(Refer Slide Time 00:00)

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

ज्ञानं परमं ध्येयम्.
Knowledge is Supreme.

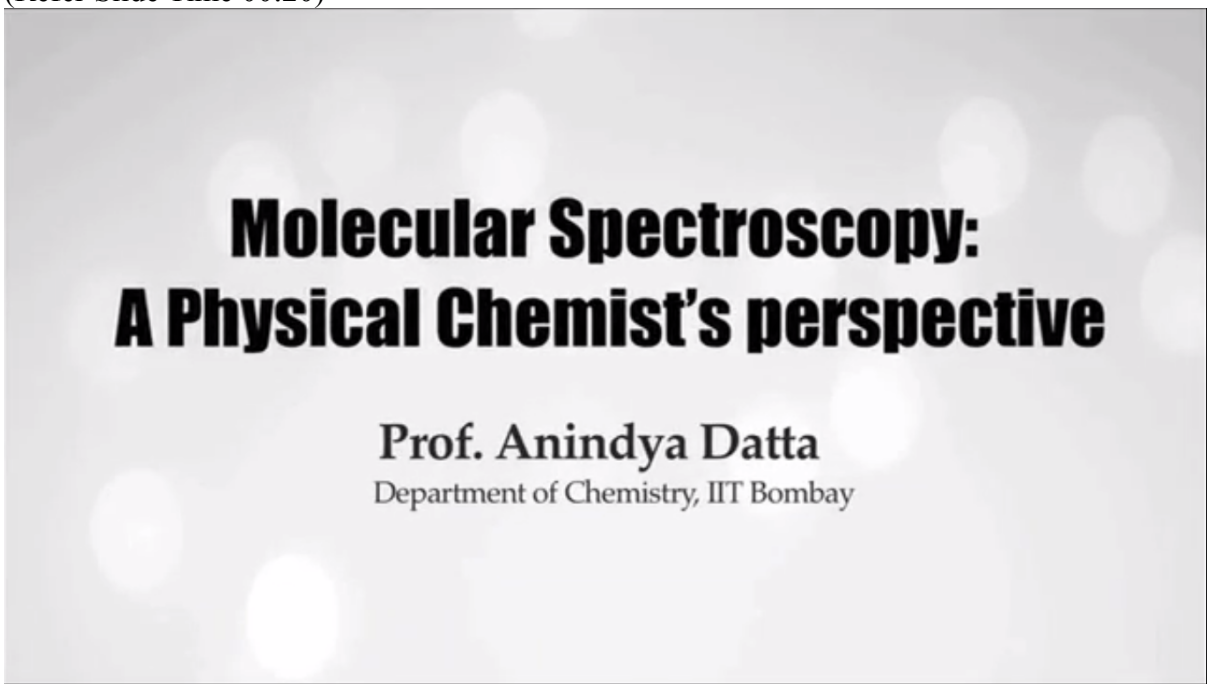
(Refer Slide Time 00:16)

NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)

(Refer Slide Time 00:17)

CDEEP
IIT BOMBAY

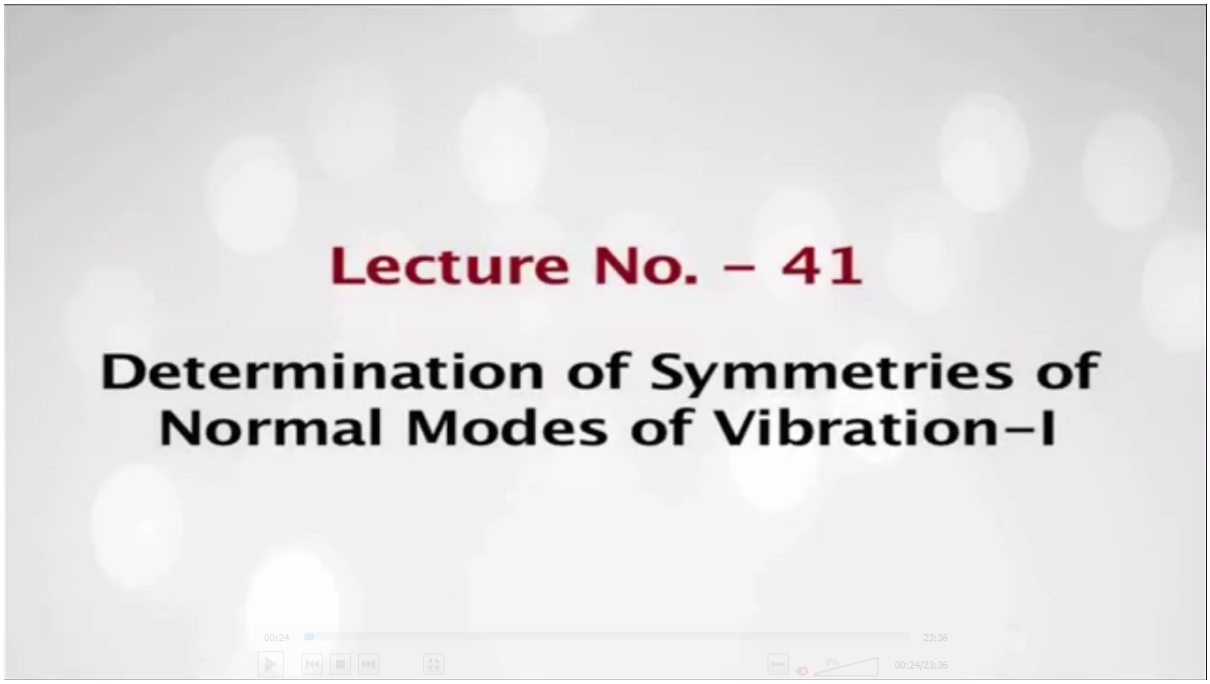
(Refer Slide Time 00:20)



Molecular Spectroscopy:
A Physical Chemist's perspective

Prof. Anindya Datta
Department of Chemistry, IIT Bombay

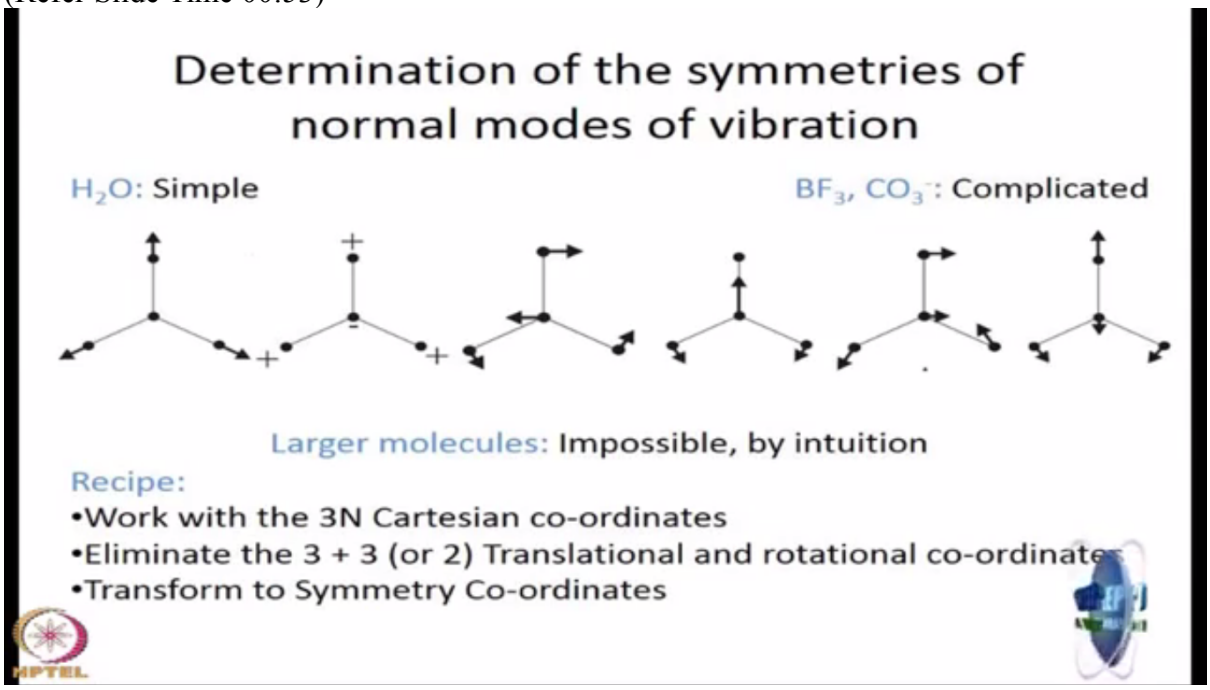
(Refer Slide Time 00:24)



Lecture No. - 41
Determination of Symmetries of
Normal Modes of Vibration - I

We are discussing the problem of symmetry of normal modes of vibration. Right? And we have said that for water it is rather simple to figure out what the normal modes look like. And when we closed the discussion the previous day, we have said that it is not going to be so simple if you think of a molecule with one more atom, okay, say BF_3 or carbonate ion.

(Refer Slide Time 00:53)



It is like water with one more atom added to it, right? This is what it is. This part looks like water. You have added one more atom. We have told that we are going to have six normal

modes of course and I am showing you the pictures of those normal modes. These are the normal modes of vibration for a D_3H molecule with 4 atoms like BF_3 or carbonate.

Now if you look at these, you could have perhaps guessed this one. The symmetric stretch. Okay. And this one. What kind of motion is this? This plus and minus means, plus means coming towards you; minus means going away from you. So this is called doming motion. Dome. You know a dome. You see on top of a mosque or Gurdwara or some churches, you have domes, right? Gumbaz. Gumbaz. Right? That's a dome.

So here it's a planar, trigonal planar structure. If the bonds come towards you, of course, to keep the centre of gravity in place, the central -- central atom has to go away from you behind the plane of the projection. That is called doming motion, right? A planar structure becomes a dome. That is called doming.

So this doming motion also perhaps you can kind of guess. This is like a symmetry -- this is like a bending motion. You can perhaps guess, but you don't know by how much this will go up. I cannot guess this one. Definitely not this one and if I can guess this one, I don't know the difference between this and this. Okay.

So it is not simple. You cannot figure out, but of course since I have drawn those arrows, there must be some way of knowing what the normal modes look like for even these molecules. Okay.

So there is something called Wilson's FG matrix by which you can actually figure out the frequencies and amplitudes of all these normal modes of vibration. Okay. Amplitudes mean amplitudes of each individual internal motion.

So the point is it is impossible to do it by intuition, right? So what we will do here, I told you what we will not do. I should also tell you what we will do. We will try to use symmetry to figure out as much as we can of this problem. What we should will be able to do is will be able to tell how many normal modes of which symmetry are present. When I say which symmetry, I mean which irreducible representation? Okay.

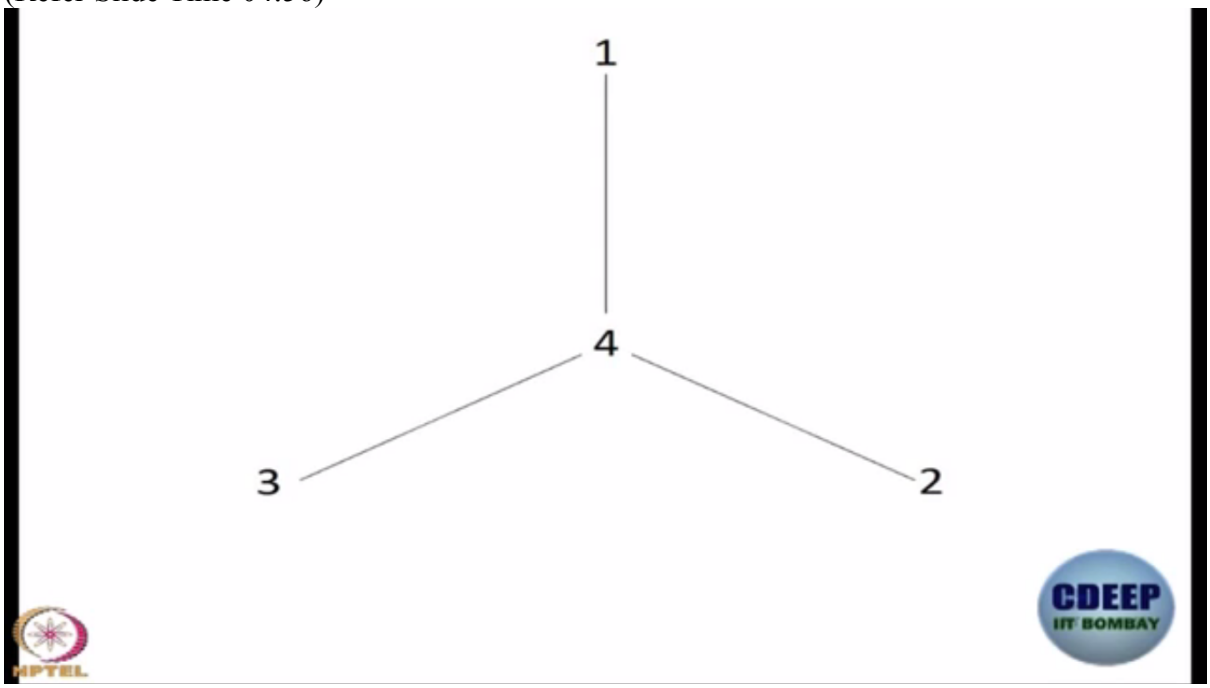
You will see we will be able to do that and we will also be able to tell which of these are IR active, which of these are Raman active and while doing that, we will arrive at something called Mutual Exclusion Principle for central symmetric molecules, and the way we do it is this is our recipe.

We go back to basics. What was the basic? How did we get this number 3N-6? We said that of these N atoms, each is associated with 3 co-ordinates X, Y or Z, right? So we work with these 3N Cartesian co-ordinates X, Y, Z attached to each atom.

Then what we will do is we will figure out the symmetries of these ensemble of 3N Cartesian co-ordinates. From there we will eliminate the 3 translational and 3 rotational co-ordinates, and then we will not really do transformation to symmetry co-ordinates, but to some extent we will be able to tell what is the contribution of which internal motion to each of these

normal modes. Okay. Part of it might sound like Greek and Latin or Hebrew at this moment, but let us be brave and take the first step. Things will become clearer as we go.

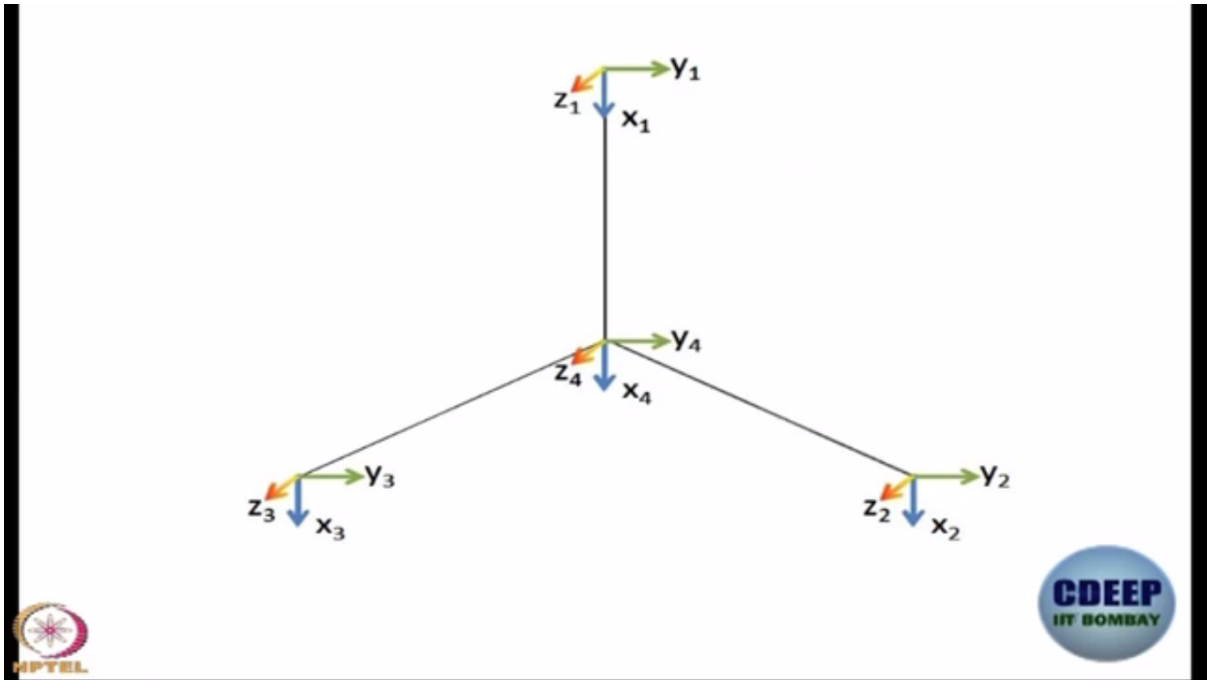
(Refer Slide Time 04:56)



So this is my molecule, okay, BF_3 or carbonate. We will just write 1, 2, 3, 4 as the identifiers for atoms. What is the first step? I must -- oh, by the way, this discussion is there in many books. I am following Cotton's book, but more or less identical discussion is there definitely in (inaudible 05:17) book and I think even McQuarrie and Simon, but I'm not sure about that. Okay, but Cotton symmetry and chemistry is fairly commonly available. You can follow it. So this is what it is.

What will I do to start with? I will assign X, Y, Z to each of these. Okay. And what we will do is we will follow Cotton's convention and draw the X, Y, Z axes like this.

(Refer Slide Time 05:42)



Would I have drawn it in some other way? Of course, I could have drawn. Okay. But I have to start with some convention. This is the convention that we use. So it's important to understand the directions of X, and Y and Z and this is where -- yes. This is X-axis pointing downwards, right? How do I define it? If this is the carbon atom, if this is not carbon atom, whatever atom, if this is atom number, what was it? 1, right? Yeah. It's written there. If the top atom is atom number 1, then X-axis is aligned with the 1, 4 bond and of course the other X-axis have to be parallel to it. Okay.

How have I drawn Y? Perpendicular to X-axis like this. Okay. The other X-axis, sorry, Y-axis, Y-axis is perpendicular to this X-axis. The other Y-axis have to be parallel to that first Y. Are you clear about that? This is the central one of course.

What about Z-axis? Z-axis is pointing towards you. This is for 1. This to for 2. This is for 3. Okay. It's easier for you to understand if I act the molecule. So, okay.

Now what I will do is I'll -- how many co-ordinates do I have then? How many atoms? How many co-ordinates? 12. So you understand for each of these operations, we are going to deal with 12 co-ordinates. So we will actually try to work out the transformation matrices.

So those will be 12 x 12 matrices and then we will see what we see, and by the time we are done, we will actually learn a couple of very useful tricks, which will help us to reduce the dimension, right? You will see we will not have to deal with 12 x 12 matrices actually and next day we will actually learn a very easy mathematical expression, which we can use as a black box. But it will not be a black box for us. We will learn how it comes. Okay.

So to start with, what is the -- what is the symmetry point group? What is the point group of this molecule? B_3H. Very good. What are the symmetry operations? First one I can say easily. E. E. What about E? E is there. Next, C3. Then 3C2. Where are the C2? Along the bonds, isn't it? This is the C2. This is the C2. This is the C2. Okay.

What else? σh. What is σh? Molecular plane. Very good. What else? But wait. Is there any other axis? You talked about the simple axis of symmetry. Is there any compound axis? S3 is also there, right? C3 is also S3. Okay.

Now what about any other σ? This, this, this perpendicular planes. Okay. I. Do we have point of inversion? No? Okay. Let's begin.

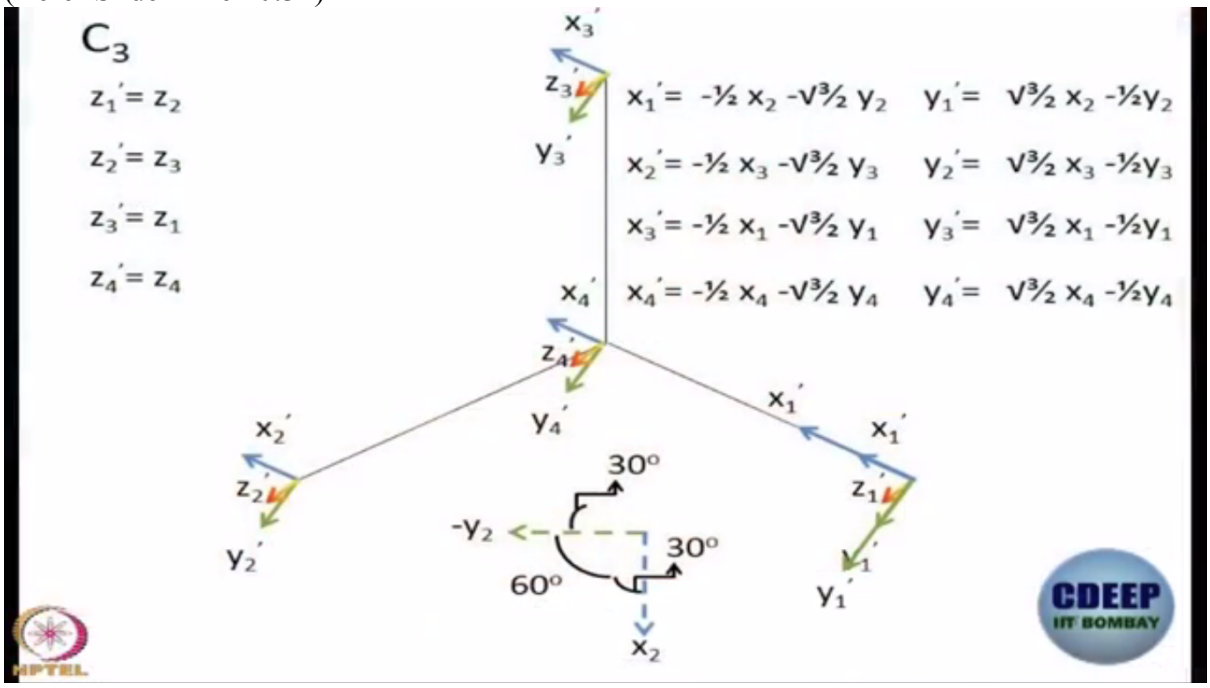
So first one, what is the first matrix? Matrix for E. E. What is E? E means doing nothing or multiplying by 1. Right? So what are -- what are the co-ordinates I have? (X_1, Y_1, Z_1), (X_2, Y_2, Z_2), (X_3, Y_3, Z_3), (X_4, Y_4, Z_4). 12 co-ordinates, right? So what is the matrix for E for a 2M-dimensional basis? It's a 12-dimensional unit matrix, isn't it? 1000, then 0100, 0001 so on and so forth.

So what is the character? 12. So if you remember character of the unit matrix is equal to the dimensionality of the basis. This is something we have learnt earlier.

What is the next operation? C3. So we have to understand what happens to the coordinates when I apply C3? Let's start with 4. 4 is easiest to understand. This is Z. Right? What happens to Z_4 when I do C3? It remains Z_4. Simple.

What about Z_1? This is Z_1. So I'll do it like this. So I'll turn in that direction. Okay. This is Z_1. Turn by 120 degrees. What happens? It becomes Z_3. Z_2. Okay. What about Z_2? Turn by 120 degrees. It becomes Z_3. What about Z_3? Turn by 120 degrees. It becomes Z_1. Are we clear?

(Refer Slide Time 10:34)



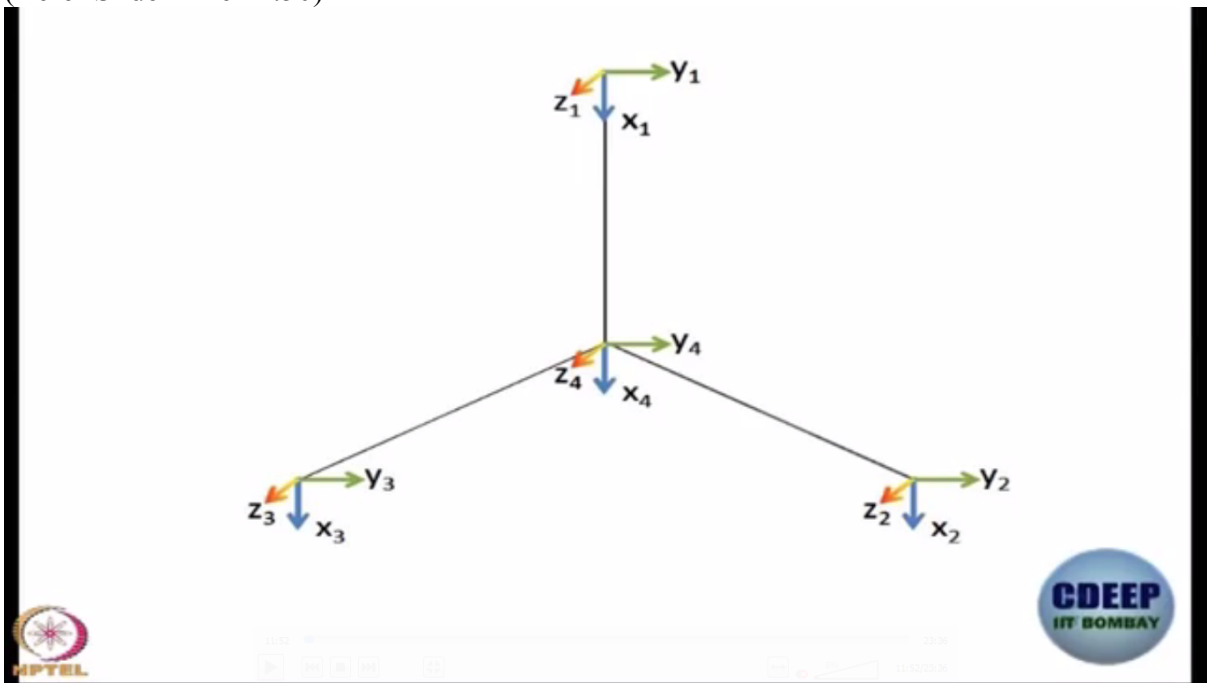
Actually, I have shown everything here, but Z I think you have understood, right? So I will write that first. Z_1' is Z_2. Z_2', okay, write itself. Z_3. Z_3' = Z_1 and Z_4' = Z_4. Right? So when I use a ', I mean transformed coordinate. Fine.

Now let's work with X and Y. Okay. So let's understand carefully what happens to X and Y. Again, X_4, Y_4 are easiest to understand. This was the original X_4. Right? I have turned by 120 degrees and I went like this. If this is X_4, 90° and 30°, 120°. This will be the direction of X_4. Okay.

In fact, it is perhaps easier to understand if you think in terms of X_1. Where is X_1? This is X_1. Isn't it? Right? You turn by 120°. This is the direction of X_1. This is the tip of the arrow. Are we clear? Okay. Z is okay. Are you all?

Now we are talking about X. So this is the X_1 arrow, right?

(Refer Slide Time 11:50)

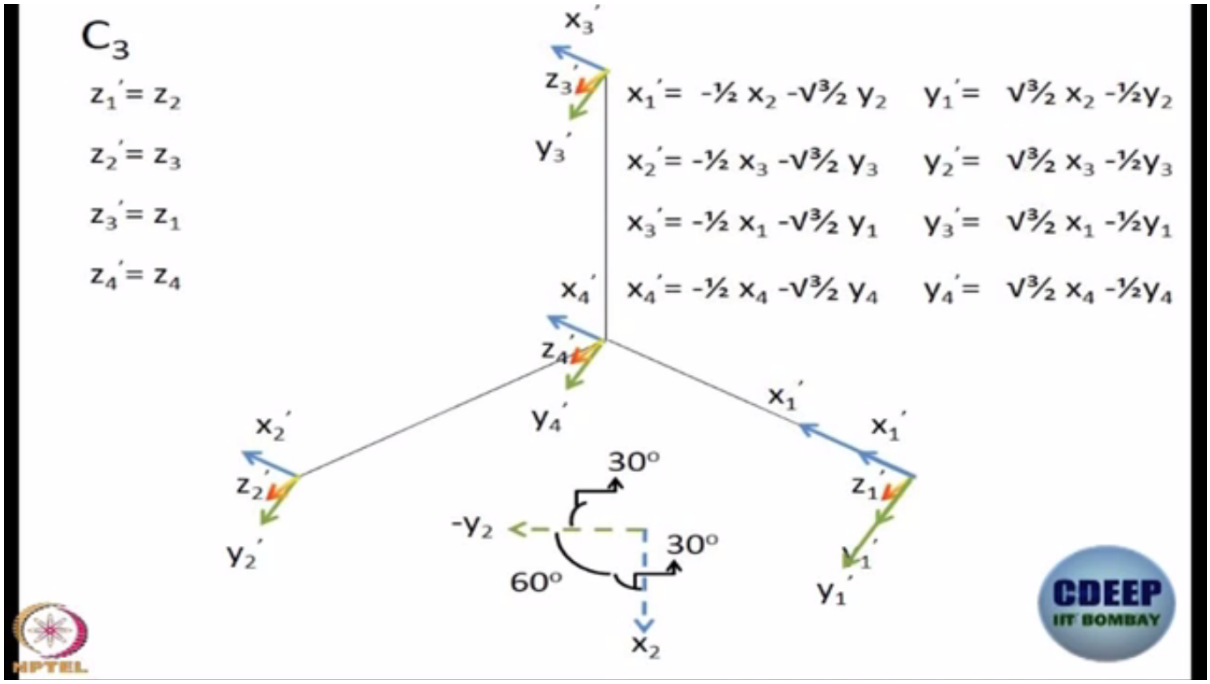


This is X_1. This is the tip of the arrow. Now what am I doing? I am turning by 120° like this. It's almost as if I am turning the hand by using this lever. Right? So now X1' will point this way. If you understood X_1, you will understand everything else. Okay. And all other transformed X co-ordinates will be parallel. Okay. X is also easy to understand. This is what it is initially, 90°, 30°, 120°. X_1 is easy to understand. This is X_1'. Okay.

What about Y_1'? Or rather let us finish with the X's. What about X_2? What was the original direction of X_2? Like this, right? Where will it go? It will be something like this. Right? Parallel to this and parallel to this. Right? So I hope you have understood the X's.

And what about Y? Where was Y? Well, go back once again. What about Y? This was Y. Right?

(Refer Slide Time 13:15)



Again, for Y_4, this is Y_4 and we are turning like this 90°, 30°. Well, parallel to X is all you need to understand. 1 again is easy to understand. This is X_1, sorry, Y_1. This is the new position of 1. So this is the position of Y_1'. Are we clear? So that is something I can show generically like this. This we have done already. Yeah. So this is X_1'. This is Y_1'.

Now see what have I done? I have rotated by 120°. So as usual you have to denote the transformed co-ordinates X_1', Y_1' in terms of the original co-ordinates, right? But this time the difference from our earlier discussion is that now the original coordinates are not (X_1, Y_1). What are the original co-ordinates? (X_2, Y_2). Why? Because atom 1 has now gone to where atom 2 was. So X_1' and Y_1' have to be written in terms of X_1, Y_1. Are we clear about that?

So how do you know that -- so what he is asking is why do we need vectors? We need vectors because how do I know that I have 3N-6 normal modes of vibration? There are N atoms. So the very basic initial formulation is that each atom is associated with X, Y, Z, that is three coordinates. That gives me a total of 3N co-ordinates. Then take away 6 from that. You are left with only vibrational co-ordinates. So that is what I am doing.

So we are working with the 3N co-ordinates right now. We have understood this, right, that X_1', Y_1' will now have to be expressed in terms of not X_1 and Y_1, but X_2 and Y_2. Similarly, X_2' and Y_2'will be expressed in terms of X_3 and Y_3. X_3', Y_3' will be expressed in terms of X_1 and Y_1 and X_4' and Y_4' will be expressed in terms of X_4 and Y_4 like what we have seen for Z.

See Z_1' is Z_2. Z_2' is Z_3. Z_3' is Z_1. Z_4' is Z_4. The positions of the atoms, if they change, then you have to use the co-ordinates of the original atom, the position of which is now based upon transformation and that is something that will lead to a very, very useful piece of information in say (inaudible 16:00) now. Go ahead. Okay.

Now the job is decide the expression. So what I want to write is X_1' is equal to something into X_2 plus something into Y_2. Y_1' is equal to something into X_2 plus something into Y_2. Okay.

How do I do that? You do that very simply. Recognize the angles. Right? So now tell me what will it be? X_1' is equal to what multiplied by X_2? What is the X_2 co-ordinate of X_1'? First of all, this is plus. So it will be minus, isn't it? This angle is 30.

So what will be the X_2 co-ordinate of X_1'? Sin 30 or Cos 30? Sin, right? And will it be plus or minus? Minus. Yeah.

Student: (inaudible 17:00).

Prof. Anindya Datta: You need vector along the axis. Yes. We are working with unit vectors along X_1, Y_1, Z_1. Yes. When we talk about co-ordinates, of course, we have to work with the same length. That is why all these arrows are drawn as same length. So what will it be? -Sin 30°. How much is that? -1/2. Is that right? -1/2 or -√3/2? I always get confused between the two. -1/2. Sure?

So this, yeah, I have given you the other answer also. So X_1' turns out to be -1/2 X_2 and what is the Y_2 co-ordinate? Already it is along -Y_2. So it will be - √3/2 Y_2. Simple? And it is not very difficult to see that for everything you will get these for X_2.

What about Y_1'? What will Y_1' be? Y_1' will be how much multiplied by X_2 plus how much multiplied by Y_2? This is 30°. So +Cos 30° into X_2, how much is that? √3/2 X_2 and what about Y_2? It's along -Y_2 and sign, right? So how much will it be? How can Sin and Cos both be √3/2? 1/2. Okay. So Y_1' = √3/2 X_2 -1/2 X_2. Are we clear with that? Sure?

And then the rest is simple. X_2', Y_2'. Same coefficients. Sure? Same coefficients. X_3', Y_3' same coefficients. The only thing that you have to careful about is which atom you are working with. Okay. Any question? No question, answer? Okay.

X_4', of course, X_4 is the only atom that does not move. Sorry. Atom 4 is the only atom that does not move. So X_4' is -1/2 into X_4 - √3/2 Y_4. Clear? Okay. Right.

So now what do we want to do? What are we trying to do here? We are trying to get the transformation matrix. How do I get the transformation matrix? Let me write the equations first.

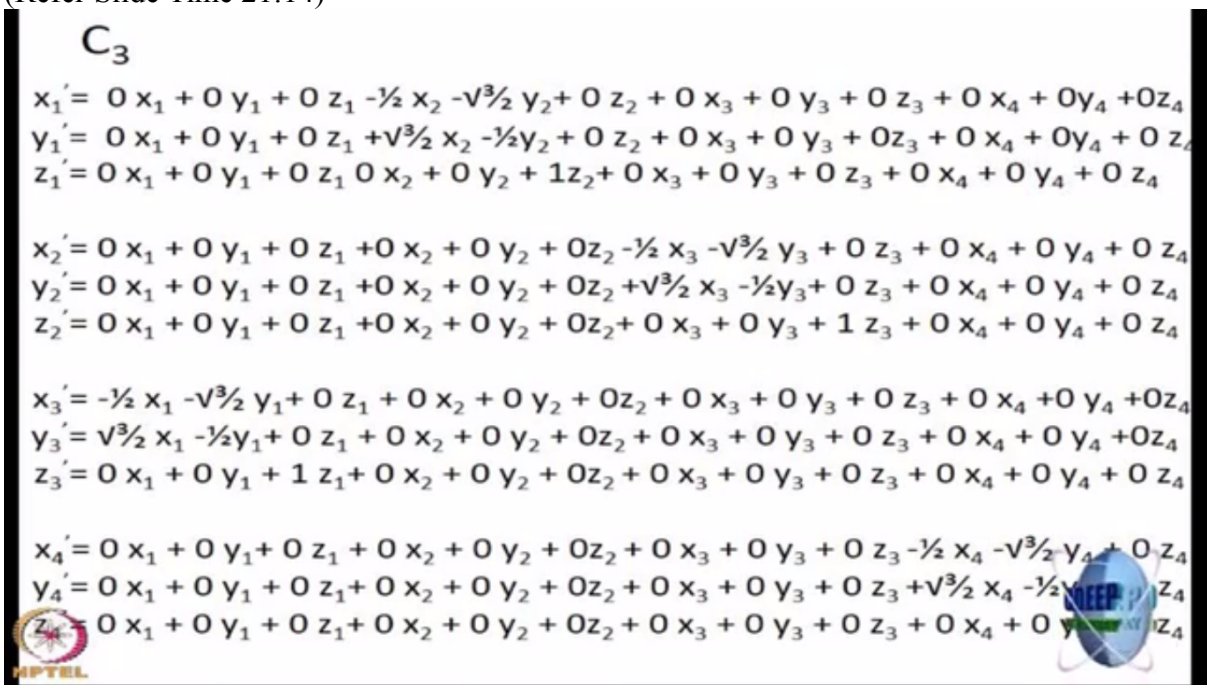
I think the question is can I write one general equation? Okay. So general equation would be X_i' or rather, yeah, X_i' = -1/2 X_j - √3/2 Y_j. Y_1', sorry, Y_i' = √3/2 X_j - 1/2 Y_j where i denotes the transformed coordinate, j denotes the original co-ordinate. That will be the general form of the equation if that's what you are asking for. We are working with the 3N co-ordinates associated with each atom. Right?

We are, finally, we want to talk about internal co-ordinates. We are talking about motion of one atom with respect to the other. If we use the laboratory fixed co-ordinate system, then it is difficult to see. It's much easier if you go and sit on one atom and see how they move with respect to each other. You are working with 3N co-ordinates associated -- one sets of three co-ordinates associated with this atom. So you have to do this. Right?

(Refer Slide Time 20:47)

So I have erased the diagram and let me write it in a little neat fashion like this. So what I have is a set of three equations for every atom. Okay. Now I want to write it in the form of a matrix. Of course, you understand that when I want to write in the form of matrix, what I'll have is I have a lot of zero coefficients, right?

(Refer Slide Time 21:14)

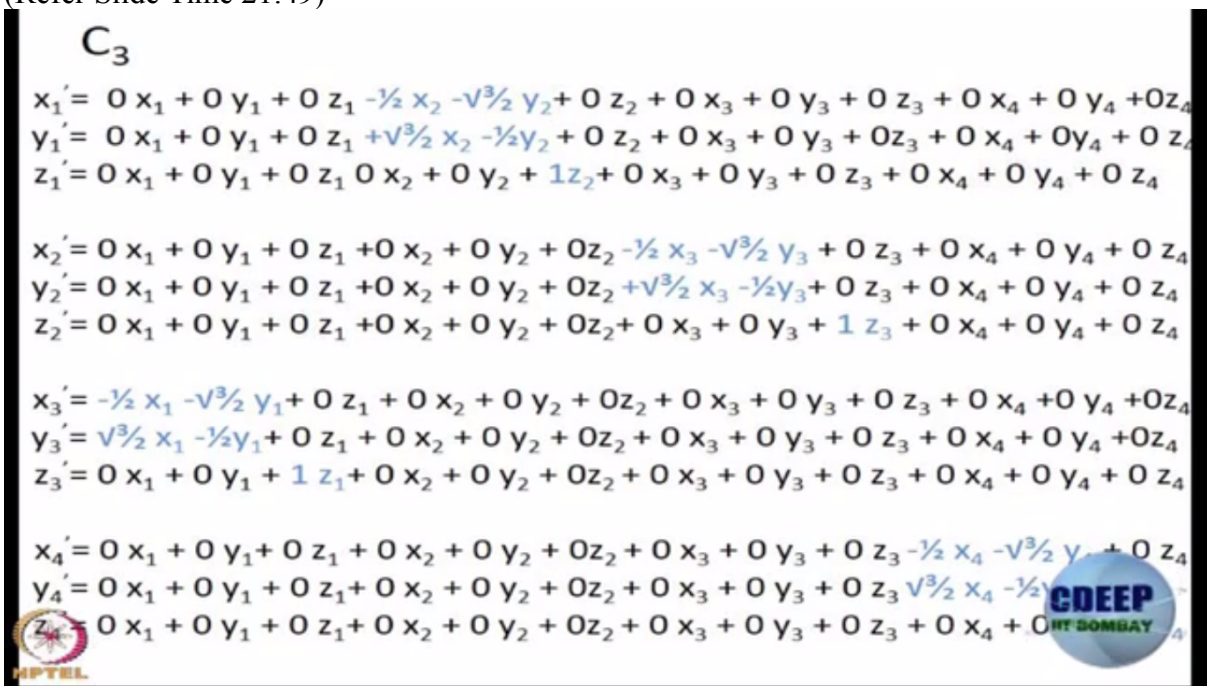


For example, this X_1' is -1/2, but what is the -- what is the co-efficient of say X_1? 0. So I have to write something like $X_1' = 0\ X_1 + 0\ Y_1 + 0\ Z_1 - 1/2\ X_2 - 1/2\ X_2 - \sqrt{3}/2\ Y_2$ and then everything else is 0 once again. Why am I all of a sudden importing so many zeroes? Because

I have to write the matrix. Right? I hope this is not very difficult to understand. This is -- these are the equations that you write.

So just so that we see things a little better, what we will do is we will show you the non-zero blocks in a different colour. Okay.

(Refer Slide Time 21:49)

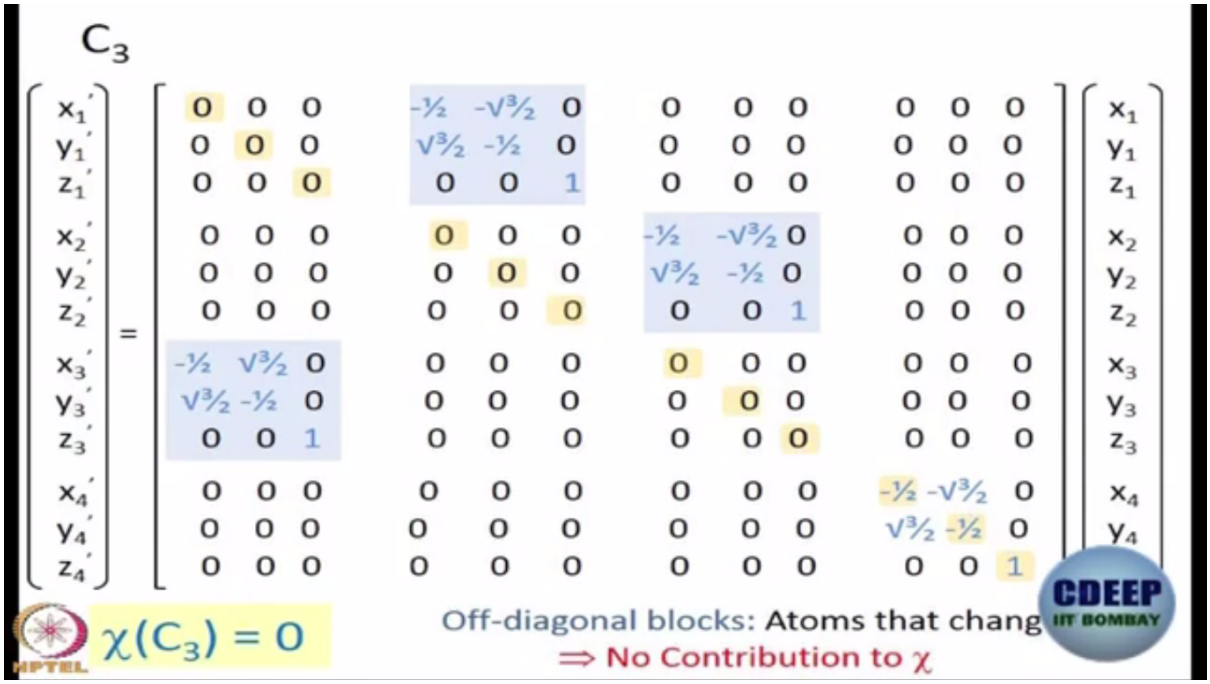


So these blue ones are the blocks that we have worked out in the previous stage. All right? Clear so far? This part is easy I hope.

Now, can you write the matrix now? Left-hand side X_1', Y_1', Z_1', X_2', Y_2', Z_2' etc., etc. Write the whole thing as a column matrix.

Right-hand side what I will do? X_1, Y_1, Z_1', X_2, Y_2, Z_2, X_3, Y_3, Z_3, X_4, Y_4, Z_4 as a column matrix. That will be left multiplied by the transformation matrix. The transformation matrix will be a collection of the coefficients. I hope there is no difficulty going from here to here. Raksha? Easy? Okay.

(Refer Slide Time 22:40)



So this is the matrix. First, let us work out the character. Then we will talk. What is a character? Character is sum of all these diagonal elements. So what is it? 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0. Now we have something -1/2 -1/2 and then 1. So, finally, after all this, we get a 0. So character of C3 if you work with the 3N co-ordinates of the molecule turns out to be a 0. Okay.

Prof. Sridhar Iyer
NPTEL Principal Investigator
&
Head CDEEP, IIT Bombay

Tushar R. Deshpande
Sr. Project Technical Assistant

Amin B. Shaikh
Sr. Project Technical Assistant

Vijay A. Kedare
Project Technical Assistant

Ravi D. Paswan
Project Attendant

Teaching Assistants

Souradip Dasgupta

Hemen Gogoi

Bharati Sakpal
Project Manager

Bharati Sarang
Project Research Associate

Nisha Thakur
Sr. Project Technical Assistant

Vinayak Raut
Project Assistant