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IIT BOMBAY

**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

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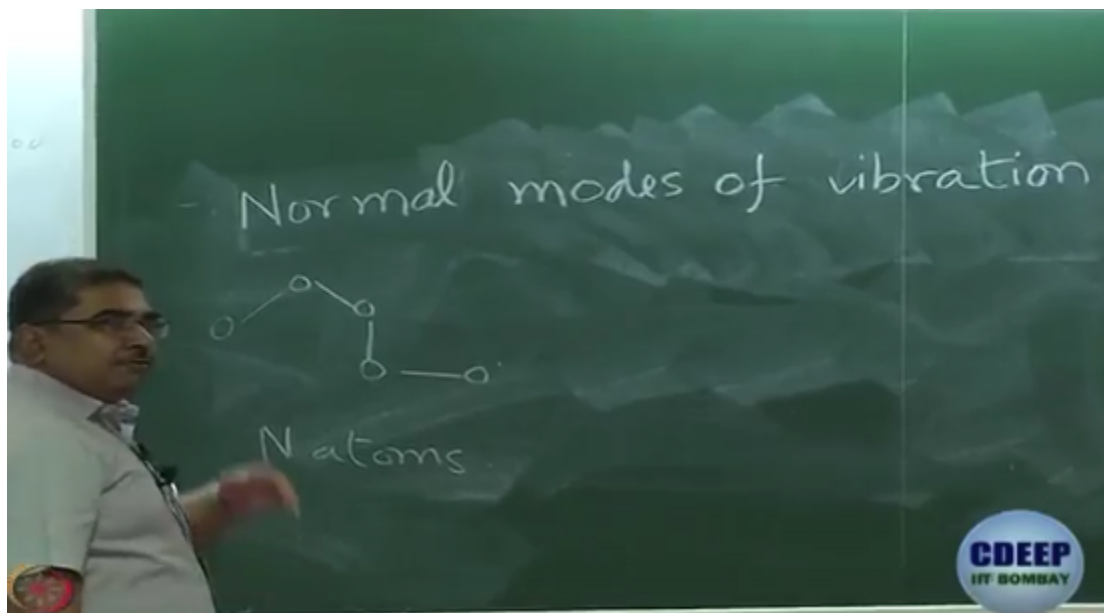
**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

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**Lecture no. – 40
Polyatomic Molecules: Normal
Modes of Vibration**

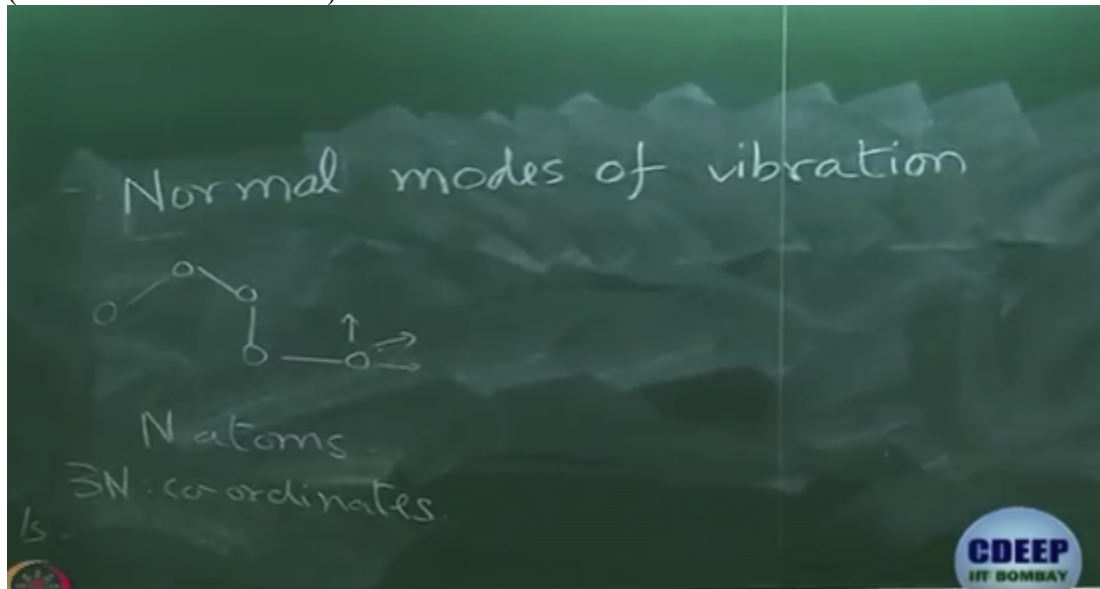
Earlier we have discussed vibrations of diatomic molecules, okay, and we have discussed that you can model the atomic molecules as a first approximation as harmonic oscillators and then since the atomic molecules must break eventually if the vibration is too much so that is why what we have is you have to use un-harmonic oscillator model if you want a little more accurate picture, right.

So now when you talk about polyatomic molecules how do I handle the problem? You might remember from your elementary physics course or maybe you've studied it in thermodynamics course in chemistry as well that when I have a molecule with say N atoms, some molecule like this, N number of atoms,
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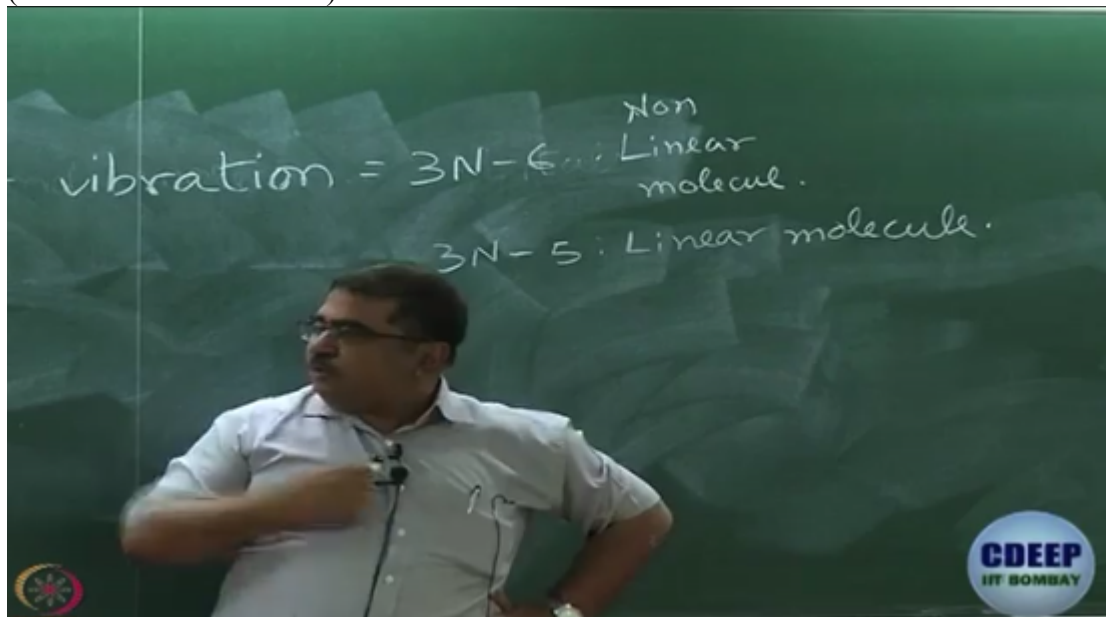
the way you formulate the problem of motion of these atoms is you consider three axis to be associated with each of this atoms, right, so what is the total number of coordinates? $3N$ number of independent coordinate whenever I say coordinates what is implicit is that they are all independent of each other.

What is another word for independent in this context?
(Refer Slide Time: 02:07)



Yeah X, Y, Z are independent of each other, if I want to replace the word independent by another word, what would I say? Yes, orthogonal to each other, very good, what is another word I can use? Yes, decoupled is okay but another name of orthogonal in this context, are they normal to each other? Right so this normal modes of vibration I talk about that I don't mean that there are crazy modes of vibration, no abnormal mode of vibration, what I mean is I'm talking about vibrational coordinates, independent modes of vibration, okay, we'll come back to that.

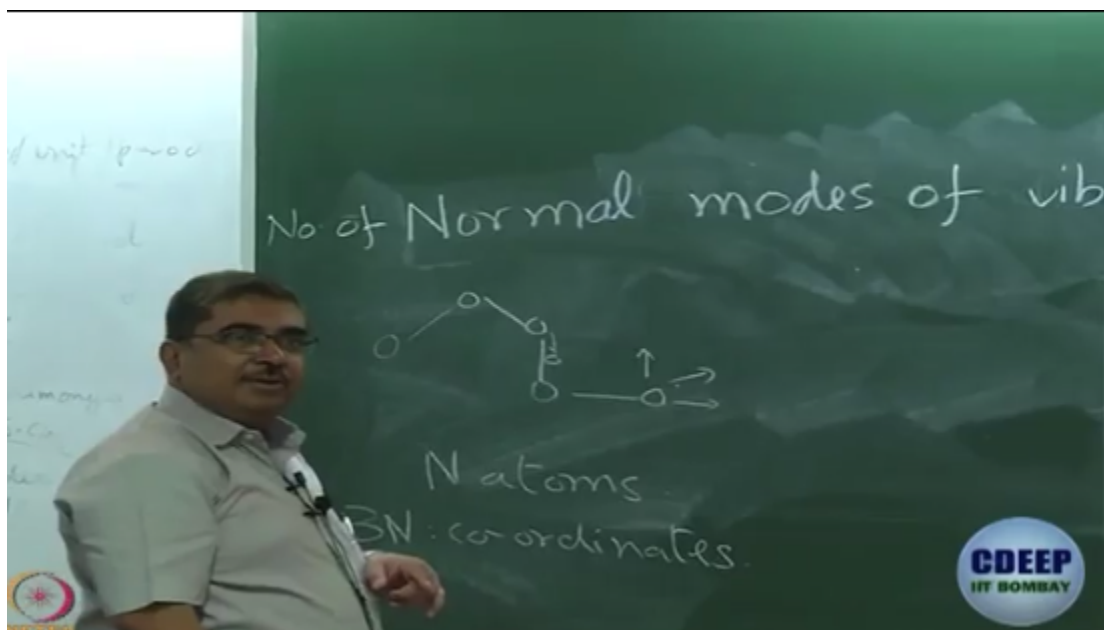
So total you have $3N$ number of coordinates and then how many of this should be reserve for translation? How many for rotation? 3, R_X , R_Y , R_Z we discussed yesterday remember, so number of, I can do it here, number of normal modes of vibration = $3N - 6$ for a linear molecule and $3N - 5$, the good thing about a chalk board is that if you forget something you can always write it later, so $3N - 6$ for a nonlinear molecule, $3N - 5$ for a linear molecule, alright.
(Refer Slide Time: 04:00)



Now so I think you know this right that a molecule has $3N - 6$ vibrational degrees of freedom, so normal mode is just another word for a vibrational degree of freedom, but it is important because we should not forget that we are talking about vibrations that are independent of each other. And since we've taken the 6 out we are talking about pure vibration, what's the meaning of pure vibration? No change in, well pure vibration means there is no rotation, no translation.

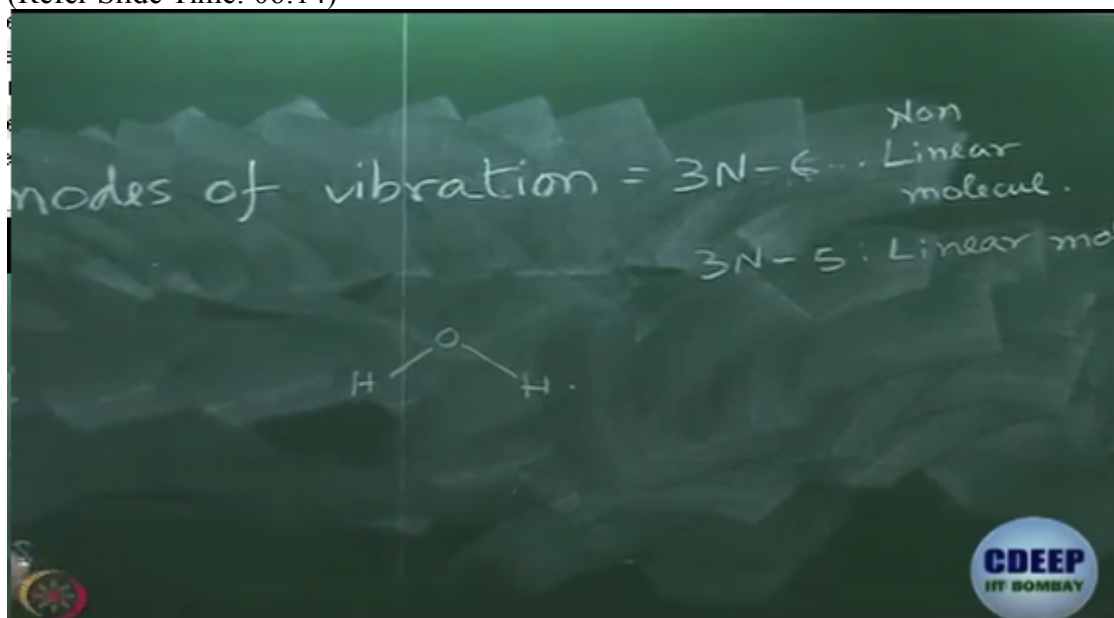
What is the meaning of translation? Change in, if you put in very simple terms, change in the position of center of mass of the molecule, if the center of mass moves than it is translation, so when we talk about vibration what we say is that the center of mass remains in place, if the center of mass moves then it is no longer pure vibration, it is vibration + translation, so in this normal modes of vibration center of mass does not move, it's very important to remember that, we've taken out 6 coordinates already.

Now so if that is the case you can understand that when we talk about vibration let us come to this hypothetical molecule, what is the meaning of vibration? Relative motion of the nucleus, of the nuclei, so let us say this, let us just only consider this bond, if you want to say that I have vibration only along this one and nowhere else, then what will happen? This atom will say move here, okay,
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but would that be a pure vibration? If only this atom moves and nothing else that would not be a pure vibration, isn't it? Because if only this atom moves that means the center of mass has moved, is that right or not? Center of mass would have moved, so to compensate for that other atoms also have to move in some way so that center of mass position is not changed, okay, it's perhaps a little easier to understand if you draw a more tangible molecule, water.

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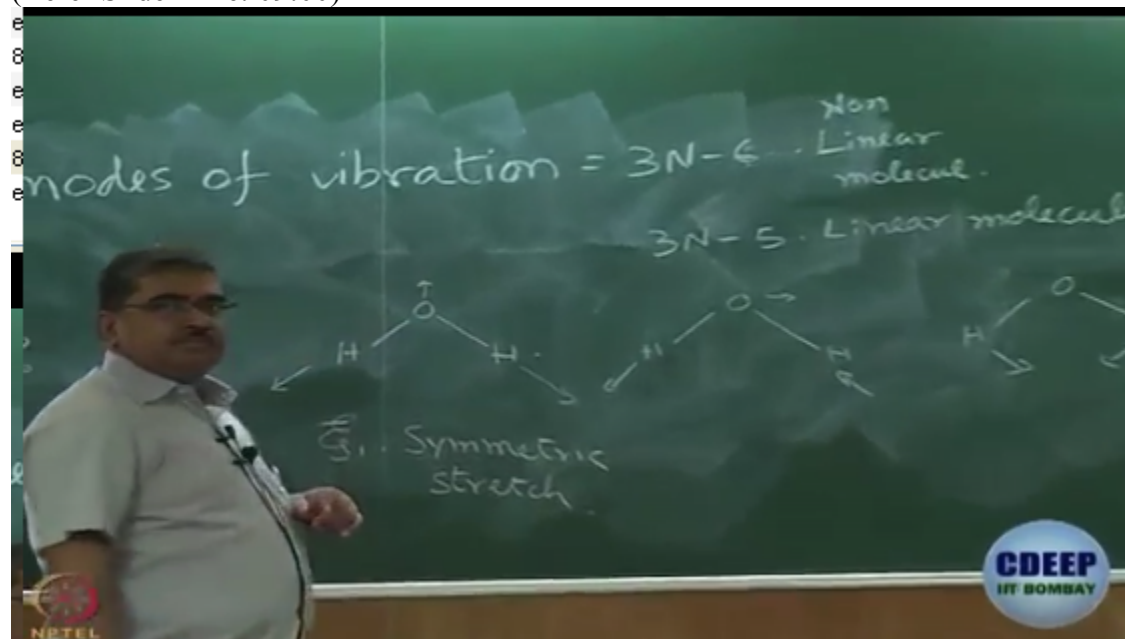
Let us consider that I have a vibration in which this OH bond is getting stretched, so you can understand that if this OH bond becomes stretch like this, center of mass would move, how can I compensate for this movement of center of mass? I can pull the other hydrogen atom out as well, so I can compensate for the stretch of this bond by stretching the other bond, let's see. So how can I compensate for that? And since oxygen is so much heavier than the hydrogen atoms oxygen has to move only little bit, okay, so if I draw the arrows like this, this is a valid pure vibrational

coordinate, okay, I could also do something else, this one stretches I can say that I'll move this hydrogen, I'll make the other wage more shorter, okay.

Now in which direction does oxygen have to move? Now what I am saying is that I'm trying to compensate for the vertical movement by moving hydrogen towards oxygen. So the horizontal movement has to be taken care off, in which direction does oxygen have to move? This or that? Yes, this is another kind of vibration it can have, or I can do something else. I can have this kind of motion, I think you guys already know this, I'm just repeating, but I'm repeating because this will help us go somewhere, this what kind of vibration is this? Bending, you can say scissoring, bending is more common.

So here you see what is the difference between the first and the second? In the first kind of vibration the 2H bonds stretch at the same time and get compressed at the same time, okay, so this is called symmetric stretch, will usually denote normal modes by the letters I, so this is the first normal mode symmetric stretch.

(Refer Slide Time: 09:00)



This is not very difficult to guess what this will be, here when 1 1 gets stretched the other bond gets compressed, so it's this kind of motion, what is it called? A symmetric stretch, xi 2 a symmetric stretch and this is the bend, so let's say this is xi. So between stretch and bend which one do you think has higher energy, which one has lower energy? Stretch has higher energy, bending requires a smaller energy, you go to a circus sometimes you find strong men who can bend an iron bar, have you ever seen a strong man who can stretch an iron bar? So that would require the strength to be much higher, right. So what we'll do is, we'll just show you unfortunately I've forgotten to include it here so we'll show you the character table of C2V.

And now let us convince ourselves that these normal modes also form bases for some symmetry species or the other before that, what is the meaning of normal modes once again? Modes that do not have components along each other, okay, which are independent of each other, how do I convince mass myself that these are actually normal modes. For water we can do it intuitively,

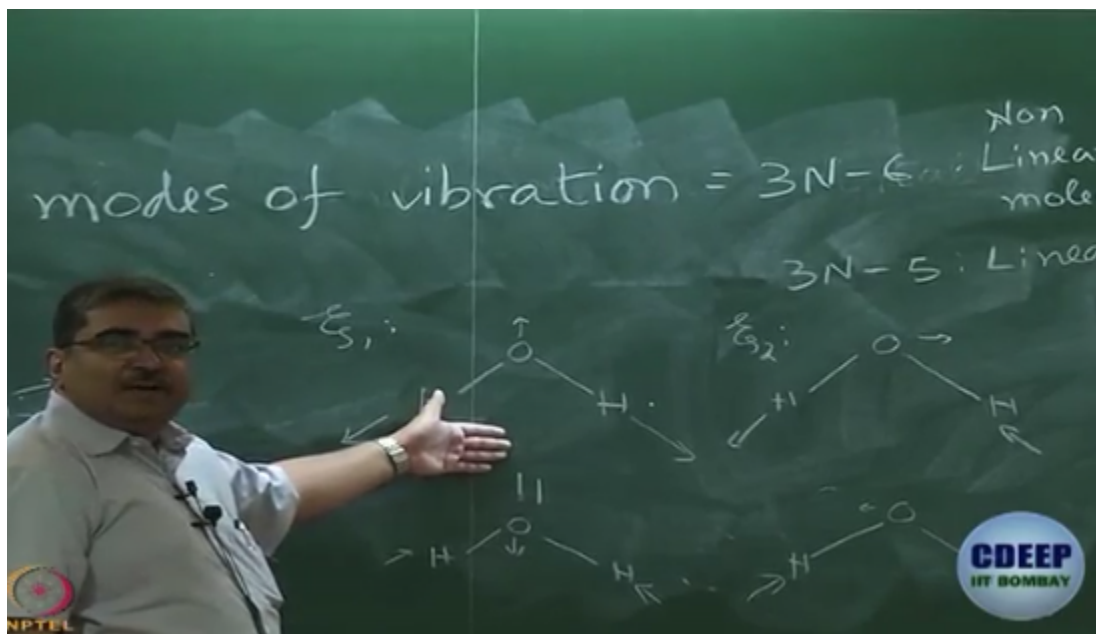
there is no way in which you can write this as a linear sum of this one and that one, okay, we'll do carbon-dioxide after this and then we will see what happens when things get a little more complicated, okay, but don't forget that these are modes that do not have components along each other.

Does this mean that water vibrates only in these three modes? Not necessarily, actual vibration can be a mixture of these three with different coefficients. Those of you who have taken dance lessons would know that first they teach you what to do with your feet, right, so initial lessons are just how to move your feet in a particular rhythm, okay. Next they teach you what to do with your hands. Finally in certain forms they teach you what to do with your head, and then when you actually do a dance what you essentially do is you do different linear combinations of movement of feet, movement of hand, movement of head, right, those are the normal modes of dance and you obtained different kinds of dance by just changing the coefficients in the linear combinations that you use. I've said this to a student who danced two successive years I said that you're only change the coefficient show is not amused, but then no matter whether you amused or not that's what it is, right, so this is the meaning so what we are trying to do is we are trying to work out the normal modes of molecular dance, that's all.

Now let's look at symmetric stretch, now if I call this ξ_1 we need to understand also what is $-\xi_1$? If this is ξ_1 , what is $-\xi_1$? $-\xi_1$ means all the movement has to be reversed so bonds get compressed, this oxygen moves a little down, if this is ξ_2 , you just reverse all the arrows that is all, so if this is plus this is minus, that's all, and the first one if this is plus this is minus, in case of bending if this is plus this is minus.

So let's look at ξ_1 , where does it belong? Apply E to ξ_1 , of course it remains the same, so what is the character for E? 1, what is the next symmetry operation? C2, apply C2 what happens? This hydrogen goes there, this hydrogen goes there, but we are talking about normal mode, so we need to worry about the arrows. Do the arrows go out or do they come in? They still go out, so is it ξ_1 or is it $-\xi_1$? It is still ξ_1 right, if it is $-\xi_1$ then the arrows would have gone in. Are we clear about this? If you understand C2 you understand everything, so character for C2 is also 1.

What is the next one? Sigma V, all atoms remain in their own place,
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all arrows remain in their own place, so character is 1.

What is the next one? Sigma V dash, the two hydrogen atoms interchange but arrow still go out they don't come in, okay, so it is +1, so what is the symmetry of this symmetric stretch? A1, right, so this is, we call this an A1 vibration.

What about bend? What about bend? Character for E is 1, what happens when you apply C2? This is bend, this is +bend, this is -bend, okay, when you apply C2 does sai 3 become -sai 3 or does it remain sai 3? It remains sai 3, are we clear? So character is 1.

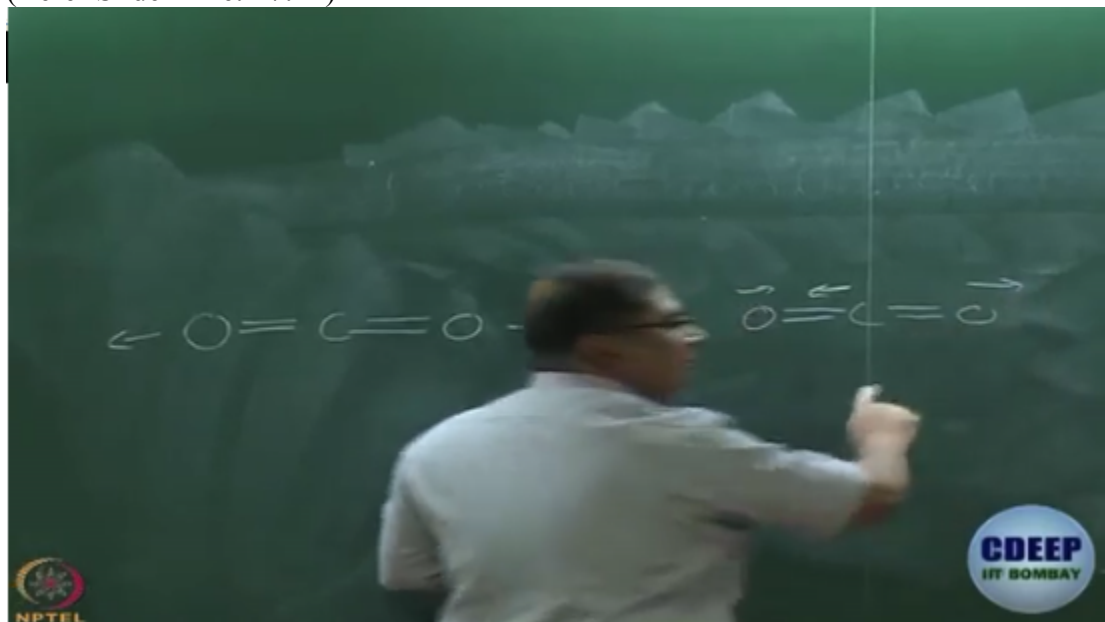
Sigma V, what is the character? 1, sure? Sigma V dash, this is plus, this is minus, this is plus, this is minus, I'm applying this mirror, is it 1 or is it -1? 1, sure 1, so this is also A1.

Let us talk about this, let's not forget what this is, this asymmetric state sai 2 is this, right this is plus this is minus, alright, see it's normal mode, this is also like a dance, alright.

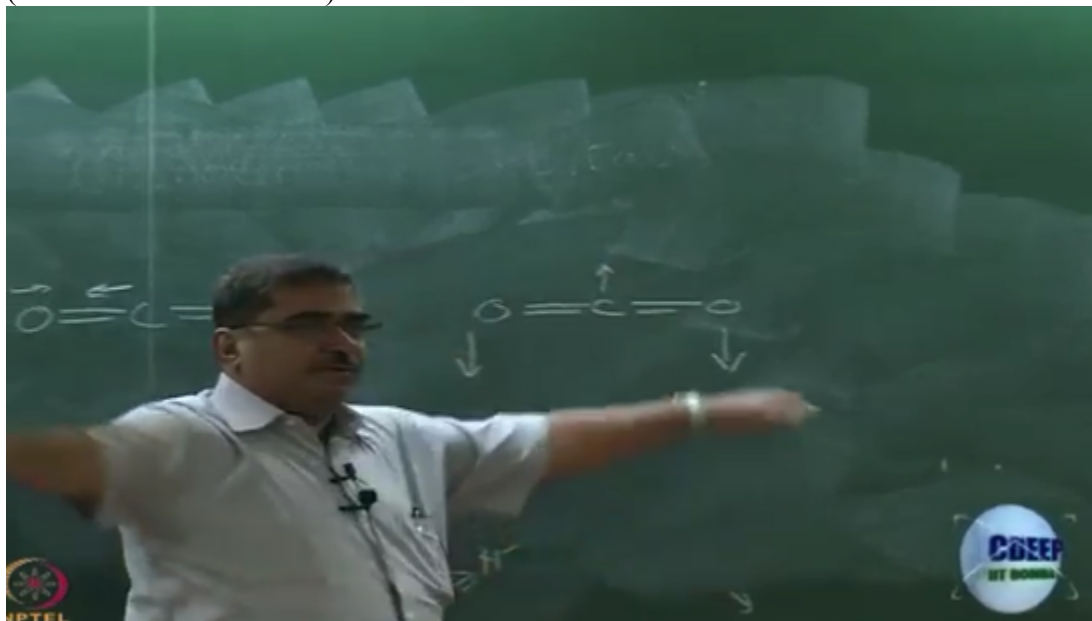
What is the character for E? 1, what is the character for C2? Plus, minus, yes, apply C2 what happens? This becomes this, isn't it? So -1, sigma V + 1 sigma V dash, -1 convinced? So 1 -1, 1 -1 which symmetry species is that? I don't even have to look at the character table, principal anti-symmetric with respect to the principal axis so it is not A it is B, symmetric with respect to that sigma V, so it is 1, so it is B1. So hereby what we've been able to do is, we have been able to perform a symmetric classification of the normal modes of water, okay.

How many atoms are there in water? Okay, let us think of another kind of triatomic molecule, carbon-dioxide, is carbon-dioxide linear or bend? Linear, how does it affect the vibration? Instead of 3 and -6 vibrations I should have 3 and -5 vibrations, so how many vibrations? 4 vibrations, what will it be? Like water there will be a symmetric stretch, and in this case carbon doesn't have to move, carbon is at the center it's a linear molecule, so the CO bonds stretch this

is plus, this is minus, you can have a symmetric stretch where this bond becomes smaller, this bond becomes larger
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without a change in the position of center of mass that's important to remember. And you can have bend, so I can draw bend like this in the plane of the board, these oxygen atoms go down, carbon go up, okay, linear this is bend.
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Where is the fourth vibration? So this is one kind of vibration, one kind of bend, you can have this kind of bend also, 90 degrees, can I not have this kind of a bend? Why am I not calling it a normal mode of vibration? Because I can easily write it as a linear combination of this and this, okay.

Another question, the moment this vibration happens doesn't the point group change from D infinity H to C2V? Actually in the approximation level at which we are working it doesn't, because don't forget we are talking about harmonic oscillation, harmonic oscillation means angular displacement is less than 4 degrees, I have harmonic vibration, so we can still work with the same character table, okay, where do this belong quickly? This one of course is totally symmetric right, what is totally symmetric for D infinity H? It is sigma G+, so this is called a sigma G+ vibration.

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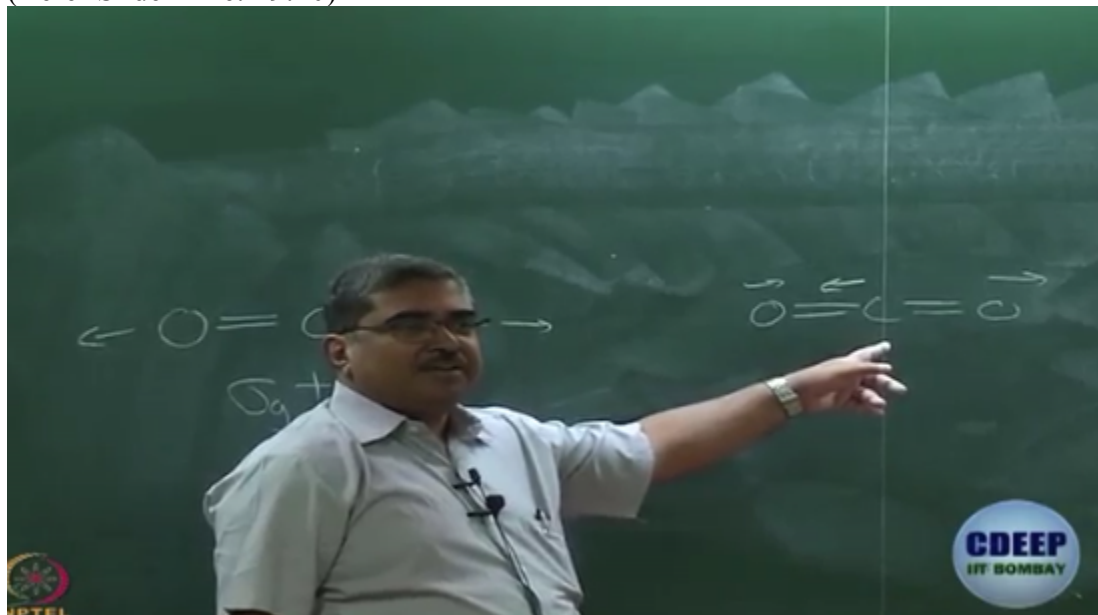
Homonuclear Diatomic Molecules: $D_{\infty h}$

	E	$2C_{\infty}$...	$\infty\sigma_v$	i	$2S_{\infty}$...	∞C_2	linear functions, rotations	quadratic
$A_{1g}=\Sigma_g^+$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma_g^-$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	$2\cos(\phi)$...	0	2	$-2\cos(\phi)$...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$	2	$2\cos(2\phi)$...	0	2	$2\cos(2\phi)$...	0		(x^2-y^2, xy)
$E_{3g}=\Phi_g$	2	$2\cos(3\phi)$...	0	2	$-2\cos(3\phi)$...	0		
...		
$A_{1u}=\Sigma_u^+$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u}=\Sigma_u^-$	1	1	...	-1	-1	-1	...	1		
$E_{1u}=\Pi_u$	2	$2\cos(\phi)$...	0	-2	$2\cos(\phi)$...	0	(x, y)	
$E_{2u}=\Delta_u$	2	$2\cos(2\phi)$...	0	-2	$-2\cos(2\phi)$...	0		
$E_{3u}=\Phi_u$	2	$2\cos(3\phi)$...	0	-2	$2\cos(3\phi)$...	0		
...		

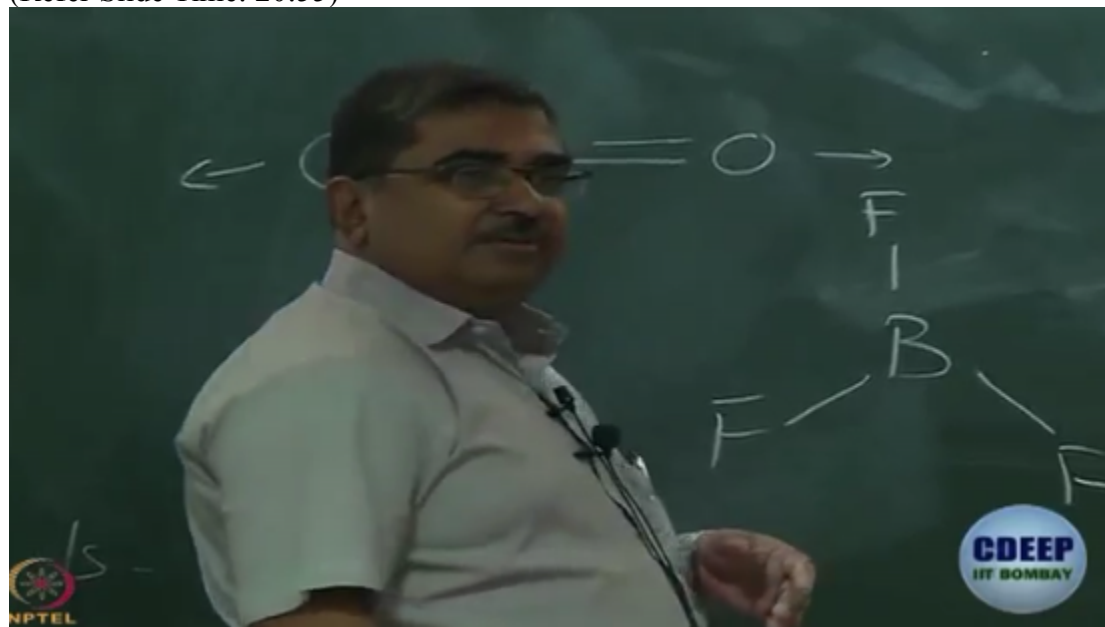
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What about this? What about this?

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This will be like Z actually, this will be like Z right because you can write it as an arrow isn't it, an arrow along the inter nuclear axis, inter nuclear axis is Z axis, so it will have the same symmetry as Z so that is going to be σ_u^+ , please work it out if you have a problem you ask me next day, this is called σ_u^+ vibration. What about these? These are 2 degenerated vibrations, okay, degenerated vibrations same energy and they are along X and Y, so they will have the same symmetry as X and Y, what is the symmetry of X and Y? π_u , so these are π_u vibrations. The reason why we are doing this is that as we'll see later by using symmetry we'll be able to say which of these normal modes are IR active which are not, which of these are normal modes or raman active which are not, but before we go there let me ask you, let me leave you with question, we could figure out the normal modes quite easily for triatomic molecules water and CO₂. The moment I add one more molecule, suppose I make it BF₃, planar molecule right, (Refer Slide Time: 20:55)



what is the point group? D_{3h}, D_{3h}, it doesn't remain so easy anymore.

What is the number of normal modes of vibration? 4 atoms are there so $3N - 6$? 6, right, will you be able to guess what these 6 vibrations looks like? Not so easy, so we need some way by which we can work out at least the symmetries of the normal modes of vibration by using character table, so next day Thursday what we'll do is we are going to work with BF₃ and we'll try and see how we can work out the normal modes of vibration without even knowing what they actually look like, right, and then we'll talk about IR and raman activity.

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