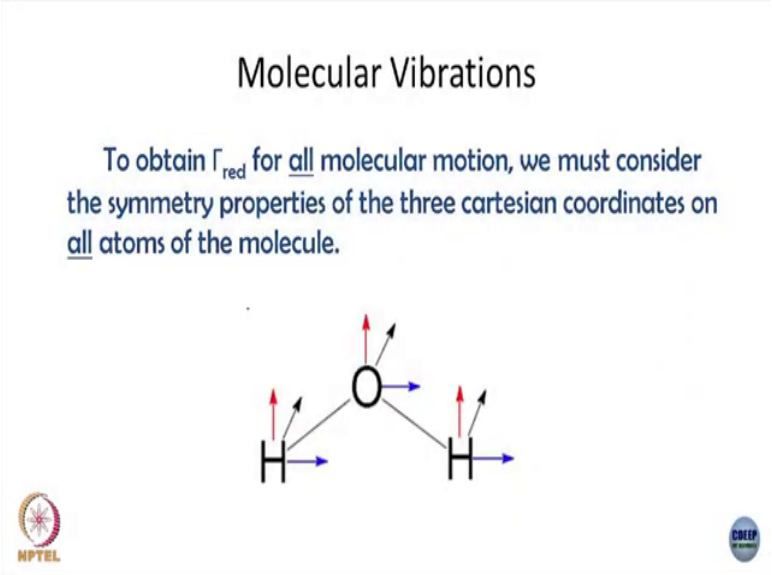
Group Theory Methods in Physics
Prof. P. Ramadevi
Department of Physics
Indian Institute of Technology, Bombay

Lecture – 32
Vibrational representation of character

(Refer Slide Time: 00:17)



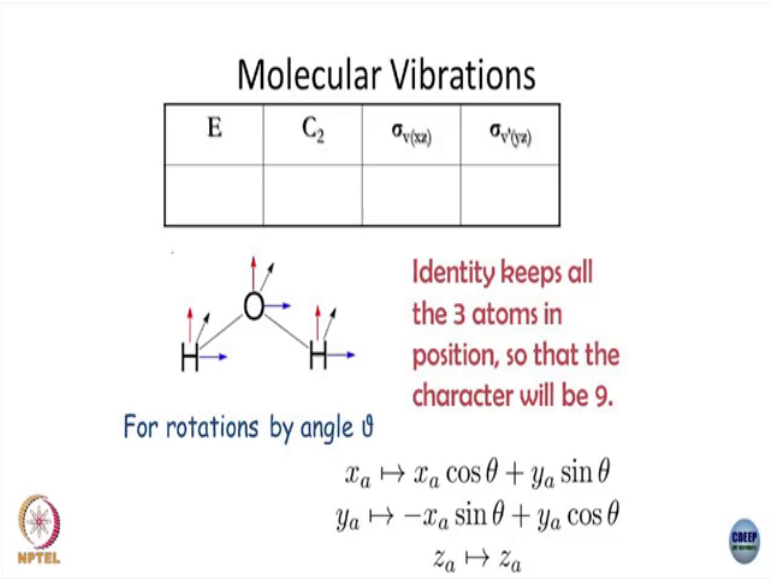
So, let me continue today showing a little easier method one of you already pointed out that we do not need to write those matrices to find which irreps the molecular vibrations belong to ok. So, I thought let me just brief you on that before we get on to the groups.

So, whatever we did I hope you remember, we went through an elaborate exercise for a non-linear triatomic molecule where two of the masses were identical; one of the mass was capital M and the other two was small m, it is exactly like the water molecule. And to find the

reducible representation for all molecular motions including translation rotations everything you put in 3 degrees of freedom for every atom in that molecule clear.

So, all these atoms will have three Cartesian coordinates and we need to work out the reducible representation or characters for the reducible representation which can account for all the molecular motions ok. So, to do that what we can do is we did the sensor products of states and so on, we do not need to really do that.

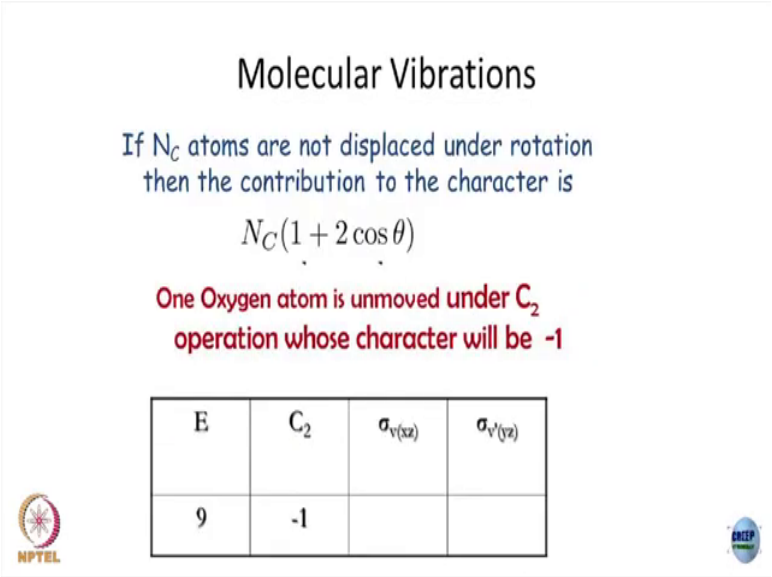
(Refer Slide Time: 01:57)



What we have to remember is if you do an identity operation on this molecule each atom remains in its own place right. So, each atom remains in its own place so, you will have character for each atom you know if you add up all the 9 degrees of freedom you will get the character associated with the identity element to be 9 ok. So, that is what you will get.

But, if you want to do rotation by an angle theta I am taking theta to be arbitrary which will be different for different groups, but discrete value ok. So, if you take rotation by theta you know the x, y and z coordinate for every atom will undergo this transformation. So, if you take this and try to find the trace if you write this matrix which does this transformation, the trace will give you 2 cos theta right and there will be a one for the z a. So, it is exactly 1 plus 2 cos theta for an atom in the molecule, if there are N C atoms which are not displaced ok.

(Refer Slide Time: 03:13)



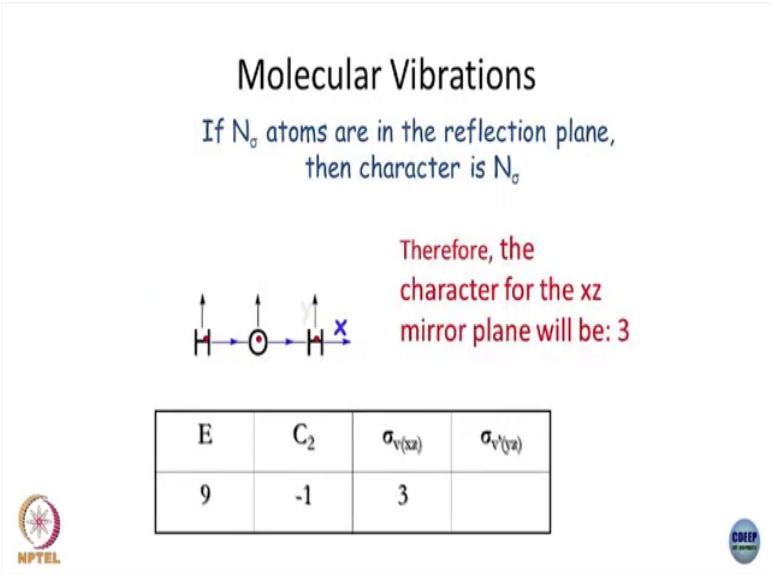
So, in this particular example when you do a C 2 rotation, what happens? These two atoms get displaced the number of atoms which do not get displaced is just 1. So, the N C will be 1 in that case. So, if N C atoms are not displaced under rotation then the contribution to the character will be N C multiplied by the character which is the trace of the 3 by 3 matrix which is 1 plus 2 cos theta. Is this clear to you? So, one oxygen atom is unmoved under C 2

operation and you are doing C 2; C 2 means theta will be pi right. So, cos pi is minus 1 minus 2 plus 1 will be minus 1 and N C is 1. Is that clear?

So, that will be the character; identity operation of course, is identity matrix for each of the atoms so, the trace of that matrix will be 9. C 2 operation for a general theta operation C n where theta is 2 pi by n this is the formula where N C is the number of atoms which are not displaced under such a operation.

So, using that because N C is one here and C 2 is only a 180 degree rotation we get the character associated with the C 2 operation for this non-linear molecule is minus 1 ok. I am not writing matrix representation, I am just directly writing the molecular motion of this molecule what should be the character for a reducible representation. I am not even writing the matrix form. Is that clear? So, let us do the same thing for the other two elements also.

(Refer Slide Time: 05:43)



If N sigma atoms are in the reflection plane then character is just N sigma ok. So, suppose you take this to be the xz plane which we were discussing in the lecture, all the three atoms are in the xz plane. So, if you do a reflection in the xz plane three atoms are there, so, N sigma is 3, so the character will be 3 ok. You can prove it rigorously, but I am giving you a final answer. So, therefore, the character for the molecular motion reducible representation is going to be 3 for reflection in the xz plane. What will happen for the yz plane can somebody tell me?

Student: (Refer Time: 06:45).

Ha?

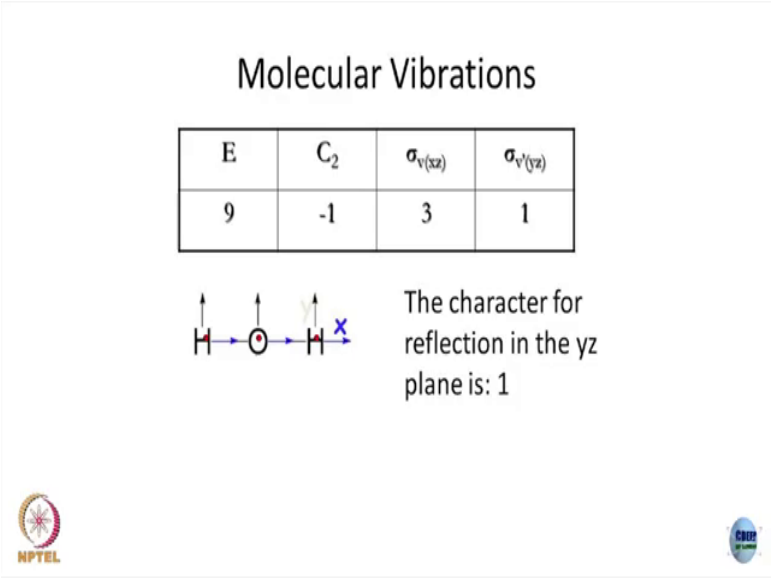
Student: 1.

1.

Student: (Refer Time: 06:49) oxygen.

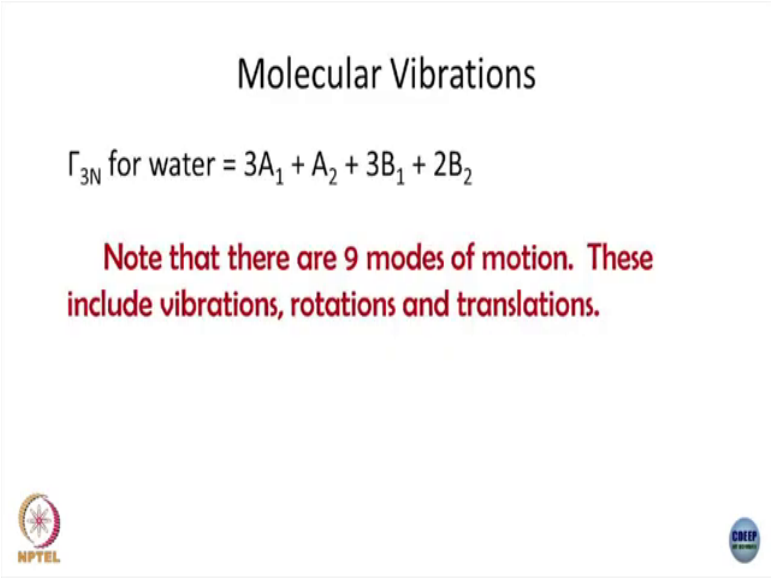
Oxygen is in the yz plane.

(Refer Slide Time: 07:03)



Yeah, so, the character for reflection in the yz plane is again 1. So, you write this out, once you do this the rest of the steps follows.

(Refer Slide Time: 07:23)



Given a reducible representation of a molecule with 3N atoms you know how to do the decomposition into irreducible representation and you find that there are totally 9 modes of motion right; three 1-dimensional irreps, one 1-dimensional irreps, 3 plus 1 is 4 and the everything is 1-dimensional. Why?

Student: (Refer Time: 07:56).

It is a C 2v symmetry. The molecular is a C 2v symmetry, it is a non it is an abelian group. So, all the irreps have to be 1-dimensional and all the motions should add up to give you the total degree of freedom. So, 3 into 3 is 9 degrees of freedom and this 9 breaks up into linear combination of. This breaking I have not worked it out here, but we have done enough exercise problems that given a reducible representation with this character you should be able

to work out the irreps into which it can decompose ok. So, this part I am not doing, but you need to do this ok. Any questions?

Student: (Refer Time: 08:49) 9 for (Refer Time: 08:51).

9 for.

Student: E (Refer Time: 08:52).

Because see finally, I am going to take these as the degrees of freedom right, xyz for atom a, xyz for atom b, xyz for atom c. So, when you do an identity operation xyz it will go to xyz. So, 3 times 3 which will be 9 is that right. So, you can put even here theta to be 0 if you want. In this expression which I have written you can take theta to be 0. If you do that then you will get 3 and 3 are unchanged 3 into 3 is 9, is that clear? Yeah, any other question?

So, once we have this we have the 9 modes of vibrations sorry, 9 modes includes translation, rotations and vibrations ok. So, this splitting which I have done here in order to do this you do not need to write the matrix representation to do this. You can do this argument to actually figure out how many vibrational modes are going to be 1-dimensional; that means, that frequency will occur only once.

If suppose you had another group like C 3v the way I have given it in the assignment, if it belongs to a 2-dimensional irrep then you can looking at it you can say that experimentally if they start looking at the spectra they will see degenerate frequency. They will see two spikes with the same frequency ok.

So, these are things which you can guess by just working out with the groups, is that clear? So, in this C 2 v case you have each irrep to be 1-dimensional. So, each frequency has to be distinct. Did you work it out? Sachin was supposed to do the discriminant. No?

Student: (Refer Time: 11:05).

Frequencies are different or?

Student: Yeah, frequencies are different.

Very good. So, why is it different now you know. It has to be different because it is 1D irreps. So, none of the frequencies can be degenerate. If you find the eigenvectors and two eigenvector shares the same frequency.

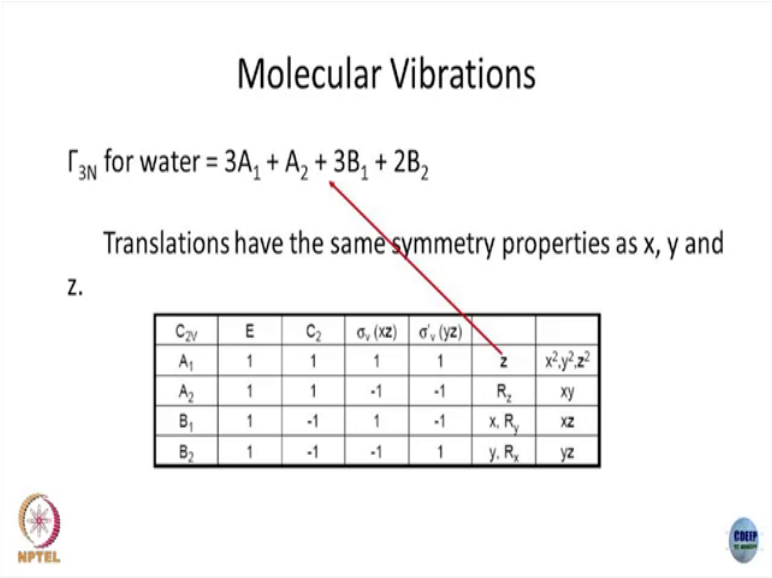
Student: The expression does (Refer Time: 11:28).

Eigen vectors are very big.

Student: Yeah.

Not simple I see maybe you can show it to me and I will simplify it to you ok fine.

(Refer Slide Time: 11:47)



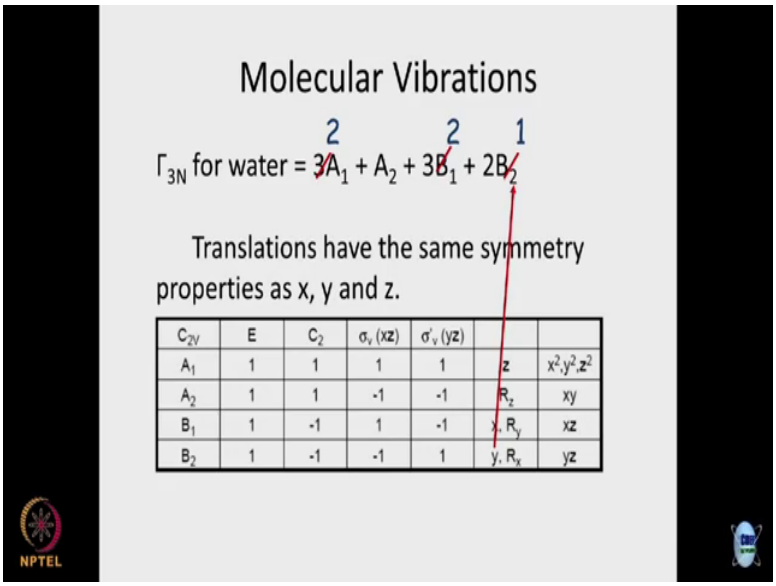
So, what I want is this we have already done. Once we have broken it up into this irreps, then you have to subtract out, what I did last time was I treated it as if we are in the 2D plane, now I have just taken it someone was saying is it important to work in 2D. So, now, today I am showing that even if you work in 3D you will get back the same vibrational modes, that is all I am trying to justify by using this shortcut way of writing the characters for the reducible representation ok.

So, 3D if you take the motion to be in 3D you will have 3 into 3 which is 9 degrees of freedom to start with. Earlier when we were doing we were taking it as a 2D and then I said 2 into 3 which is 6 degrees of freedom, so that is the way we started with ok.

So, here I am doing it as if it is a 3; 3D situation and then you have to remove the translation and the same procedure, there we did only the translation along x and y we subtract it, but

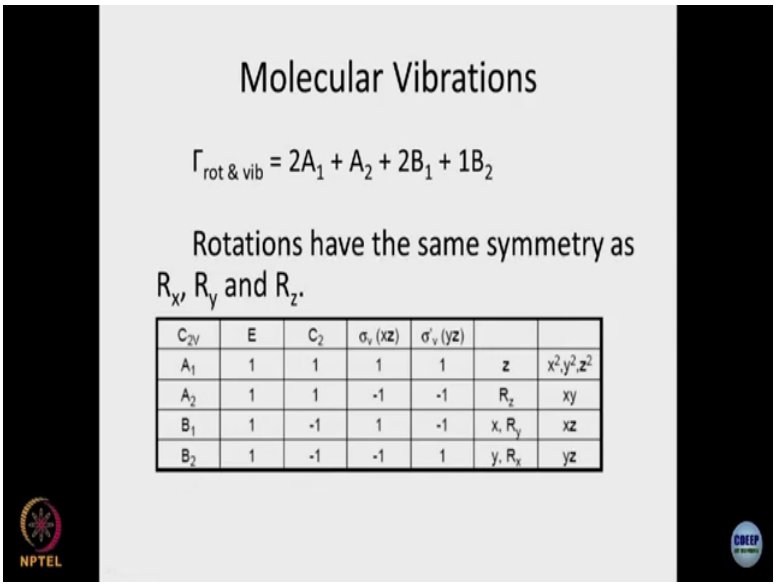
now you have to also subtract the translation in the z coordinate because we are doing it like a 3D problem. So, associated with the z; associated with translation along z you will have an A 1 which should get removed ok.

(Refer Slide Time: 13:23)



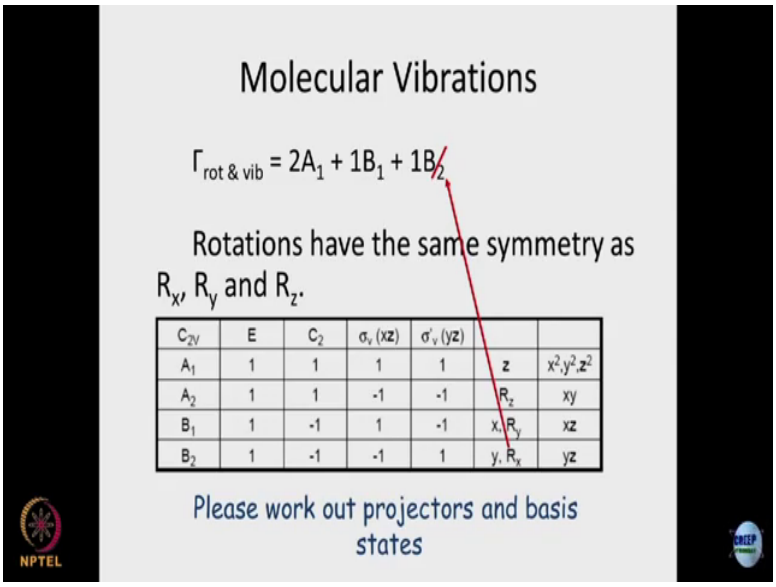
Associated with x translation you have to remove one B 1 and similarly y translation will remove one B 2 out ok. So, essentially it becomes 2A 1 plus A 2 plus 2B 1 plus B 2, is that clear? This is after we were removed the translation in the x, y and z direction.

(Refer Slide Time: 13:59)



So, now, what we are left with is whatever we have got after subtracting the translation is the rotational irreps plus the vibrational irreps ok. So, now, I have to remove the rotational irreps out of this then what will remain will be the vibration modes. So, rotations you can see about z axis is A 2, about y axis is B 1, x axis is B 2 ok. So, I need to subtract them.

(Refer Slide Time: 14:39)



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

So, once I do that I get the, I probably missed out there is a B 1 rotation and what happened A 2, B 1. So, the answer will be there should be 3 rotations know? What happened?

Student: (Refer Time: 15:12).

Ah?

Student: (Refer Time: 15:14).

Louder. Did I miss something some factor?

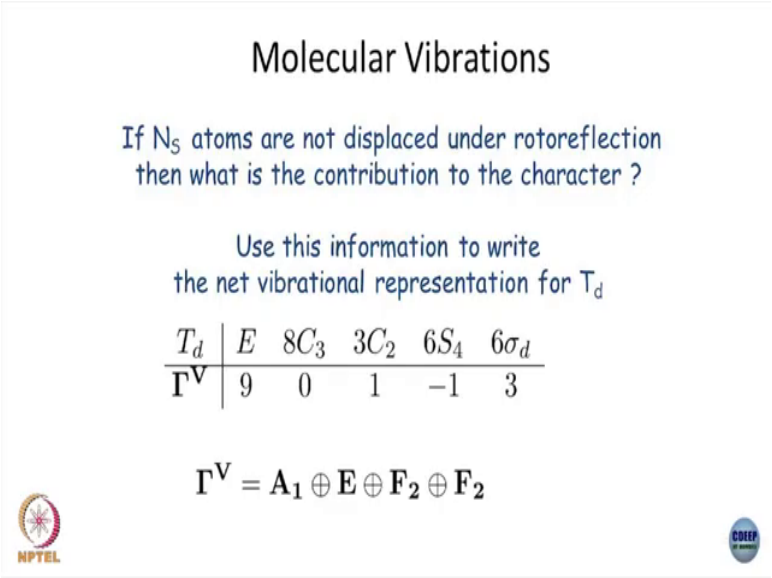
Student: (Refer Time: 15:19).

So, it is one A 2 and then the B 2 will also get removed; B 2 will get removed and one B 1 will get removed ok, excellent. So, what we have essentially irrespective of whether we looked at it as a 2D problem or a 3D problem the vibrational degrees of freedom should have to be 3 and the irreps which it belongs to will not change we did this in a long process.

One was using the normal coordinates and the other process where I said let us look at it as a tensor product of 3 atoms with xy coordinates, there also we got 2A 1 plus B 1. Now, I have shown you by doing it as if it is a 3D problem still we get the vibrational modes to belong to irreps 2A 1 plus B 1. Is that clear ok?

So, this anyway I worked it out for you the projectors and basis states in 2D you can try to redo it for the 3D case ok. Just as an exercise you can write the matrix representations for the reducible one which I have here. For this case you can work out the matrix representation, find the projectors, subtract out the projectors for translations, you can do that elaborately here again you will start getting a similar expressions. It is tedious, but it is straightforward ok. That is why when I did it in the class last time I just confined to as if it is constrained to move on a plane and then it became a little simpler ok.

(Refer Slide Time: 17:13)

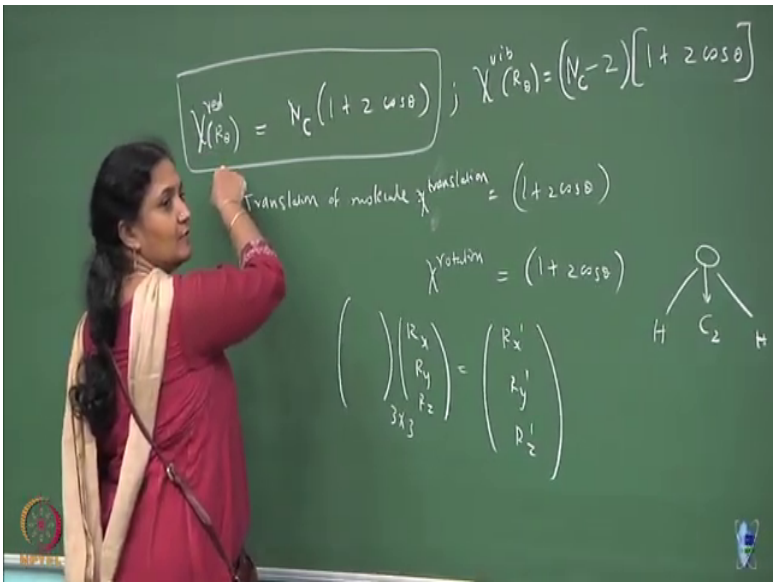


So, I have not really discussed if you had rotoreflection operation what happens to the contribution to the character I will leave it you to try it out and see what happens when you do a rotoreflection. If N S atoms are not displaced under rotoreflection then what is the contribution to the character? That is one I will leave it to you and if you use those information for rotation which I have already discussed, you could actually work out the character for the molecular motion of let us say a molecule with T d symmetry ok. Which molecule has a T d symmetry tetrahedral?

Student: (Refer Time: 18:14).

Methane has this which we saw in the video.

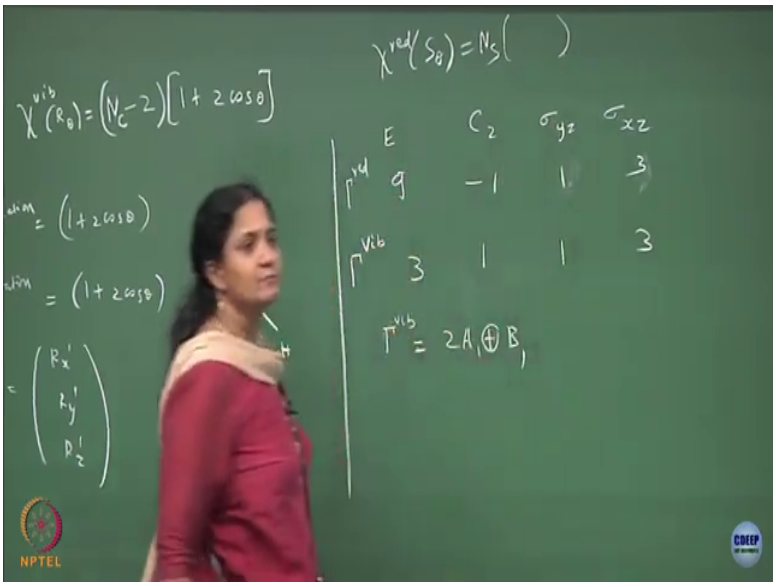
(Refer Slide Time: 18:39).



So, there you could also do one more stuff that you can directly so, the way I wrote here so, I said N C atom with 1 plus 2 cos theta is the character for a reducible representation for a specific rotation which you are doing. What you could do is that you can also remove the translation of a molecule that will be one the character for that character for translation is 1 plus 2 cos theta.

Again, you can write character for rotation you can take R x, R y, R z basis how it transforms under rotation it will transform exactly like your position coordinates, rotations are proper transformations right. If you take R x, R y, R z the operation which you are going to do will give you R x prime, R y prime, R z prime right. What will that be? Any change or same? Still the same 1 plus 2 cos theta ok. So, you could try and remove. Reflections do not add to your translation or rotations ok.

(Refer Slide Time: 20:21)



So, instead of the earlier one where we wrote the gamma reducible wrote this as 9, 9 as 1, 1 was 3 and the other one was 1 right or the other way round, this was 3 right. You could write there vibration alone, reducible representation for vibration alone. So, there you can try and remove these two. So, if you try to do that chi vibration for rotation by theta will be N C minus translation minus rotation. So, it will be N C minus 2 that will be the expression for the vibrational it will only look at the vibrational degrees of freedom ok.

So, what will that be? So, for theta equal to 0 all the three atoms 3 minus 2 is 1, 1 into 3 that will give you directly 3 and you know vibrational degrees of freedom are 3, identity matrix has to be a 3 cross 3 identity matrix it has to be 3. Now, what about this? That had one atom right. This one atom when you do a theta rotation on the H 2 O molecule oxygen, hydrogen, hydrogen when you do a C 2 rotation about z axis these two get displaced only one atom is

undisplaced. So, N C has to be 1 minus 2 and then 1 plus 2 into cos 180 degrees because I am doing a C 2 operation right.

So, what will that be? Minus 1. So, this is this is plus 1 finally. These things will not change fine. And now you can use the character table to see how the gamma vibration I am claiming that it will be twice A 1 plus B 1 ok, but I want you to check it out ok, please check it. So, this is the only non-trivial operation in the water molecule, but if you go to the methane molecule you have other operations, you can do a rotoreflection. You can do a rotation by 90 degrees and then do a reflection right if you have seen those slides and played on this animation you will see that you do have a rotoreflection.

So, this character table when you start doing I also want you to check how the under rotoreflection the characters change, how the characters change you I want you to fix it. Just like this expression this is for rotations. For rotoreflection I am going to call it as S theta I want you to find out if ns atoms are undisplaced under rotoreflection, what will be this factor? I will leave it you to check it out and once you know that you can again play around also rotoreflection you will have translations and rotations to be removed out of it ok. Rotoreflection has a rotation component in it unlike your reflection alone ok.

So, you have to remove those degrees of freedom and if you write down the vibrational degrees of freedom the character for that. How many will be there in methane molecule? 5 atoms; 5 into 3 is 15, 15 minus 6 is 9, 9 vibrational degrees. So, the identity element has to be 9 which is true here. You can see that the N C which is the N C minus 2 will be 5 minus 2 which is 3, 3 into 3 is 9 for theta equal to 0 ok. So, that is why the identity element is 9, rotation by 120 degree is cos theta will be half minus half. So, this gives you a minus 1 and a plus 1, this will become 0. Is that clear? You all with me?

So, that is why the character for when you consider the C 3 operation turns out to be 0. C 2 you can check it out how the C 2 axis is fixed on the T d plane and see which atoms are getting displaced, which atoms are not getting displaced and then you can figure it out that this is one.

For the rotoreflection I have not really worked it out for you, but I want you to first do that and then you can figure that out it is minus 1. After you have written this writing this down is very straight forward. You know how to find the number of times in a reducible representation each irrep (Refer Time: 27:08) for that you need the character table and using the character table you can fix it.

But, what do we observe from this final answer? There are the vibrational degrees of freedom will have one non-degenerate frequency, two degenerate frequency, two types of 3-fold degeneracy, is that clear? This is the interpretation. You have totally 9 vibrational modes, but, the number of frequencies are only 4 distinct frequencies in this case.

In the water molecule all the frequencies were distinct, but here I am not finding the frequencies, but I can at least tell an experimentalist if you are going to make these atom interact with the electromagnetic field of certain frequency you start seeing spectra and you will be able to see that spectra from there they can find what is the frequency. And, you can tell them that you should be able to get 2-fold degenerate, you should be able to get 3-fold degenerate ok. I am not doing anything other than using only the tools of great orthogonality theorem and of course, the symmetry of the molecule ok.

So, this is what you saw in that video today maybe you can go and replay it again and see in the methane molecule they say that you have three different vibrations with which has the same frequency they can superpose and you get as superpose mode of all those frequencies, is that clear? Interesting you know, I just want you to appreciate the fact that this is really useless information to write the net vibrational representation in T d which I have not worked it out here, but please try it out.