Symmetry and Group Theory
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Lecture -61
Symmetry of Normal Modes of Vibration

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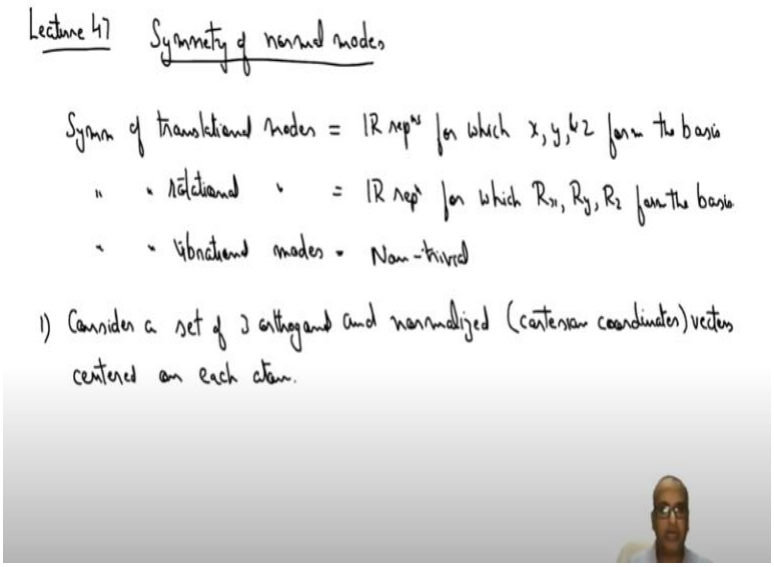

So, welcome back. In today's lecture we will be looking at symmetry of the normal modes that we have seen in the last class. So, we have seen that there are three N total modes or total degrees of freedom present, out of which three are translational two or three are rotational and rest of them are vibrational. So, now let us try to see if we can actually visualize those vibrational symmetry of the vibrational modes and actually visualize how the vibrations are going to look like in different molecules.

So, let us start the discussion with symmetry of normal modes. So, in this the symmetry of translational and vibrational modes is easier to identify, so what is that? Let us see, symmetry of translational modes is basically the IR representations under that particular point to which the molecule belongs. So, IR representations for which x, y, and z form the basis. So, this information can be easily obtained from the character table that what unit vectors.

So, unit vector are forming the basis for which IR representation and that will be the symmetry of the translation modes, because translational modes go with motion in x, y, and z direction. So, similarly symmetry of rotational modes is equal to IR representations for which the rotational unit vectors that is Rx, Ry, Rz forms the basis, so that is easy to see. Now, how to find out symmetry of vibrational modes this is nontrivial, it is not as trivial as it is for.

So, let us see how to do this. So, first of all, let us go step by step, so consider a set of three orthogonal and normalized that is Cartesian coordinates, normalized vectors centered on each atom, we will go through this step-by-step but let us first see what are the steps in there?

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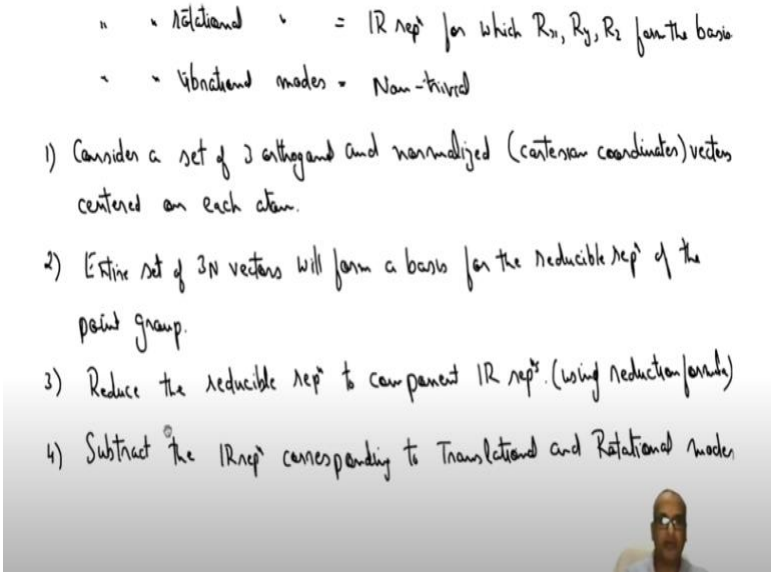

So, this all of this which we are doing is to find out the symmetry of vibrational modes. So, first you have to do is, consider a set of three vectors which are orthogonal and normalized that is Cartesian coordinates, which will be centered on each atom. So, that would mean that if there are N atoms, there would be 3N such vectors. Now, entire set of 3N vectors will form a basis for the reducible representation of the point group.

So, we can create so, we have vectors on each atom. Now, we can create a reducible representation of the point group using this as the basis. Now once we have the reducible representation, next step is reduce the reducible representation to component irreducible

representations. So, that also we have learned and we have practiced enough. So, we know how to do it, this is done using reduction formula.

So, now I will not go through all the calculations, I will just tell you how to do it step by step and we will look at the answer. So, I expect now you do the calculations at home using different molecules. Now, what you have to do is so after you reduce so now you have got a total set of IR representation, which are basically the symmetry of the full normal modes all the normal modes. Now, what you have to do is, out of this subtract the IR representations corresponding to translational and rotational modes.

So, once you subtract this what you have got is, you will get symmetry of your IR representations which will corresponds to the vibration modes. So, let us take an example of water and C2v, we have been discussing this a lot.

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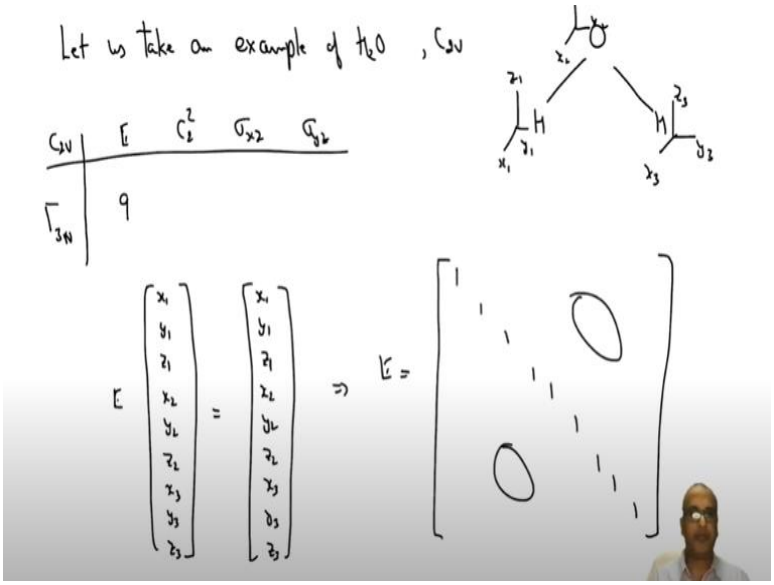

So, now first step is to put so you have water. So, first step here is to place x, y, z on all three atoms, so three vectors on each atom. So, this is x 1, y 1, z 1, x 2, y 2, z 2. Now, create a reducible representation, so under C2v point, this is C2v, what are the symmetry operations we have C2z, sigma x z and sigma y z and we are trying to create tau 3N. Now for E, so now there are 9 vectors so the dimension has to be 9 cross 9.

So, for E let us see how to do this? So, the matrix will be matrix for these vectors will be written like this, x 1, y 1, z 1, x 2, y 2, z 2, x 3, y 3, z 3. Now all of it will remain unchanged, so I am not going to write the whole thing. So, the same thing will remain are let us just write down for completeness x 2, y 2, z 2, x 3, y 3. Now, this implies that my E matrix is nothing but a unit matrix of 9 cross 9 order.

So, all my diagonal elements 1, 2, 3, 4, 5, 6, 7, 8, 9 the rest of everything will be 0. So, I am not going to write all the elements. So, everything else will be 0 and you have diagonal as 9, so my trace will be coming as 9. So, everything will contribute.

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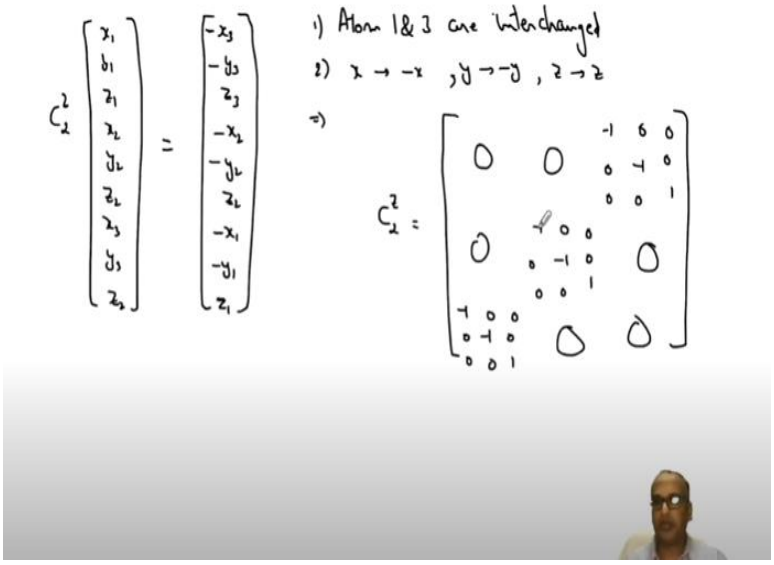

So, now let us go to second symmetry operation, which is C2z. If we perform C 2 z onto the same matrix again x 1, y 1, z 1, x 2, y 2. Now what happens? What is the change which is happening? Let us go back to the molecule and see. So, if we are doing C2z that means atom number 1 will be replaced with atom number 3 and what else will change if atom number 1 and 3 will be interchanged and x will go to - x, y will go to - y, z will remain as positive.

So, these are the changes which will have to create in this matrix. So, x 1 will be replaced with x 3 and there will be a negative sign, y 1 will be replaced with y 3 and there will be a negative sign, z 1 will be replaced with z 3, x 2 the atom remains at the position. So, x 2 goes to - x 2, y 2

goes to - y 2, z 2 remains as z 2, x 3 is replaced with x 1, so this goes to - x 1, - y 1 and z 1. So, that means under C 2 z we can say atoms 1 and 3 are interchanged.

And, the second effect is x goes to - x, y goes to - y and z remains as z, these are the changes which are happening. So, then how would my matrix look like here, because we need to write the matrix to be able to write the character. Now, let us see x 1, y 1, z 1 goes to x 3, y 3, z 3 and with the negative sign. So, I will write - 1, - 1, 1 over here and 0, 0, 0, 0, 0, 0 and my x 2 remains at x 2, y 2, z 2 remains at its own position.

So, that will not change the block, so that means I will have -1, -1, 1, 0, 0, 0, 0, 0, 0. Now, x 3 has gone to x 1 position, so I will write -1, -1, 1 over here 0, 0, 0, 0, 0, 0, rest everything will be 0. So, now if you see that the trace is only contributed by x 2, y 2, z 2. So, the trace will be -1,-1,-1, +1. So, this will be -1, so let us write down the trace over here. So, our trace is now -1. Now similarly, let us write down the trace for sigma xz.

So, I will do it for water and I will give you a little bigger molecule so that you can try it out by yourself at home.

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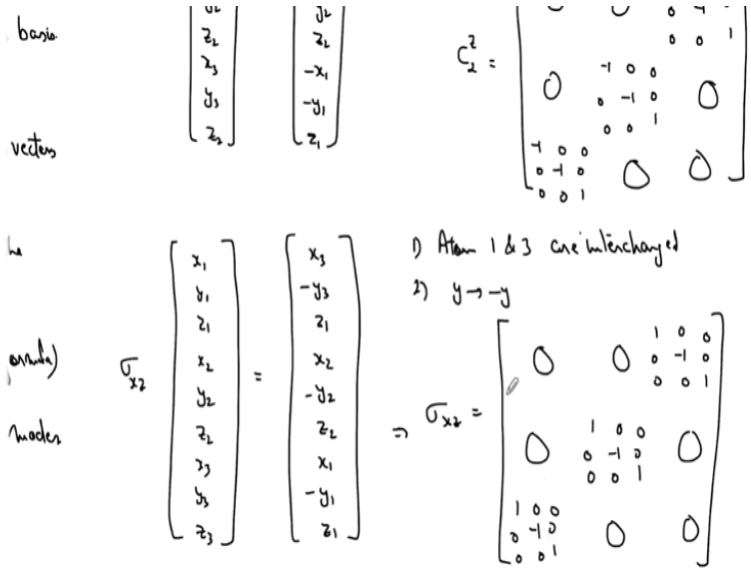

Now, let us do for sigma xz, so it is important to understand how to work this out. So, again we will write the same matrix. Now let us see what is the effect of sigma xz? So, effect of sigma xz

which is the plane going through this and reflecting atom one and atom three. So, again one is reflected with three and only y changes it is sign x because the plane is x, so x and z will change its sign.

So, I will write down effect is atom one and three are interchanged and second change is y goes to - y, x and z will not change its sign. So, that means I can write x 1 goes to x 3, y 1 goes to - y 3, z 1 goes to z 1, x 2 remains such it is own position, just that the y changes it is sign and x 3 goes to x 1, - y 1 and z 1. So, this will give me sigma xz as let us try to write down again. So, again x 1 and 3 are replaced, so I will write one block over here.

So, these two blocks will be 0 and I will have 1, -1, 1, 0, 0, 0, 0, 0, 0, x 2 remains such it is own positions I will have 1, - 1, 1, 0, 0, 0, 0, 0, 0. So, this block is 0 this block is 0, this block is 0, x 3 and x 1 as interchanged. So, I will have 1, - 1, 1 but again, the trace is contributed only by the atom which is not moved. So, I will have + 1 as a trace now and we are working with only trace. So, that is why we want to know what is the trace over here.

Now, let us do the same thing for sigma yz. Now for sigma y z is the plane of the board. So, that means none of the atoms will move now and x goes to - x that is the only change because now the plane is yz.

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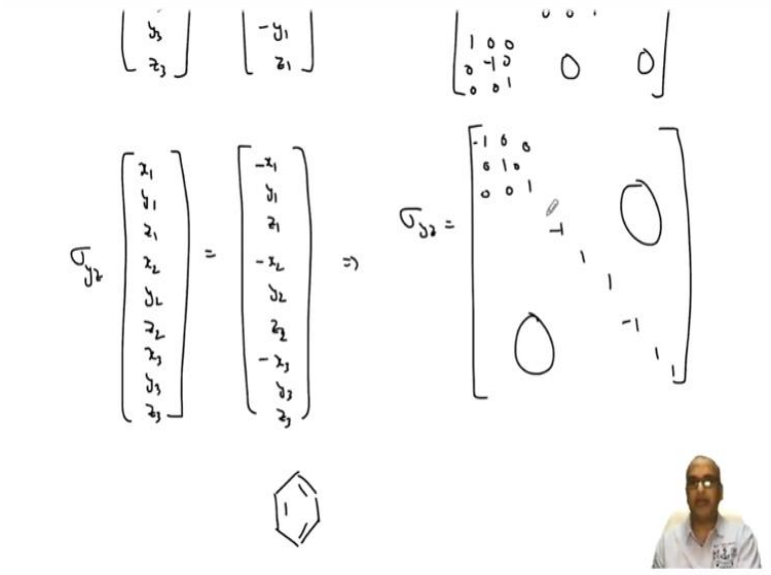

So, let us sigma yz, so none of the atoms are moving. So, that means I am not going to change the position only the x, sign of the x will go negative. So, this implies that my sigma yz, the matrix will be - 1, 1, 1, 0, 0, 0, 0, 0, 0, - 1, 1, 1 - 1, 1, 1 let us get everything is 0. Now, the trace is contributed by all 3 atoms because they are unmoved and there are 6 positives, 3 negatives, so I will have + 3 as the trace. So, I will write down trace as + 3.

Now, that you have determined the trace. So, you can easily reduce this, like reduce this 9, - 1, 1, 3, but before we actually do that, let us see an easier way to do this calculation. Finding the tau 3. So, why we are saying that let us say if we want to work with the benzene molecule. So, let us say if you want to work with benzene how many atoms are there? Six carbons and then six hydrogens.

So, there in total there are 12 atoms and 12 atoms means three vectors on each atom that would mean 36 dimensional matrix. So, 36 dimensional matrix, you will have to write down and any mistake in writing in any of this will screw up the whole calculation and all the vibrational modes will go wrong. So, we do not certainly we do not want that. So, let us see how to handle such a situation when you are dealing with large molecules.

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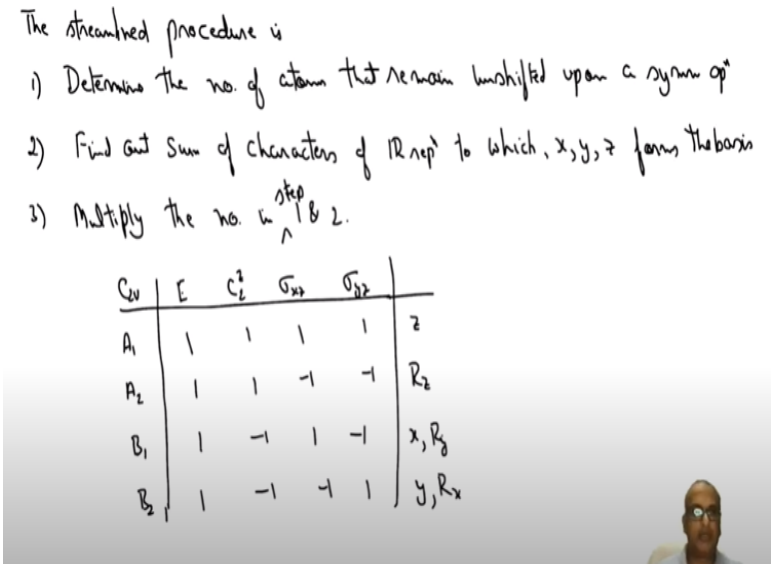

So, the easier trick is the streamlined procedure, see it is important to know how that streamlined procedure is developed and for that you need to know the lengthy procedure also. First step is

determined the number of atoms that remain unshifted upon a symmetry operation, that is easy to identify. How many atoms would remain unshifted, we will see again the case of water and see how easy it is.

Find out some of characters of IR representations to which x, y, z forms the basis, multiply the numbers in one and two in step one and two. So, for that we need to write down the character table of C2v. So, E, C2z, sigma xz, sigma yz. So, you have A1, A2, B 1, B2 all positives, for A 2, you have both sigmas negative, for B1, 1, - 1, 1, - 1, 1, - 1, - 1, 1. Now, if you see that the unit vector transformation is the basis. So, unit vectors are z over here Rz, x, Rx and y sorry x R y over here and x.

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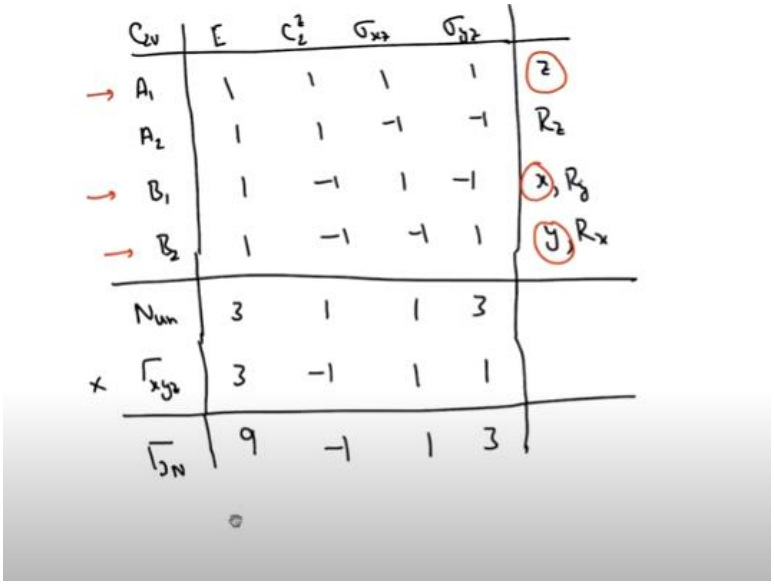

Now, what is the first step, first step is to find out number of unshifted atoms. So, when you do E operation all three atoms will remain unshifted when you do C2 z, only one will remain shifted sigma x z all three will remain unshifted sigma yz all three will remain unshifted. Then second step is to find out sum of characters for IR representation for which x, y and z are forming the basis. So, tau x y z, so 1 + 1 + 1, so z is the basis here x is the basis here y is the basis here.

So, I am going to summation these three, so now 1, + 1, + 1 is 3; 1 + - 1 - 1, so I will get - 1 over here, then1, 1, -1, so I will get + 1, 1 – 1, 1 so I will get + 1. Now, I multiply these two and this will be tau 3N, which we had written using all sorts of matrix writing thing. So, now if you just

multiply these two so multiply these two you will get 9, - 1, 1 and + 3 and this was the trace which we were getting which we got when we actually wrote the complete matrix. So, once you had obtained tau 3N then the next step is easy.

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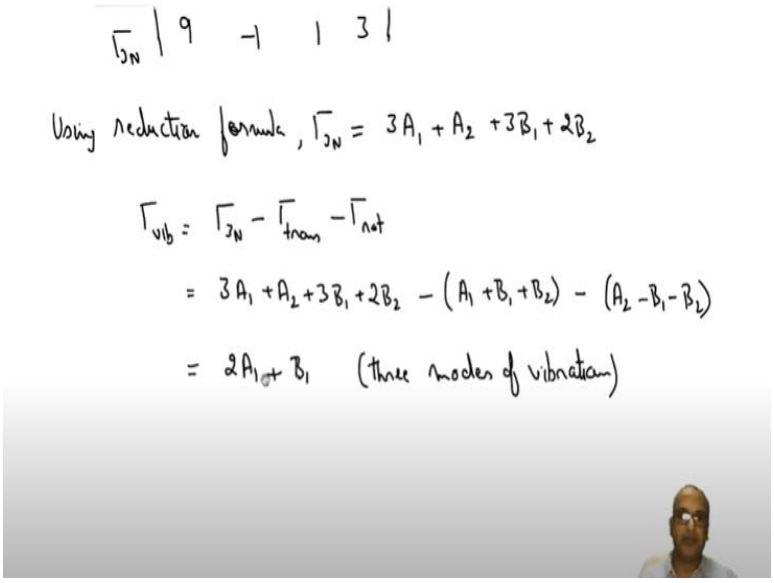

So, next step is just reduce this, so using reduction formula you can write down tau 3N is equal to I am just noting down the answer, which is 3A1 + A2 + 3B1, please do it yourself and check this calculation if I am not made any mistake + 2B2. Now to obtain tau vibrational, what you have to do is you have to subtract the tau 3N you have to use tau 3N and subtract tau translational and tau rotational.

Now, tau 3N is this, so I will write 3A1 + A2 + 3B1 + 2B2 minus, what is tau rotational now, sorry tau translational, translational is x y and z. So, A 1, B 1, B 2. So, A 1, B 1, B 2 and similarly for rotational, rotation will be for which R x, R y, R z will form basis, so that will be A 2, B 1, B 2. So, this is A 2, B 1, B 2 now do this simple maths and what you will get is 2 A1 + B1. So, this tells you that there are 3 modes of vibration.

And, if you actually record this vibrational spectrum of water, you will get 3 vibrational modes. So, now but we do not know what are those vibrational modes that we will look at later, in the next lecture but at least now we know that how many lines are expected from vibrational spectrum, if you record vibrational spectrum of a molecule. So, purely this is purely theoretical

basis but without having to record vibrational spectrum, you know beforehand only that you must be getting three lines, because there are three modes of vibration which are coming.

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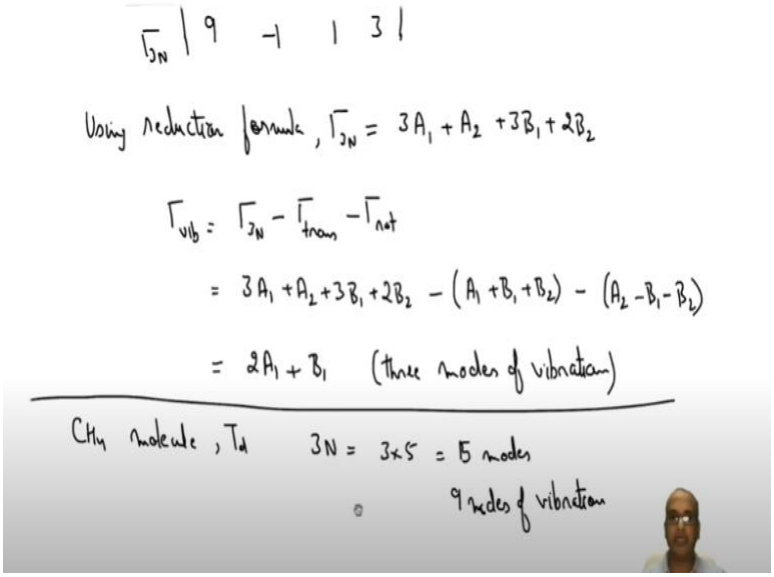

Now let us quickly take another example of little higher, bigger molecule, so let us say CH4 molecule, point group is Td. Now here 3N is equal to 3 into 5. So, remember that there are 5 atoms now 1 carbon and 4 protons. So, you will have 15 total modes out of which 3 will be translational 3 will be rotational. So, how many vibrational modes will be there? There will be 9 modes, so 9 modes of vibration.

But that is not necessary that all 9 modes will give you 9 lines, there can be some degeneracy which we can only tell once we actually calculate the IR representation or symmetry corresponding to those 9 modes, that is the reason I am discussing this example here. So, in this in the water case we had only 1D representation. So, 1D representation mean all 3 modes will give you 3 different lines, there is no degeneracy possible.

Accidental degeneracy is a different thing but theoretical degeneracy is not possible but in case of Td point group you have 2D and 3D representations. So, if 9 modes of vibration may show some degeneracy, so that is why we wanted to test this case.

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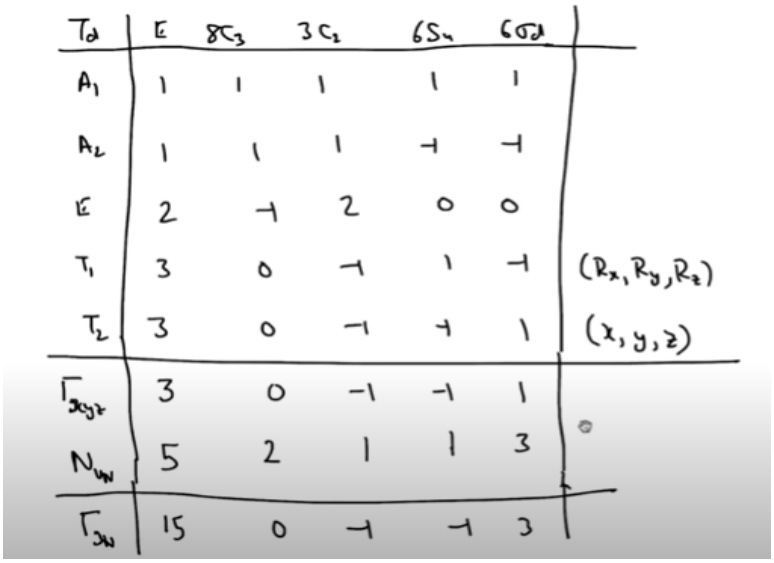

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)
T_2	3	0	−1	−1	1	(x, y, z)
Γ_{xyz}	3	0	−1	−1	1	
N_{un}	5	2	1	1	3	
Γ_{3N}	15	0	−1	−1	3	

So, now let us go to that character table, so that without having to write the whole matrix we can just write down the tau 3N. So, Td we have E, 8 C3, 3 C2, 6 S4 and 6 sigma d. This is for the basis set and we have A1, so I am just writing the character table nothing fancy about it. So, now x, y, z together forms the basis for T2, Rx, Ry, Rz together forms of basis for T1. So, that means we do not have to take the sum also it is very easy now.

So, tau x y z is basically same as T2 so you have 3, 0, -1, -1, 1. Number of atoms which remain unshifted that we have to estimate by imagining the operation which we have to. So, under E it will be 5, all 5 atoms will remain unshifted, under C3. So, C3 it will be 2 atoms proton and carbon, rest of the three protons will remove, so, you have two unshifted, in C2 you have only one unshifted, in S4 again, there is only one unshifted sigma d plane will be formed by at least three atoms, so you have 3 unshifted.

Now in calculate tau 3N which will be 15, so it is a 15 dimensional matrix. So, E will have 15, 0, - 1, - 1, 3 now you have got tau 3N.

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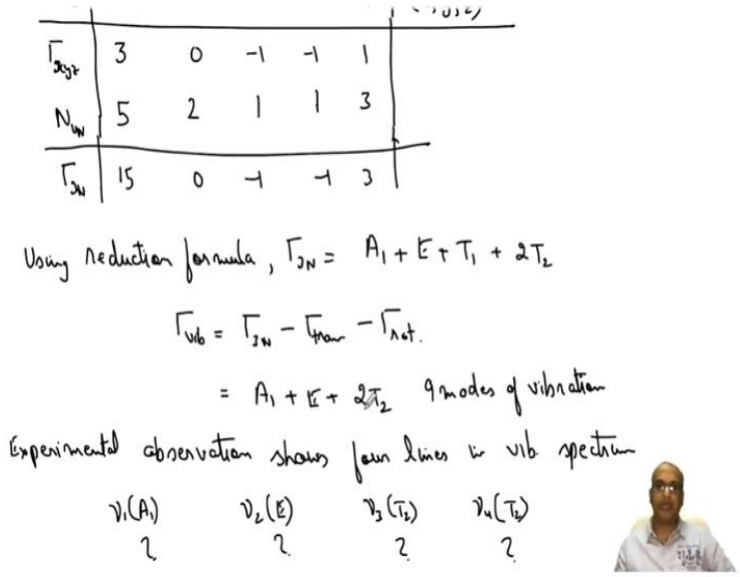

So, using reduction formula you can easily reduce tau 3N using reduction formula, tau 3N is equal to A1 + E + T1 + 2T2 this is the total of tau 1. Now, for tau vibrational we have to subtract the rotational and translational root of it, tau 3N minus tau translational minus tau rotational. So, this will give you A1 + E + 2 T2, so you can count whether you are getting 9 modes because initially we saw that out of 15 modes, 9 modes should be for vibrational.

So, you are getting one here two here because this is doubly degenerate. So, 1 + 2; 3 and 2 of them are triply degenerate. So, 6 over here, so total nine modes of vibration, you are getting. So, your calculation is correct, 9 modes of vibration, if you make any mistake, you will not get nine modes here. So, now if you compare the experimental observation, shows 4 lines in vibrational spectrum.

So, all those the modes are 9, but we only see 4 lines, why do we see 4 lines? Because there are 4 modes. So, two of them are degenerate here and three of them are degenerate in one and three of them are degenerating one. So, you should see maximum four lines and not more than that, which is defined by four set of IR representations in vibrational spectrum. So, you will get nu1 for which is with A1 symmetry, nu 2 with E symmetry, and these are two degenerate modes, we do not know here whether these are stretching modes or bending modes and so on.

Now nu3 with T2 symmetry and nu4 with T2 symmetry but what are these modes that we still do not know. What we have done is we have isolated, we have identified that there are out of nine modes of vibration, we should be observing four lines in the spectrum. Now, these four lines will correspond to what whether there is a symmetric stretching, anti-symmetric stretching what kind of bonds will be stretching, what kind of bonds will be compressing all those things also we can do but that we will learn in next class.

So, meanwhile try to practice take different molecules and see if you can get to this stage of finding the IR representations corresponding to tau vibrational, pick up any given molecule for which we have done previous calculations like BF3, NO3 or take an octahedral molecule take any big molecule and see if you are able to get and then find out if it matches with the theoretical description of vibration spectrum, that is all for today. Next class will see how to visualize these vibrational modes.