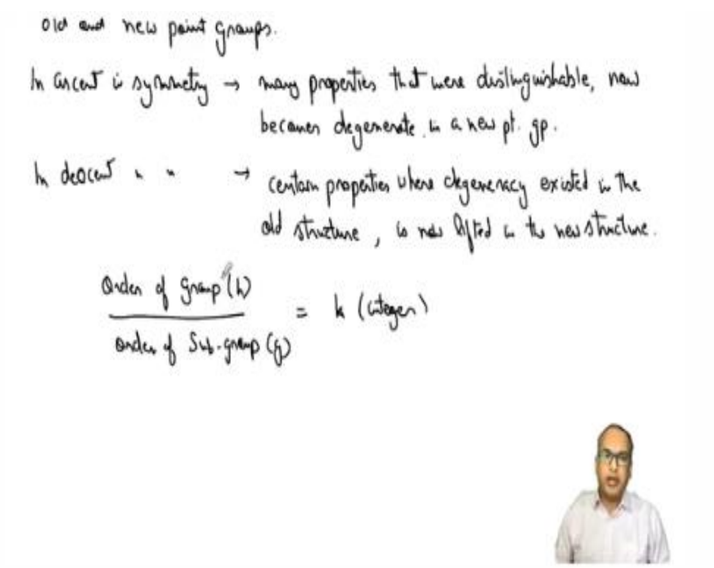

So, the important point is that in either case, we will say very often, because it is not always and we will discuss those cases also where it is not the case. In either case there is group-subgroup relation between old and new point groups. I mean so if you are going from one point group to another point group, very often, if the overall molecular geometry is preserved then there is a group-subgroup relation.

So, in case of ascent in symmetry in many degenerate properties, no, if you are going from lower symmetry to higher symmetry. So, we should say many properties that were distinguishable now becomes degenerate. We will see how that happens, in a new point group or new structure or new molecule. And in descent in symmetry certain properties where degeneracy is actually existing in the old structure, is now lifted.

So, degeneracy lifted meaning that they are now acting independently, is now lifted in the new structure. So, also if there is a group subgroup relation so we can say that the order, if this is only to remind, order of group which is defined by h and the order of subgroup, let us call it as g, must be equal to k, where k is an integer. So, it must be an integral divisor of the order of the group. So, if there is a group-subgroup relation the two must follow the rule of group-subgroup.

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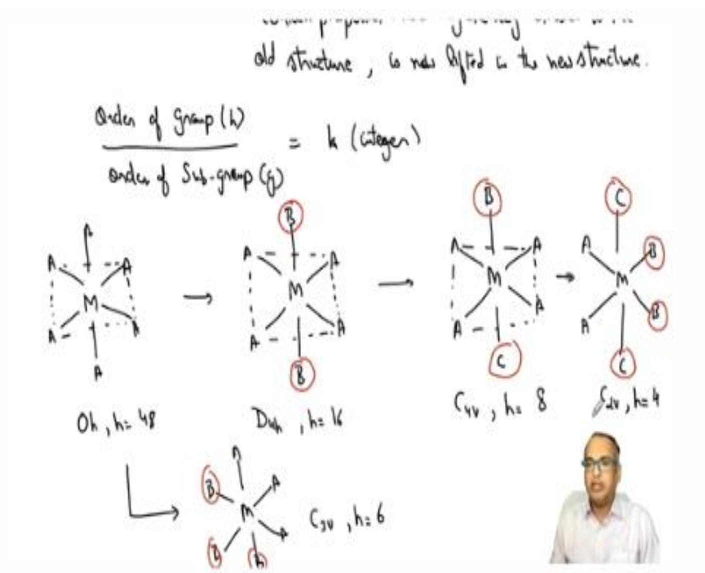

So, now let us take an example, because without example it is not easy to understand. So, let us start with the octahedral group. We know how an octahedral molecule looks like, so there is a central metal atom and there are six ligands, all bonds are equal. Now this point group is Oh and h is equal to 48, the order is equal to 48. Let us now say that if we substitute these two with B atoms, what will happen A is replaced with B? There is some reaction which does that.

So, what do we get? We get this. Now what is the point group of this? This will be D4h, I am not drawing the wedged projections and all, but it should be clear that how is the arrangement of these atoms, now the order of this group is 16. So, you can see that if you divide 48 by 16 it does form, it does come to an integer so that means there is a group-subgroup relation between Oh and D4h. Now if you go further and if you substitute now this B with C, then what do you get?

So, I will just mark where the substitution is, so we have B here so we keep one B and another as C. So, that we are killing the plane which is containing the 4 A atoms and the M atom. So, if we kill that plane what do we get? We will get, let me color this that there is a change over here. Now the new point group will be C4v and the order of this group is 8 so you are still following the integral divisor.

So, 48 divided by 16 is 3, 48 divided by 8 is also an integer, 16 divided by 8 is also an integer. So, this is the universal group in this particular case D4h is a subgroup of Oh, C 4v is a subgroup of D4h as well as Oh. So, keep on going and then what do we have here if we further replace let us say these two as B's and these two as C's, what do we get here? So, in all these cases this central metal atom has the octahedral geometry.

So, basic geometry of the molecule is still preserved, it is not changing. The point group and the symmetry is dependent on the pendant atoms also, so that is, so we are only changing the pendant atoms. So, now if you see that the point group here is C2v and order of the group is 4 and now this is still following group subgroup relation. So, these are the substitutions now. There is another way of going from here if you see that if we change three of the atoms then what happens?

Let us say I have A this will be B, B and A. So, I am making substitutions at this point, this point, this point. So, now this is a case of ammonia kind of molecule, so you have C3v and order is 6. Now if you see that this particular molecule is a subgroup of Oh so C3v is a subgroup of Oh but C 3v is not a sub group of D4h or C4v or C2v. Because here the integral divisor does not work, so this is one group-subgroup relation, this is another group-subgroup relation. So, let us write it down explicitly that what we have now.

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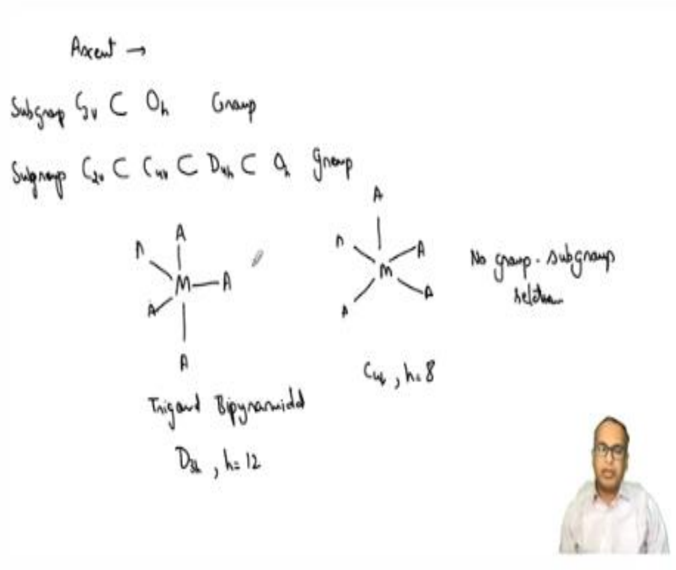

So, we can say that if we are going towards higher symmetry so we have C3v is a subgroup of O h and on the left-hand side we can say it is a subgroup, right-hand side is a group. Now the order of this is 48 this is 6, so you have group-subgroup relation. Similarly, the second one was so here also again it is a subgroup you start with C2v, C2v is a subgroup of C4v. We have seen that in that example C4v is a subgroup or subset of D4h followed by Oh.

And now this side is the group this side is the subgroup, so left side is subgroup, right side is group and this is all these are related right. So, in all these cases if you see the central metal atom does not change its geometry, but if the central metal atom changes its geometry, so let us say consider a molecule with let us say this is a trigonal bipyramidal structure. So, this is trigonal bipyramidal what will be the point group point group will be D3h here, D3h.

And order is for D3h and the order will be 12. We can verify it, now let us say if there is some sort of chemical reaction, structure of the molecule changes from trigonal bipyramidal to square pyramidal, that can happen. So, if that happens the point group changes to C4v and the order is 8. Now in this case, if you notice that 8 and 12 are not related as an integral divisor, so this is not group-subgroup relation.

So, we can say there is no group-subgroup relation observed here because there is a overall change in the central metal atom geometry. So, that is very, very important that the basic geometry of the molecule has to be preserved if they have to follow group-subgroup relation.

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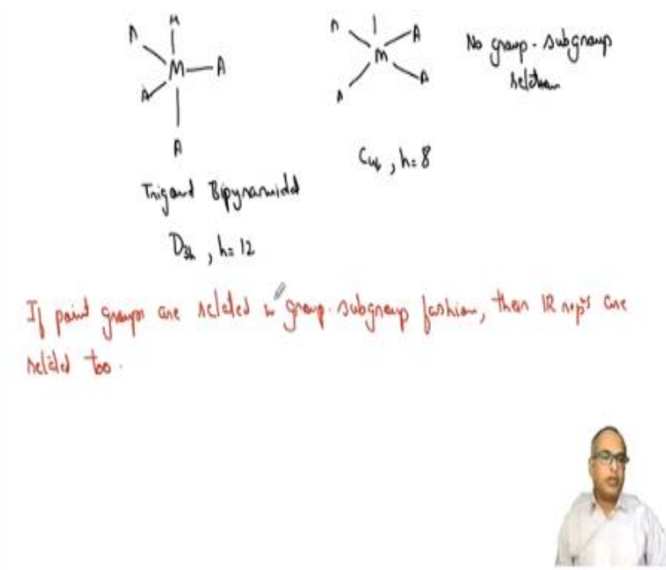

Now the important point is the most important point in all these relations is why we are discussing this group-subgroup relation and I will write it in red because it is really important. So, if point groups are related in group-subgroup fashion, then their irreducible representations are related too, how they are related, we will see but first the point is that if some of the point groups are related in group-subgroup fashion then their IR representations would also be related.

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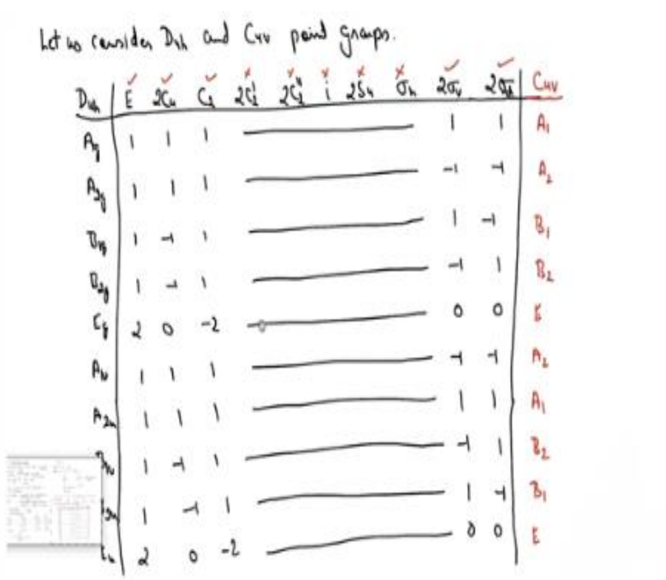

So, now let us consider the D4h and its subgroup C4v. Because if we start with Oh octahedral this will be the entire time will go in, just writing the character table so I am going to write the character table for D4h that itself is 10 class so 10 IR representations. So, let us consider D4h and C4v point groups. So, in this case D4h is the group and C4v is the subgroup, so we will write down the character table of D4h and we will see how C4v IR representations are related to D4h IR representations.

So, let us see that, so let us start with D4h, what are the symmetry elements present? So, I am just reading out from the character table now so you have E, 2C 4, C 2, 2C 2 prime, 2C 2 double prime, we have i, 2S 4, sigma h, 2 sigma v and 2 sigma d. I will draw a line over here and I will also write down the Mulliken symbols for 10 IR representations which are, A1g, A2g, B1g B2g, Eg then you have A1u, A2u, B1u, B2u and Eu. So, this is what we have.

Now the important point is that the group-subgroup relation if you remember the first week of lectures or second week of lectures, where we discussed what is a point group and what is the subgroup of it. So, subgroup should form or must form the group within the elements using some of the elements of the main group. So, for example if these are the elements of D4h some of these elements would form a complete group.

That is, it will fulfill all the criteria of a point group definition but using only some of the elements. So, if you look at the C4v character table, we will see that C4v character table only contains E, 2C 4, C 2, 2 sigma v and 2 sigma d. So, C4v point group does not contain any of these elements. So, I will just write down C4v with red color here. Now if we write down the characters from character table only for the common symmetry operations or only for the common group elements.

We will see that this is 1 1 1 and I am not going to write anything here and this is 1 1, then under A2g it is 1 1 1 and these ones are minus 1 minus 1. For B1g it is 1, I am just reading out from character table, so you can all do that, so again this is 1 minus 1 1 and we have minus 1 1. Eg has 2 0 minus 2 and this is 0 0, then again, we have 1 1 1 and we have minus 1 minus 1 here, then we have 1 1 1, 1 1. For B1u 1 minus 1 1 this is minus 1 1.

We have 1 minus 1 1 and 1 minus 1, 2 0 minus 2 0 0. So, now if we read out only these characters from C4v character table then what do we get, so and we will write down the Mulliken symbols corresponding to these characters, which are now present and do not care about the ones which I have left blank. But read out the C4v character table and write down the Mulliken symbols here. So, what do we get here?

So, we will again use red color to write that we have A1, A2, B1, B2, E, A2, A1 and B2, B1 and E. So, now you notice that C4v has 5 classes so it will have only 5 IR representations which are A1, A2, B1, B2, and E, whereas D4h has 10 classes, so it will have 10 IR representations. So, that means each IR representation of C4v must be correlated to 2 IR representations of D4h. So, how does it correlate now.

So, we can easily see that whatever is A1g in D4h it is actually nomenclatured as A1 in C4v. So, if you just write down these characters, so let me go to the next page. So, if we write down these IR representations which are now correlated.

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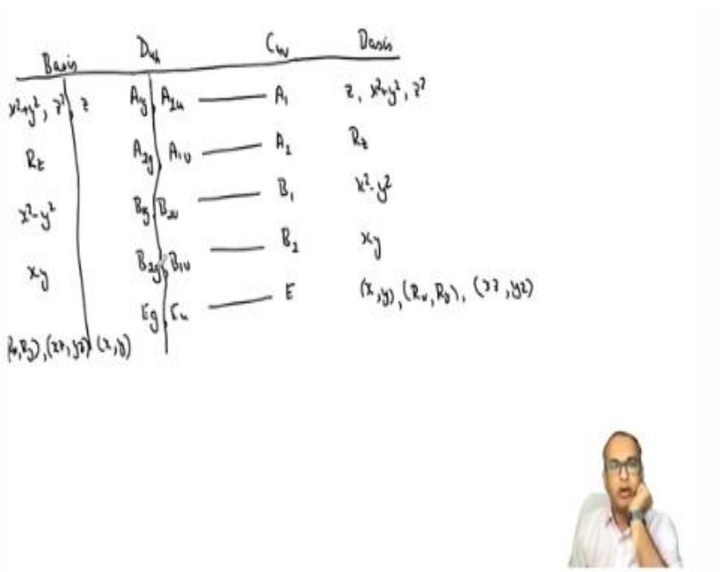

So, let us first write down on top the point group and C4v here so C4v has A1 A2 then we have B1 B2 and you have E and D4h has so A1 was correlated with A1g and A2u. So, you can say that these are the correlations, then A2 was correlated with A2g and A1u. B1 is correlated to B1g and B2u and B2 is correlated with B2g and B1u and E was correlated to Eg as well as Eu.

So, 5 representations in C4v, each representation is correlated to 2 representations under D4h point group, now if you also look at what are the basis of these IR representations under different point groups you will find that the basis are same which is a very important result. So, if you see A1 under C4v point group we find that it is z, let us also take the binary products z square, Rz has A2 as the basis then x square minus y square, then xy then x, y, Rx, Ry and xz, yz.

So, now let us also look at the bases under A1g and A2u combined here because both of them are correlating with A1. So, if we read out directly from character table, we will see that the basis are x square + y square, z square and z, so you get same basis. So, if we want to separate out these ones the basis for this, let us try to draw a line carefully between this and I will just write down the bases on the left for A1g and right for A2u.

Similarly, the left basis is for this side right basis will be for A value side. So, Rz then you have x square 2 - y square then you have xy, you have rx ry and xy and also for Eu what is the basis let me see, D4h for Eg it is this one is xz yz and Eu it is x, y. So, the point is that whatever is the basis in D4h point group for individual IR representation the correlated IR representation under the lower or under the subgroup will have the same basis.

So, that means whatever property has A1 symmetry, the same property will have A1g or A2u symmetry in D4h. So, the properties are also correlated so even though you are changing the overall conformation or overall structure of the molecule with keeping the geometry of the molecule consistent so that there is a group-subgroup relation, the properties are preserved. So, you can talk about the properties of this point group and this point group by comparing their IR representations.

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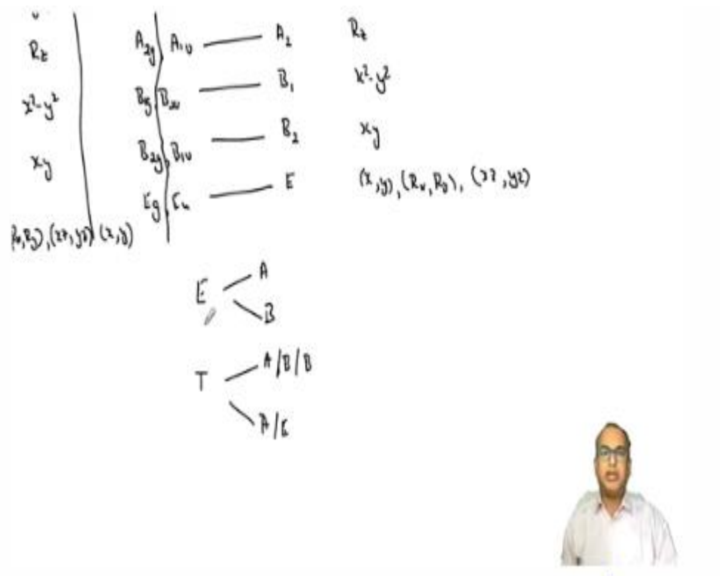

So, in many cases you will see that, so in this particular case if you see that the Eg representation and Eu representations were correlated with E, so that means the degeneracy whatever degeneracy was present in D4h is still present in C4v point group. So, degeneracy is not yet lifted. But what happens in certain cases the degenerate representation of one group may become two or three distinguishable IR representations in a subgroup.

So, in such a case what happens? For example, E representation might correlate with A or B representation or at T representation might correlate with A slash B slash B representation or it can correlate with A and E representation. So, the overall dimension has to be constant so a triple E degenerate representation can correlate with 3 IR representations or one 1d IR representation and one 2d IR representations.

So, the point is that the degeneracies may get lifted in certain cases and may not get lifted in certain other cases. So, for example in D4h to C4v there is no degeneracy which was lifted. Now let us continue that and see if we further go down in symmetry, so we have descended in symmetry when going from D4h to C4v. If we further go down in symmetry to C2v does this degeneracy lifted or not?

So, I think we will take some time to do that, so let us discuss that part in next class and till then so practice developing. So, what we have done today is we have developed a correlation table between a point group and its subgroup. So, try to do some practice of doing the same thing so find out the bigger point group try to write down the character table of it and then find out its subgroup and write down a correlation between the 2 IR representation of group and subgroup.

And we will see if we further go on to the lower in symmetry what happens to degenerate representations all. So, that is all for today, thank you.