(Refer Slide Time 00:00)

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

ज्ञानं परमं ध्येयम्.
Knowledge is Supreme.

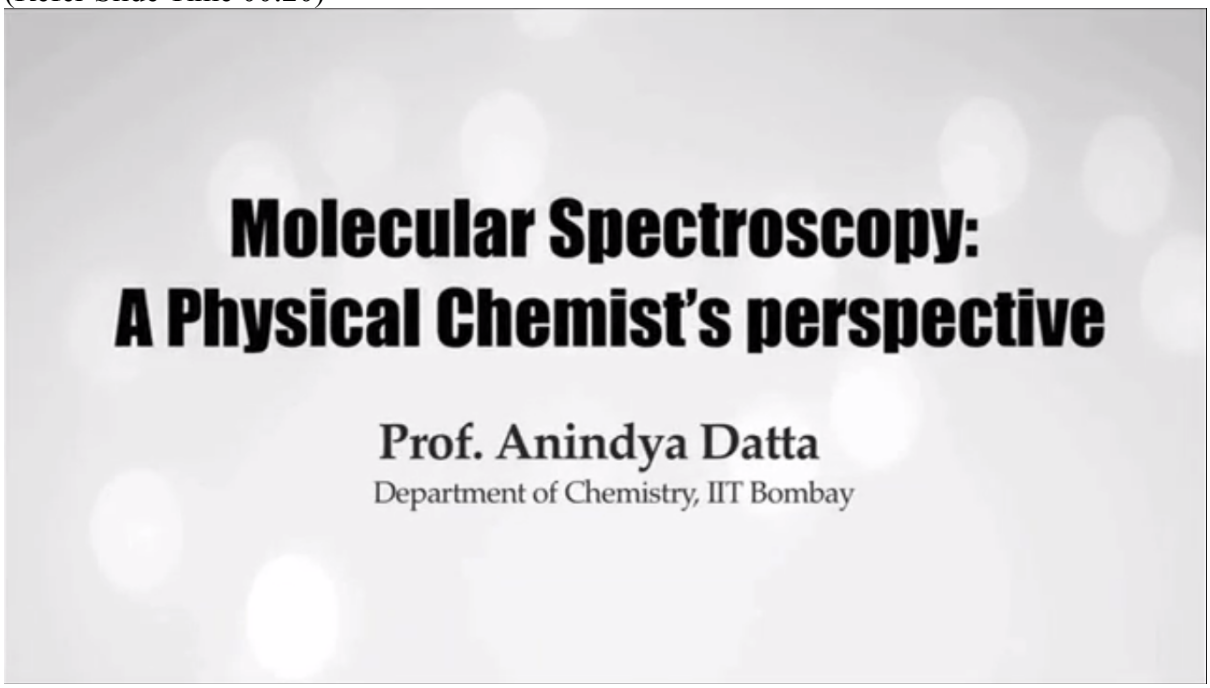
(Refer Slide Time 00:16)

NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)

(Refer Slide Time 00:17)

CDEEP
IIT BOMBAY

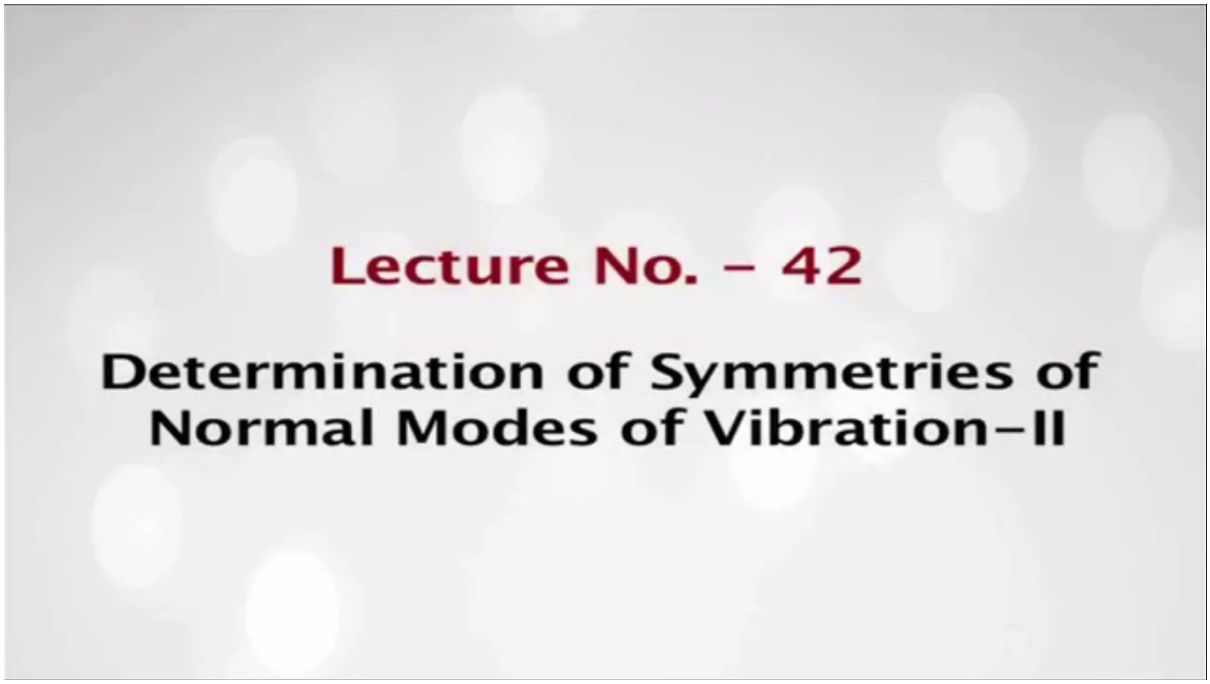
(Refer Slide Time 00:20)



Molecular Spectroscopy:
A Physical Chemist's perspective

Prof. Anindya Datta
Department of Chemistry, IIT Bombay

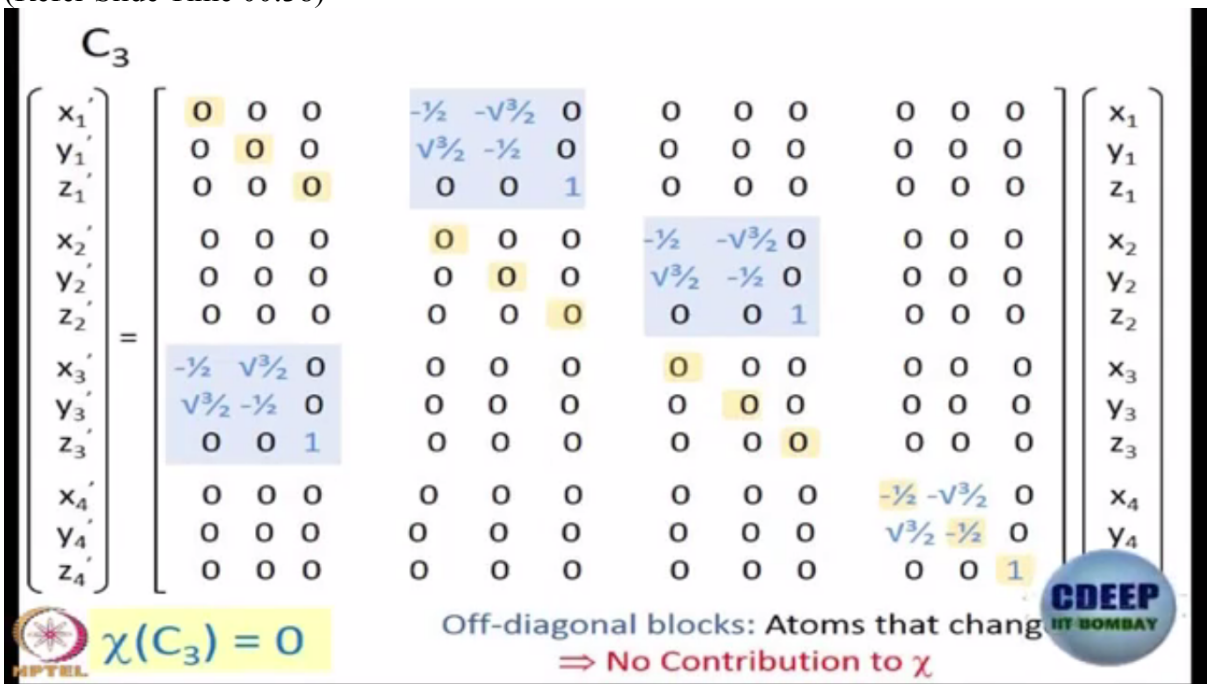
(Refer Slide Time 00:24)



Lecture No. - 42
Determination of Symmetries of
Normal Modes of Vibration - II

So we continue our discussion of this symmetry of normal modes of a D3h molecule with 4 atoms and so far we have reached this situation where for C_3 we have a 12 x 12 matrix and the character is 0.

(Refer Slide Time 00:38)



Okay. Why is it 0? Because this - ½, -½ exactly offsets +1. But we have actually learned something very, very important from this exercise. What is it that we have learned?

You see these blue blocks are what we had worked out, right, from the co-ordinates initially. What is this one? This is the contribution of co-ordinates of atom 2 in atom 1. Okay. Only the co-ordinates of atom 2 make a non-zero contribution to the transformed co-ordinates of atom 1. Why? Because atom 1 has moved from its original position to the position of the original position of 2. Only the co-ordinates of atom 1 make a non-zero contribution to the transformed co-ordinates of atom 3. Why? That is how the transformation has taken place.

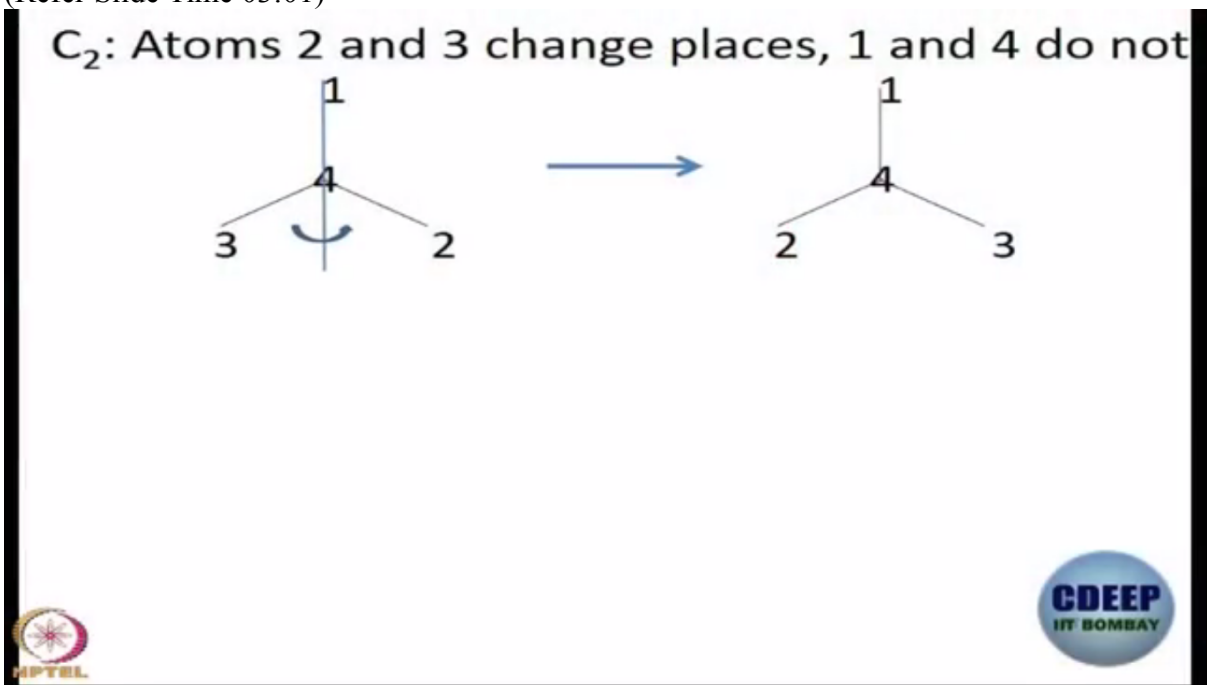
So what we see is that if atoms change place, then the non-zero blocks actually go off-diagonal. Right? What is the only atom that has made some non-zero contribution to the character? Atom 4, the only atom that has not moved from its own position as a result of the transformation. Right? This is something that is very, very important and you see to get this one matrix, we have spent like half an hour. Now we are going to get the other matrices in a matter of 2, 3 minutes each. Okay.

So the important lesson that we have learned is that the off-diagonal blocks, non-zero off-diagonal blocks are for atoms that change places, and they do not contribute to χ. Right?

So if you remember the old English proverb, rolling stone gathers no moss, right, if atoms move from their own position as a result of a symmetry transformation, symmetry operation, then they do not contribute to the character. This is something that we learned, and this is something that we'll use now. This will become very, very simple.

Okay. Let's go to the next symmetry operation. Before that, is there any question at this stage? Let's move.

(Refer Slide Time 03:01)

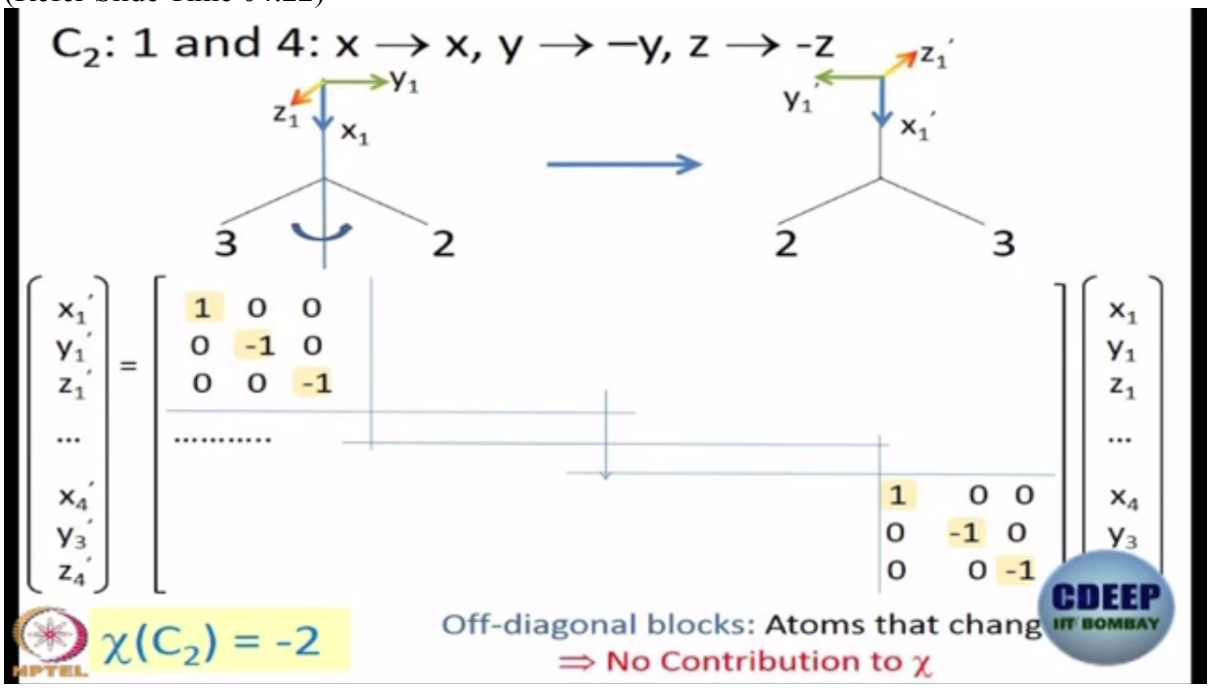


C_2. Remember where C_2 is? Where is C_2? This is one, this is one, this is one. Do they belong to the same class? C_2's, do they belong to the same class? Yes. So it is enough if you work with any one C_2. Okay. We choose to work with this C_2 that goes to atoms 1 and 4. All right.

Now as a result of this C2, what will happen? Which atoms move from their original position? Yes. 3 and 2 will interchange. Right? 1 and 4 remain in their own position. This is how the picture is going to be. So I hope it is not very difficult to understand that 3 and 4 will make no contribution to the character. Only 1 and 4 will make contributions. First. Second point is 1 and 4 will make equal contributions. Are we clear?

2 and 4 move from their original position. Therefore, they do not contribute to the character. 1 and 4 remain in their position. Therefore, they contribute equally to the character. Okay. So see now the problem has become so simple. You don't have to work with 12 co-ordinates anymore. You only have to work with 3 co-ordinates. That's all.

(Refer Slide Time 04:22)

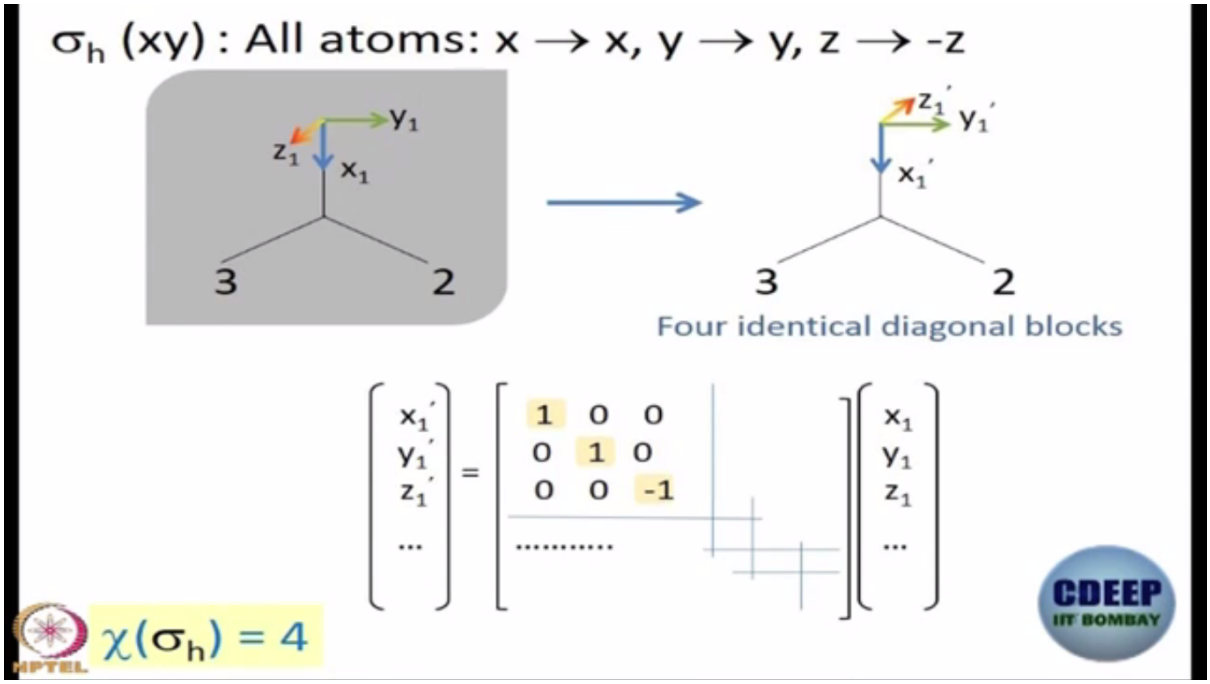


These are the co-ordinates, right? I hope you remember this is X, this is Y, this is Z. So tell me then what happens to X_1 as a result of C_2? What is X_1'? Same. What is Y_1' as a result of C_2 operation? -1 is a character. What about Z_1'? It becomes minus, right?

So this is the transformation matrix I get. I don't worry about anything else. See the only thing I worked out is this. For X_1 we said there is no change. For Y_1 it becomes $-Y_1$. For Z_1 it becomes $-Z_1$. So that block is 1 0 0, 0 -1 0, 0 0 -1 and you will have an identical block for atom 4 because atom 4 also doesn't move.

Have we understood this matrix? Okay. Why do I not write the off-diagonal blocks? Of course, they will be a similar block for 2 and 3 as well, but they will be off-diagonal. So I don't even write. The only thing I want is character. What is a character then? 2. $\chi(C_2)$ is -2.

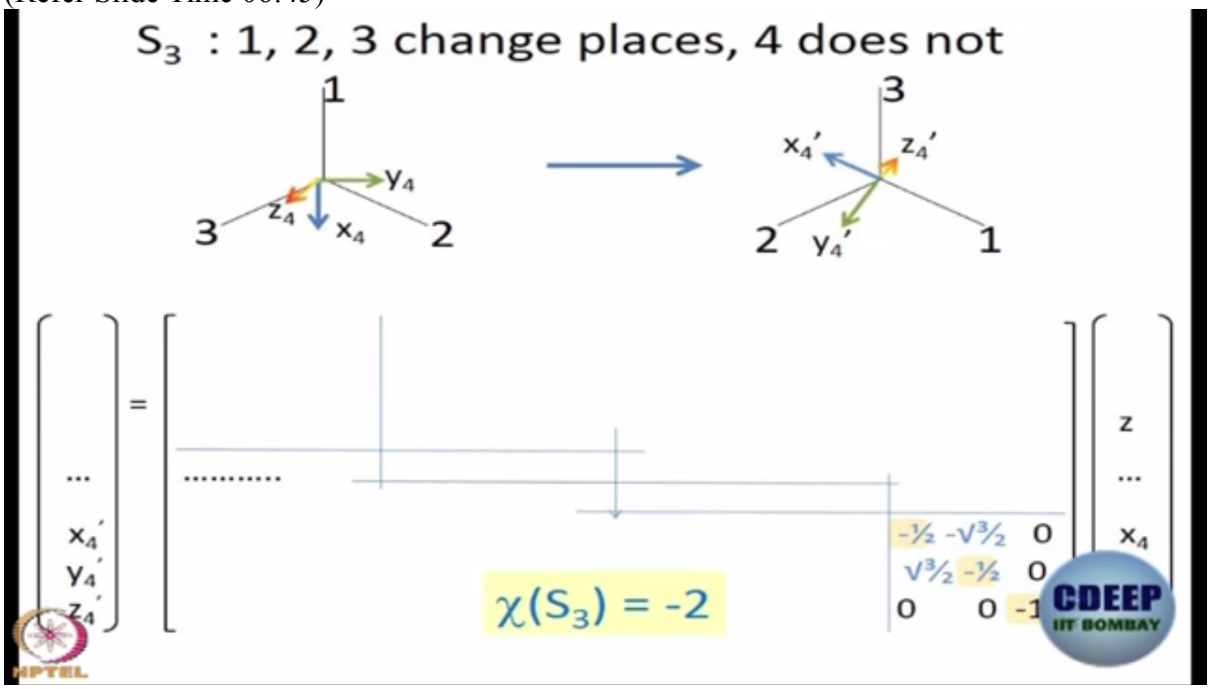
(Refer Slide Time 05:43)



All right. C_2 is done. What is next? Let's do σ_h. For σ_h, which are the atoms that move from their position? None. Does that mean we have to work with 12 co-ordinates? No. Why not? Yes, because all 4 will make identical contribution. Just work out any one. Okay. So σ_h is very easy. Isn't it?

X_1. What does X_1 become? What is σ_h? It is the XY plane. Z is your C_3 axis. So what happens to X? Same. What happens to Y? What about Z? -1. So what is the contribution to character of each atom? 1 + 1 - 1. So it is 1. Maybe you are giving me the answer when you said 1. I thought you are giving me the answer for X only anyway, and how many such blocks are there? So what is the character? Character of σ_h is 4.

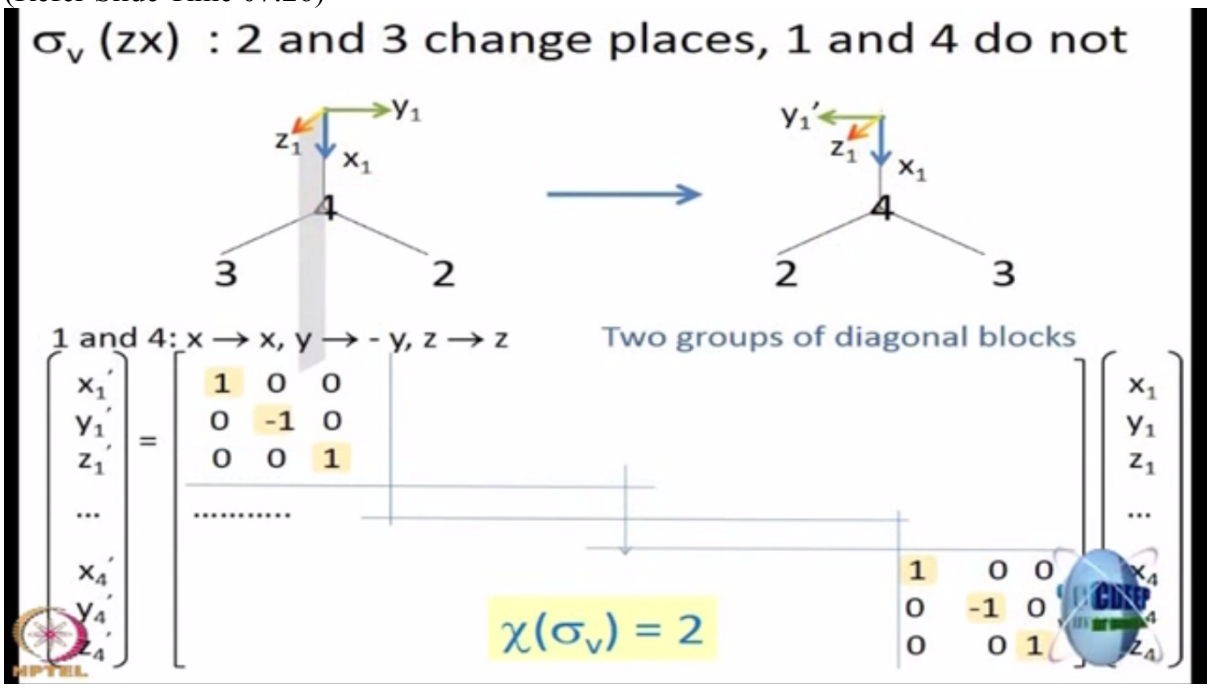
(Refer Slide Time 06:45)



S_3. What happens when I do S_3? S_3 is similar to C_3 in that 1, 2 and 3 interchange places. 4 remains in its own place. What is the only difference? You are doing an additional reflection. So Z will become -Z. That is all. Okay.

So what is it then? This is the only block you have to worry about. From X and Y, you know already you will get -1/2, -1/2. For Z you are earlier getting +1. Now you will get -1. So -1/2, -1/2, -1. -2. Okay.

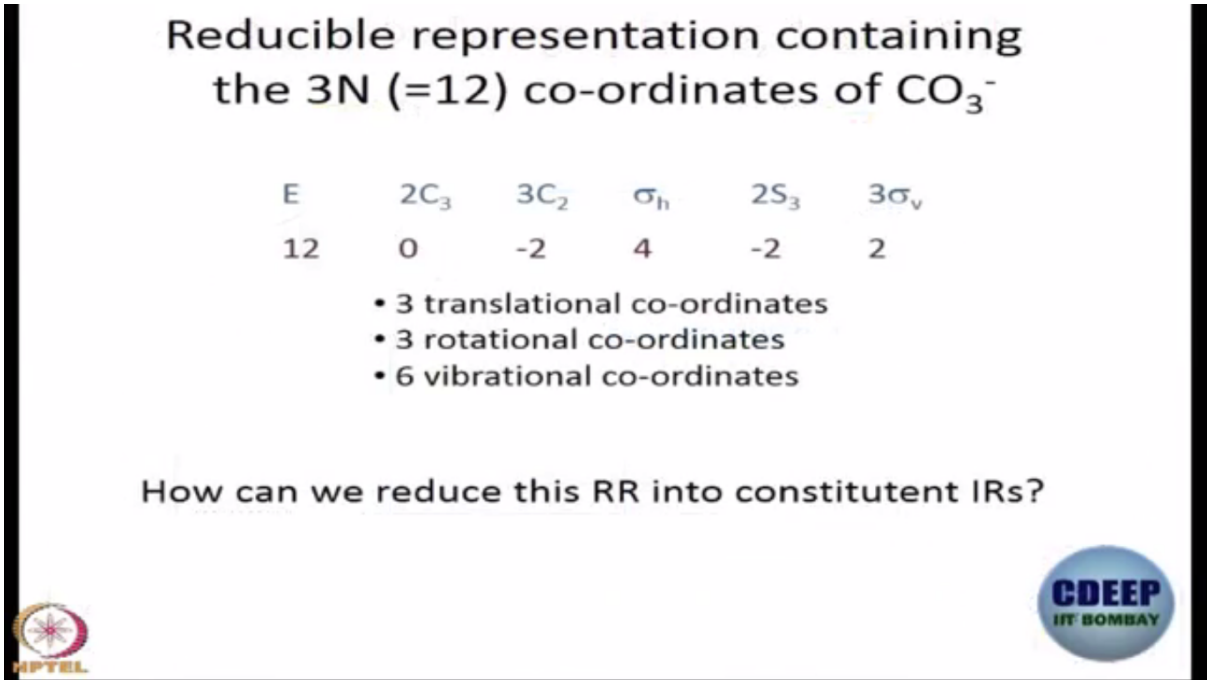
(Refer Slide Time 07:26)



σ_v. σ_v is ZX, right? σ_v is ZX. Of course, I could have taken this one, but it is more convenient if I take this. So I will take this. σ_v is ZX. So what will happen to X? No, first of all, wait. When I apply σ_v, which atoms remain in their place? Which atoms move from their place? Again, 2 and 4 interchange places, so they don't matter anymore. 1 and 4 will only matter and they will make identical contributions. Okay.

So what will happen? What will happen to X? This is X. This is σ_v. Will it change? No. So character is 1. Sorry, coefficient is 1. Why? Will it change? (inaudible 08:14) Yeah. Y will become -Y. Yeah. And Z same. So what will the character be for each atom? 1, 1, -1. That is again +1, right? See X remains same. ZX. Z also remains same. 1 + 1, 2 and Y becomes -Y. Yeah. I didn't even watch. So 1 + 1 + -1, that is 1. How many atoms contribute? Two. So 2 into 1 is 2. This. Simple.

(Refer Slide Time 09:06)



So, finally, after doing all this, this is where we are. This is the representation we have got, right, using the 3N Cartesian co-ordinates.

(00:09:15)