Symmetry and Group Theory
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Lecture – 35
Symmetry of Normal Modes: D3h : Continued

Now let us talk about C2. Where are the C2s? **"Professor - student conversation starts"** Along 1 2 and 3. **"Professor - student conversation ends."** Along, so 1 4, 1 4 or 3 4 or 2 4 something like that. I can take anyone. I will take that 1 4 bond. Right, I will take that as C2 axis.

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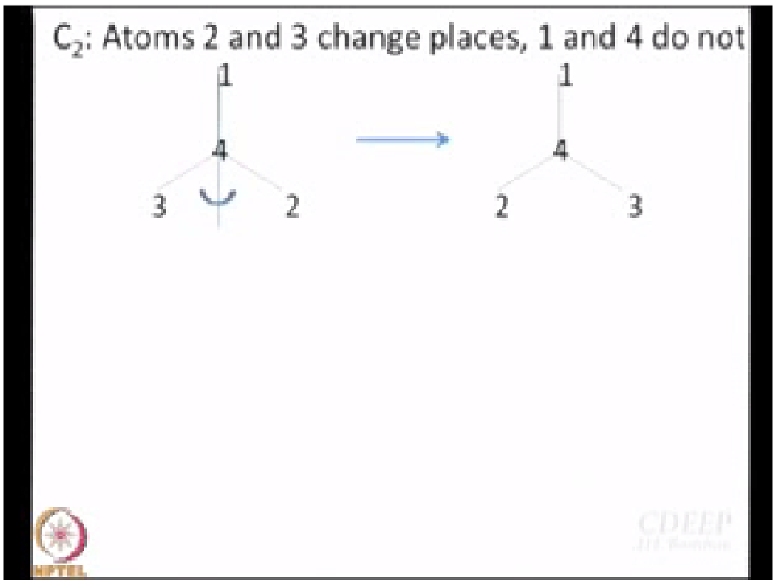

Now, if I turn with respect to the 1 4 bond, what happens? Which are the rolling stones? 2 and 4 are the rolling stones. 1 and 4 are not. So, 2 and 3 are the rolling stones, you are right. 2 and 3 are the rolling stones. 1 and 4 are not. So we do not bother about your 2 and 3 anymore, right and that is not the end of the story. Do you agree with me if I say that x1 transforms exactly as x4. X2 transforms exactly as, sorry, sorry, what am I saying.

I am getting carried away. y1 transforms exactly as y4. z1 transforms exactly as z4. No? x1 is parallel to y… x1 is parallel to x4. So they are going to transform in the same way, right. First of all they will remain in their own place and besides that they transform in the same way also. Same is y1 and y4. Same with z1 and z4. So see of all these things, so in a 12*12 matrix, how many 3*3 blocks are there? This is your 12*12 matrix.

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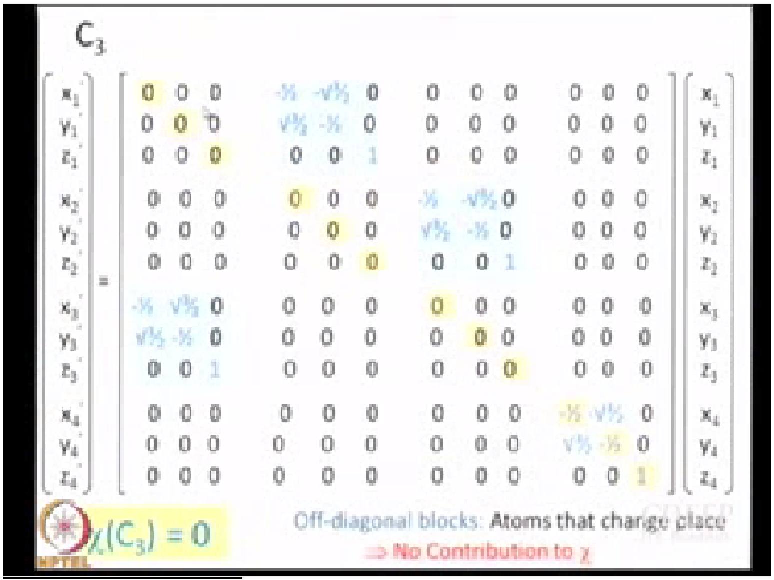

C1 2 3 4, 1 2 3 4, there are 16 3*3 blocks. You cannot all those multiply a number by another number and get the result. There are 16 such blocks. So we are worried because we thought that we are, we have to work out all the 16 blocks. Now we see that we have to work out only 1 block. Okay and just multiply it by 2 in this case. Are you clear, understood? Sure? Okay.

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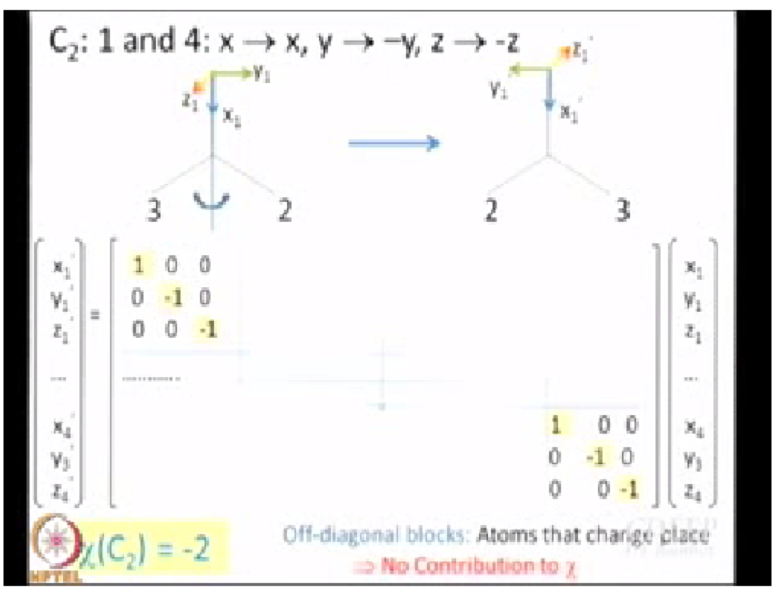

Then let me draw x1 y1 z1. Which operation am I performing? C2. So what will happen to x1 y1 z1? **"Professor - student conversation starts"** x1 remains same. x1 remains same. z1 -z1. z1 becomes -z1. y1 becomes -y1, right. **"Professor - student conversation ends."** And that happens not only for 1 but also for 4. Is not it? And you might as well have drawn the arrows of

4. So x remains x, y becomes -y, z becomes -z, okay. So you can write the block. Now what will be the block?

"Professor - student conversation starts" 1 0 0. 1 0 0. 0 -1. 0 -1 0. 0 0 -1. 0 0 -1. So to make simple life even simpler, it is a diagonal block. **"Professor - student conversation ends."** So this is how your transformation matrix should look. You do not care about anything else because all you care about is character, right. So what is the character? **"Professor - student conversation starts"** -2. -2, right, simple, very easy. **"Professor - student conversation ends."**

"Picture abhi bhi baaki hai" as you will see. Not right now, little later. What is the next symmetry operation that we have to worry about, let us say sigma h? Which are the atoms, what are the rolling stones here? No rolling stones. So you have to consider everything but still now we are not worried anymore. Now we have to understand is that since they do not change places, all I have to worry about is work it out for only 1 atom and just multiply by 4, right. It is very simple.

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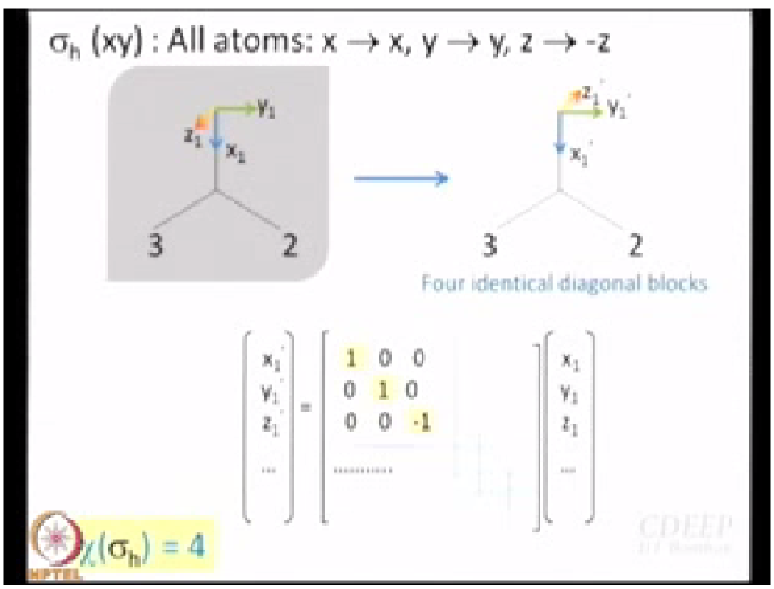

So tell me what will happen if I apply xy. Sigma h xy, when I apply then what will happen to x1? What will happen to y1? What will happen to z1? **"Professor - student conversation starts"** x1 remains same. **"Professor - student conversation ends."** x1 and y1 remain the same. z1 changes sign. So if I apply this sigma, this is what I get. And the same would hold for 2 and 3 and 4.

So you are going to have 4 identical blocks along diagonal. What will be each block, tell me now? **“Professor - student conversation starts”** 1 0 0, 0 1 0, 0 0 -1. 1 0 0, 0 1 0, 0 0 -1, very good. Alright. See now we are going so fast. Is not it? We took so much of time for C3 and now we are going very fast. What will be the character? 4. 4. Yes. This is the, I keep forgetting this all the time.

I correct it today. This is the of peril of copy paste. Be extremely careful when you copy paste. That is also a lesson. There is some other mistake somewhere, in some later slide also, please point it out so that I can correct it once and for all. Alright. This is 4. X sigma h is 4. **“Professor - student conversation ends.”**

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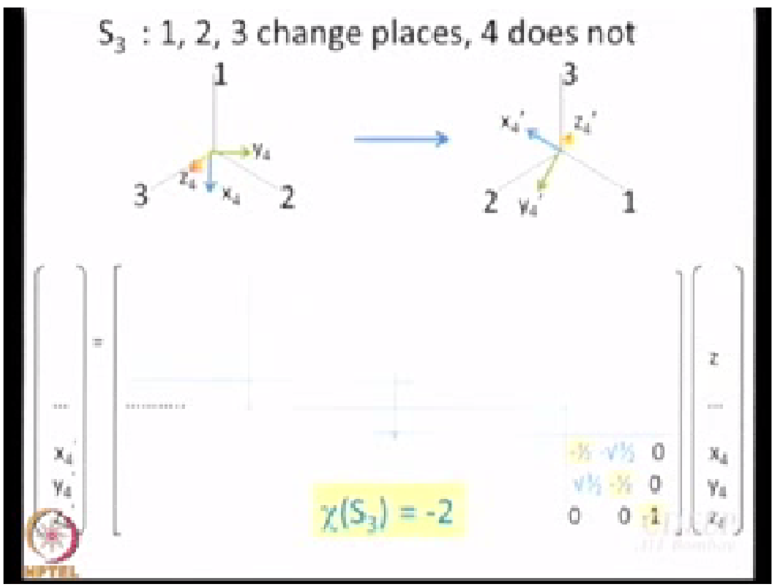

Next S3. S3 once again, it is like C3. 1 2 and 3 change places and 4 does not. The only difference is what? **“Professor - student conversation starts”** z also becomes -z, unlike the previous one. **“Professor - student conversation ends.”** So the same matrix of C3, same block. The only difference is that the 3 3 element is -1 instead of +1, right. So I can write now. What is the character? **“Professor - student conversation starts”** -2. XS3 is -2. **“Professor - student conversation ends.”** See we have worked out everything, almost.

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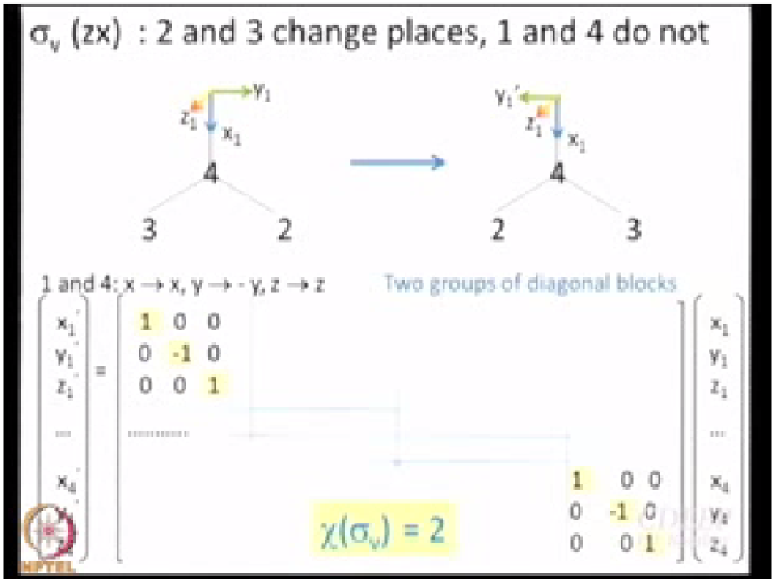

Now zx. What is zx, what kind of plane is this? **“Professor - student conversation starts”** No, no. What you, how will you write that kind of plane. What is it called. Diametral plane because it also bisects the angle between the C2 axis that are perpendicular to the principle axis of symmetry. "Tabi to D3h sahi hai." Alright. **“Professor - student conversation ends.”** So apply zx?

This is zx. Now what will happen? What are the rolling stones? **“Professor - student conversation starts”** 2 and 3. 2 and 3. **“Professor - student conversation ends.”** So ignore them. We have to work with all faithful 1 and 4, right. And what will happen when I apply this plane? What will happen to the coordinates x y z? The zx plane right. Even with our drawing, you should be able to tell what will happen.

“Professor - student conversation starts” Y changes sign. Y changes sign, the others remain the same, very good. This. **“Professor - student conversation ends.”** And now the animation looks a little annoying because it is too slow, we have already given you the answer. What will the, the block look like then? **“Professor - student conversation starts”** 1 0 0. 1 0 0, 0 -1 0, 0 0 1. **“Professor - student conversation ends.”**

How many such? 2, 2 diagonal blocks. Character? Alright, I have written it as vertical plane. I do not know why. Anyway. Even they have written it as vertical plane. So let us not get into, that is why I have done it. But it is a diametral plane. I do not why it is written as diametral, vertical, anyway, forget it. Does not really matter. 2. Any other symmetry operations left? No.

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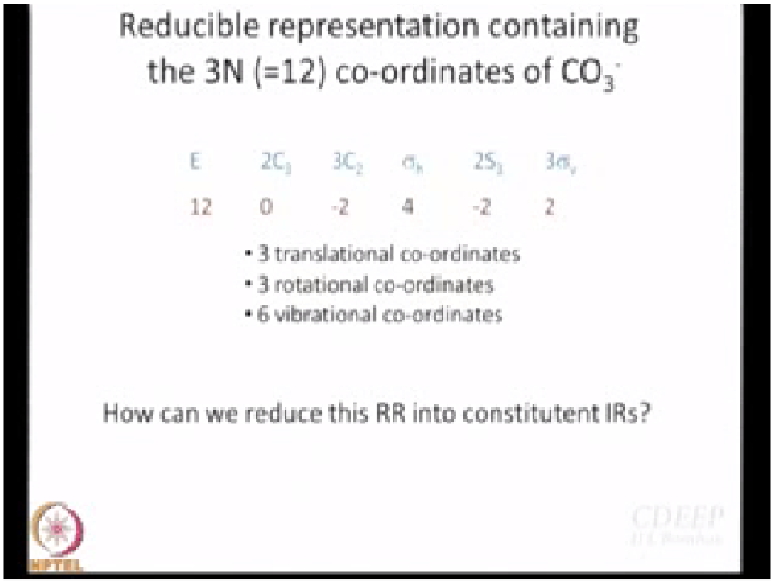

So see what we have then, we have this reducible representation containing the 3N coordinates of carbonate. And the representation is 12 0 -2 4 -2 2. Please take it down. 12 0 -2 4 -2 2. I will show you the character table also. 12 0 -2 4 -2 2. And out of these coordinates, you know that there are 3 translational coordinates, 3 rotational coordinates, 6 vibrational coordinates. So before anything else, what we could want to do is, we want to, we could want to break this down into the constituent's irreducible representations.

So how can we reduce this reducible representation into the constituent irreducible representations?

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Use that relationship. Okay. You have taken down the characters for the reducible representation, right, 12 0 -2 4 -2 2, okay. You know this relationship. If you do not know yet, please write it down. Because now you are going to work it out.

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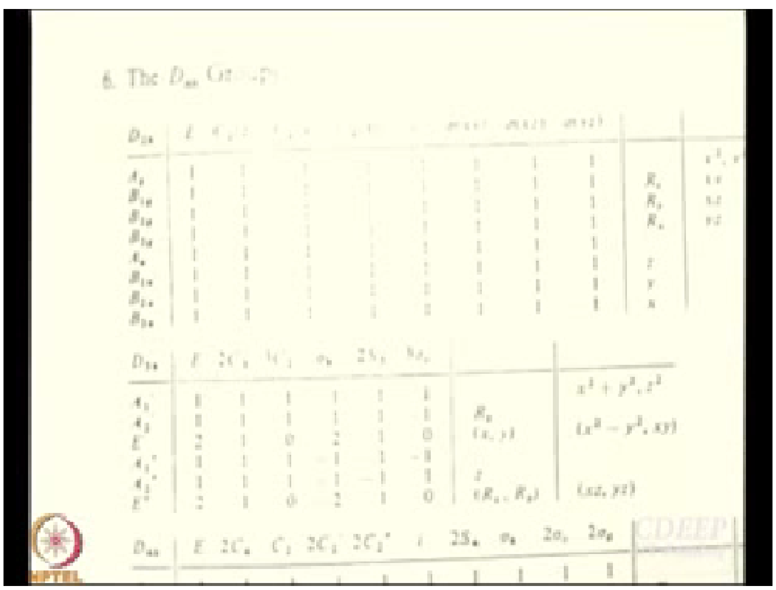

This is D3h for you. Can you work out the coefficients of each irreducible representation in that reducible representation that we have constructed. What I will suggest is going through Carter's book, I will tell you which page. Carter's book shows you how to do this in a tabular manner rather than writing out separately, okay. So that might be a little easier. This 12 0 -2 4 -2 2, these are the XR's, right.

The character table gives you the XiR's. So for each symmetric species, you have to multiply the XR's by the corresponding XiR's and then sum over all the symmetry operations. And when you sum over every symmetry operations, there is some place where you can go wrong very easily. Where is that place? Do not forget to multiply by this 2, this 3, this 2, 3, etc. Because do not forget that we are summing over all R's where r is a symmetry operation, not symmetry element.

So 2 C3 means there are 2 C3 operations. You have to sum over all the R's and when you do it in a tabular manner, it is very easy to see if you have gone wrong. So please read out that tabular presentation from your Carter's book. So what is A, A1-. **“Professor - student conversation starts”** 1. 1. What about the second one A A2-. 0. 0 that means there is no A2- kind of vibration. What is, well, not only vibration, vibration, rotation and anything.

What is AE1-? A A1--. A. A A2--. You have worked it out completely. **“Professor - student conversation ends.”** Let me write it down and see if everybody has got the right, same answer.

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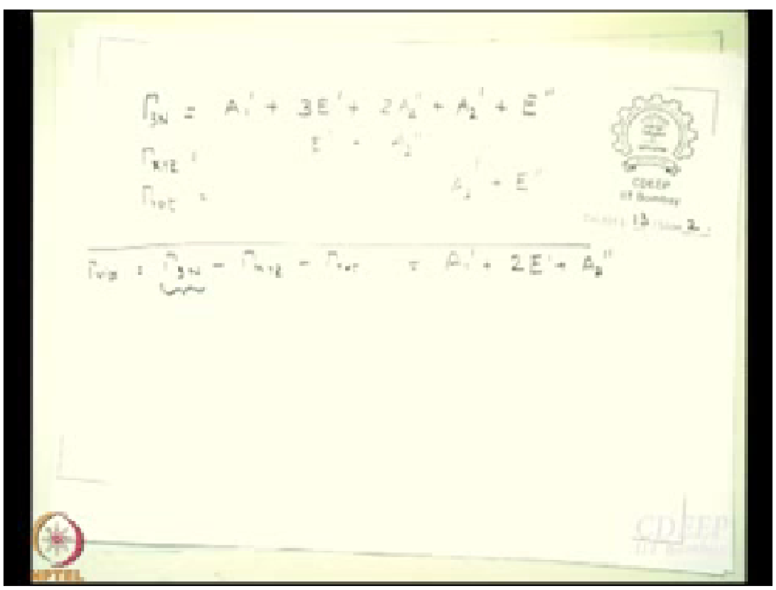

So I can write it like this. This gamma we have got, I will call this, what will I call this? **“Professor - student conversation starts”** No what will I call this, I want to give a name to this gamma. I will name my gamma, gamma 3n, okay. So that is equal to, what is A A1-? So I will write A1-+ what is A A2-? A A2-? 0. So I will not even bother writing anything. What is A E-? Your answer would better be correct.

3E-+. 2A. 2A. So nothing for A1--. 2A2--. Then what about E--? What about E--? E-- or not. Or nobody has worked it out. Even if you do not tell me anything more, I can work it out. This is a one dimensional representation. So 1, E- is 2 dimensional, 2*3 is 6, 6+1 is 7, 7+2 is 9. How will it be 3? If it is E, E--, then it cannot be 3, right. 1 2 3 6 9. So total has to be 12 but how will I make that total 12 by E--.

Something is wrong. 6, we made a mistake. A2-. I will just write the A2- here if you do not mind. So if that is the case, then I should get 1E--. You understand what I am doing, right. The dimensionality of the reducible representation should be equal to the sum of the dimensionalities of the constituent irreducible representations, right. So dimensionality here is 1, dimensionality of E- is 2 and there are 3 such.

2*3 is 6. 7, 7+2+1, +1 is 8, no 10 and E--2 that is 12. I better check if the answer is there. Yes. A1-+A2-+2A2--+3E-+E--. So congratulations, we are good in arithmetic. Now what will I do? What does this gamma 3N stand for? It is a representation for what? This was 3N coordinates, that is all. And we know that other than this 3N coordinates, because it is a non-linear molecule, 3 have to be translational coordinates, 3 have to be rotational coordinates.

So sum of these coordinates, the sum of the symmetric species that we are showing here, they are going to be because, they are going to be for the translational coordinates, sum will be because of rotational coordinates and that is something that we can read off directly from the character table. Is not it? **"Professor - student conversation ends."** So D3, you can see D3h, can you see? Now see it.

For D3h, x and y jointly form a basis for E-, right and what was your answer there earlier. C- was there. Out of that 1 E- goes for translation along x direction and y direction. Where is z? z A2--. Do you have A2-- in that expansion, you do. There are 2 A2--. So one of them goes for translational motion, z. Okay, what about rotational motion? Rz is here, A2- and Rx and Ry jointly form a basis for E--, right.

So what I need to do now is that I need to remove the irreducible representations corresponding to translational and rotational motion. Then whatever is left, will be the symmetric species of vibrational motion, simple. Let us do it. Do you take down what is what? Okay. No, then do it. Symmetric species for x y z Rx Ry Rz. So what do I take? So this is gamma 3N. What I will do is, I will write down what is gamma translation or I will write x y z, just x y z, gamma xyz means this will be the xyz components of translation, right. So what is gamma xyz, tell me?

“Professor - student conversation starts” E-. +E--. +. A2--. A2--. What do I need to take out from here? I want only pure vibration, right. I have taken care of translation. Now I need to take care of rotation. So I will write gamma rot, what will gamma rot be equal to? A2-. A2-. +E--. Is that right? A2-+E--, okay. So what I want to work out finally is gamma vib, gamma vib means the representation for the normal modes of vibration, that will be equal to gamma 3N-gamma xyz-gamma rot.

What will that be equal to? A1-. A1-+2E-+A2--, no A2-, right. A2- gets cancelled. No A--. How will I check whether my answer is right or wrong. Total dimensionality should be equal to 6. Is it 6? 1 2 and 2*2. Do not forget E- is a 2-dimensional representation, okay. Understood? Kristo? Total dimensionality is 6… Is it 6 or not. Yes. It should be 6, right. 3N -6, right. So what, what have we done?

We do not, we have not even tried to draw the normal modes of vibration. But we know the symmetric. We do not know what they look like but we know their symmetrics. If you remember we have said that we are going to play astrologer. We are going to work out the kundlis of molecules and this is what we have done, right. Ram is not born yet but Ramayan is written. So you know this the symmetries or normal modes already. **“Professor - student conversation ends.”**

But is that all or is there more? Of course, when I ask a question like that, the answer is there is more. Two things. First of all, we do not have to do all this. I can simplify this further for you. What is gamma 3N and how did we get gamma 3N, do you remember? **“Professor - student conversation starts”** (()) (22:01) **“Professor - student conversation ends.”** For gamma 3N, what you did is, you took the number of atoms, right, number of atoms that is not changed by a particular symmetry operation and you multiplied it with the character of xyz, right.

Understood what I am saying or not? So what you need to do then is that you write down this character table, just look at the character table, then below that write down what is the number of atoms that do not get changed, do not change position upon that particular symmetry operation. So what I am saying is this.

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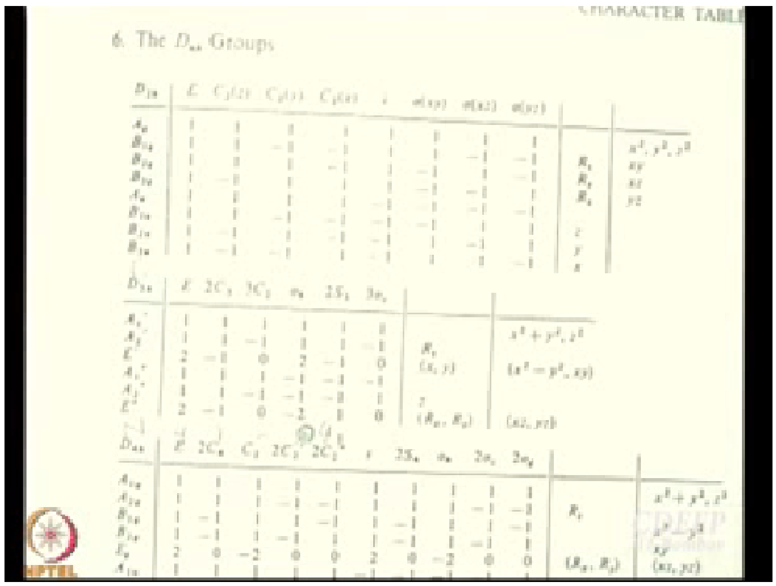

Big enough, but wrong character table. Now is it okay. Now what I am telling you is write down another line here for N. Can you read that N, yes, of course you can. What is the number of atoms that do not get changed? For E? **"Professor - student conversation starts"** 4. 4 in our case. For C3? 1. 1. For C2? 2. Sigma h? 4. S3? 1. Sigma V? So now what you can do is, you can work out gamma xyz also.

Sir, (()) (23:53) What did you write? Sigma h should be 0. Instead of 1 extreme, I have gone to another extreme which is not good. 4 atoms remain unchanged. What we are saying? What I am asking? What is the total number of atoms that remain unchanged? 4 is correct. Shantanu I forbid you from confusing me in future. **"Professor - student conversation ends."** You understand what I am saying?

What is the number of atoms that do not get change? Now see you can work out gamma xyz, I just write it here for the amount of space. What is gamma xyz? Can you tell me? This is xy and this is z. So how do I get gamma xyz character for, this is 3? Character for C3, what was the, what was the character for C3, for gamma xyz? For xy, it is -1 and for z, it is 1. So our good old friend 0.

Then 0 and -1 is -1. So on and so forth you can work out this characters for gamma xyz. Now you see if you just keep on multiplying this N by the character of gamma xyz, do not you get gamma 3N? You understood this what I wrote, what is N? You understood gamma xyz? Gamma xyz you do not understand? Gamma xyz is gamma x+ gamma y+gamma z. So gamma x+gamma y is E-, right and gamma z is A2--.

So now I will just add the corresponding characters. Now got it. So now if I multiply each, each of this characters of gamma xyz by the number of atoms that remain unchanged by that particular operation, should I not get gamma 3N?