Symmetry and Group Theory
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Lecture -62
Symmetry of Normal Modes of Vibration

Welcome back in today is lecture we will be discussing visualizing molecular vibrations using internal coordinates, so let us start the lecture.

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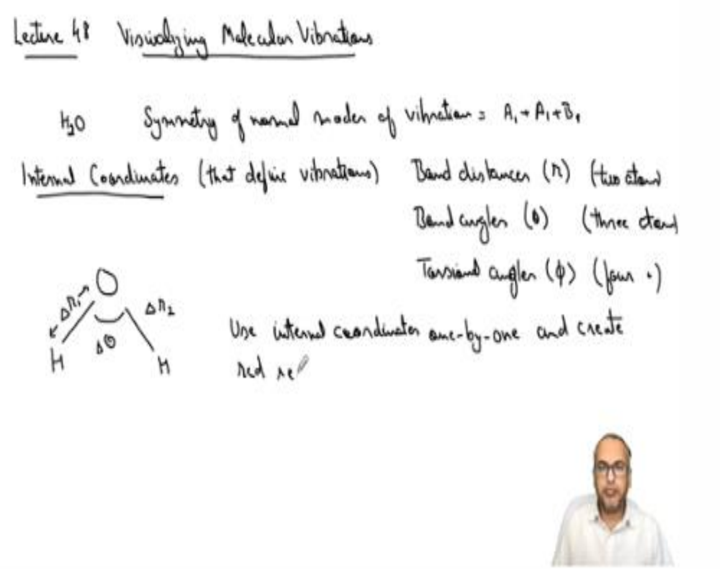

Lecture 48 Visualizing Molecular Vibrations

H_2O Symmetry of normal modes of vibration = $A_1 + A_1 + B_1$

Internal Coordinates (that define vibrations) Bond distances (r) (two atoms
Bond angles (θ) (three atoms
Torsional angles (φ) (four ·)

Use internal coordinates one-by-one and create
red re

So, what do you mean by Visualizing Molecular Vibration? So, for example, in case of water molecule in the last lecture we have seen that symmetry of normal modes of vibration, we saw that there are three vibrations modes present and the symmetry we could find out was A1 and A1 and B1. So there are two A1 modes and one B1 mode. But we do not know how does it look on the molecule.

So can we use our knowledge of symmetry and group theory to visualize these molecular vibrations, so yes, we can do that, if we use internal coordinates. So, what are internal coordinates? So, we have seen that if we use Cartesian coordinates on each atom, we can actually get to know the symmetry of normal modes. We can see the symmetry of translational rotational as well as vibrational modes but we cannot visualize them so if we use internal coordinates.

We can actually visualize these vibrational modes, so what are internal coordinates? So internal coordinates are that will define that defined vibrations. These are bond distances or even say change in bond distance also, are bond angles which is theta, and torsional angles. So torsional angles let us say these are phi. So, bond distance is to define bond distances you need two points or two atoms.

To define a bond angle, you need three atoms minimum and to define a torsional angle you need four atoms minimum. So that is the requirement so that means if you have a diatomic molecule you cannot have any bond angle or torsional angle you can only have bond distances. Similarly, if you have tri atomic molecule like water you cannot have torsional angle, you can only have bond distances and bond angles.

So let us take internal coordinates and see what do we get like how do we visualize molecular vibration. So let us start with drawing water molecule. So let us say if I have change in bond length as delta r1 over here and then this would be delta r2 and this will be my change in one angle delta theta. So now if I take the bond angles and bond distances as the basis and create a reducible representation let us see what do we get.

So, we will use internal coordinates one by one that is very important, you cannot take bond angle and bond length together and create a reducible representation that would not solve the problem, so one by one, and create reducible representation.

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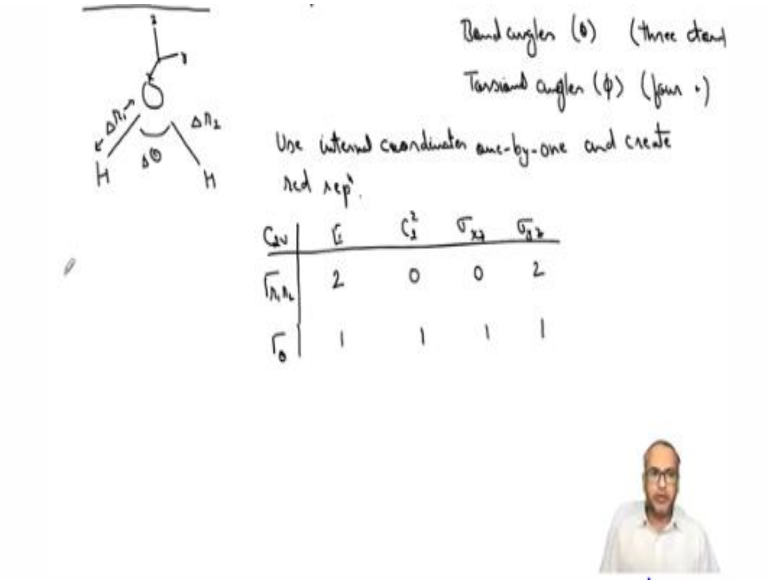

Bond angles (θ) (three [illegible]

Torsional angles (ϕ) (four ·)

Use internal coordinates one-by-one and create red rep^n.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
$\Gamma_{r_1r_2}$	2	0	0	2
Γ_θ	1	1	1	1

So, what we get, so we have C2v point group E, C2z, sigma xz, and sigma yz. Now if I have tau r1r2 this will be so these two bonds are now the basis so E will have 2, C2z will be 0. Because both the bonds are moving getting replaced with one another sigma x z, again the bonds are getting reflected so remember that this is my x y and z so my x z is perpendicular to the plane of the board.

So this is 0 sigma y z both the bonds stay at where they are, similarly we can create one for tau theta so reducible representation using delta theta as the basis, so this will be nothing will change for this angle this will be 1 1 1 1. So now this reducible representation can be broken into its component irreducible representations.

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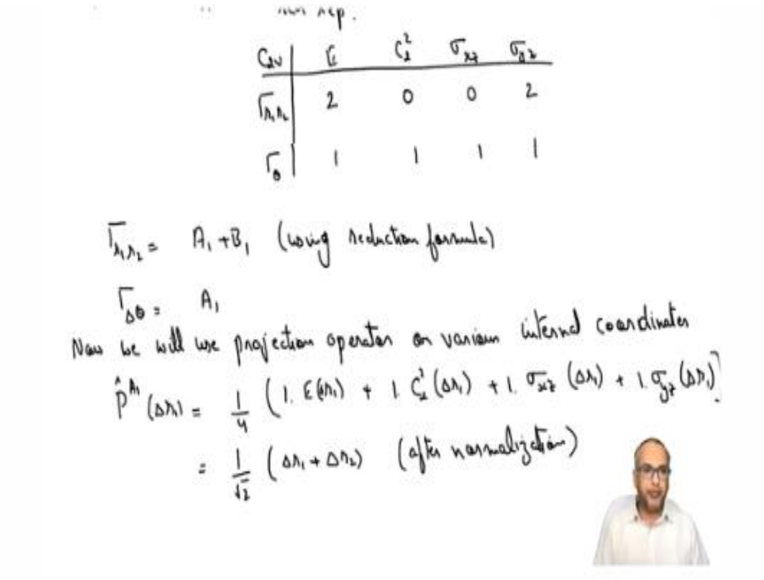

rep.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
$\Gamma_{r_1 r_2}$	2	0	0	2
Γ_θ	1	1	1	1

$\Gamma_{r_1 r_2} = A_1 + B_1$ (using reduction formula)

$\Gamma_{\Delta\theta} = A_1$

Now we will use projection operator on various internal coordinates

$$\hat{P}^{A_1}(\Delta r_1) = \frac{1}{4}\left(1.E(\Delta r_1) + 1.C_2^z(\Delta r_1) + 1.\sigma_{xz}(\Delta r_1) + 1.\sigma_{yz}(\Delta r_1)\right)$$

$$= \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2) \quad \text{(after normalization)}$$

Which will be so we can say r 1, r 2 is equal to A1 + B1 using reduction formula. So I am sure you all know how to do this. Now so we are not going to go to details of this. Similarly tau delta theta is equal to A1. That is very very clear from here itself, so by looking at the character table you know that this is the symmetry of totally symmetric representation, A1. So now what we do is now we will use projection operator on various internal coordinates.

So that means so we will do projection of A1 onto delta r1 so this will give me, I am sure you all know how to calculate this, so for A1 I will have 1 into E applied on r 1 or delta r 1 + 1 into C 2 z onto delta r 1, is 1 into sigma x z onto delta r 1 and this h comes from the, 4 comes from the h, 1 by h. So this gives me 1 by root 2 after normalization delta r 1 plus, delta r 2, this is after normalization.

See this is a 1d representation A 1, so you will get only one linear combination of the basis sets that will give you one normal mode.

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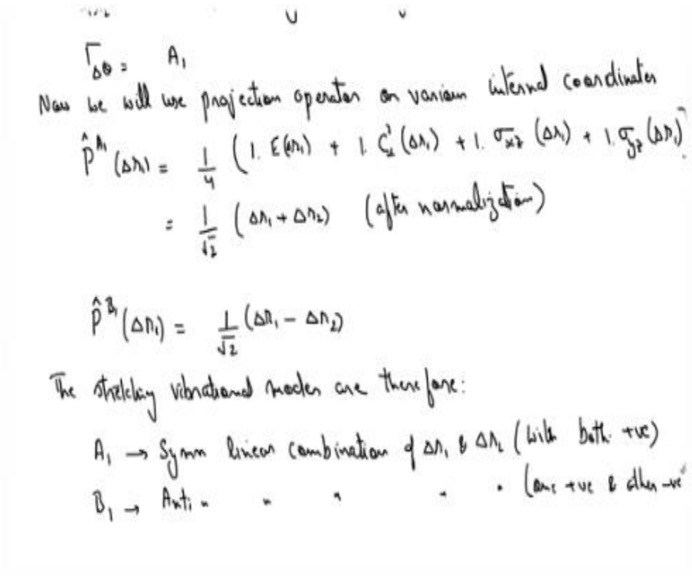

$\Gamma_{\Delta\theta} = A_1$

Now we will use projection operator on various internal coordinates

$$\hat{P}^{A_1}(\Delta r_1) = \frac{1}{4}\left(1.E(\Delta r_1) + 1.C_2^1(\Delta r_1) + 1.\sigma_{xz}(\Delta r_1) + 1.\sigma_{yz}(\Delta r_1)\right)$$

$$= \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2) \quad \text{(after normalization)}$$

$$\hat{P}^{B_1}(\Delta r_1) = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

The stretching vibrational modes are therefore:

$A_1 \rightarrow$ Symm linear combination of Δr_1 & Δr_2 (with both +ve)

$B_1 \rightarrow$ Anti " " " " (one +ve & other -ve)

Now similarly if I do on projection operator B1, which comes from again from the tau r1r2 and this is delta r1 what do I get, so I am not going to write the detailed calculation now I will get delta r 1 - delta r 2. So this linear combination is obtained when you apply the projection of B 1 symmetry onto delta r1. So let us also do it for so let us see so the stretching vibrational modes are therefore, the stretching, so A1 means it is a symmetric linear combination of delta r1 and delta r2. So, because both are positive, with both positive, we have delta r 1 positive and delta r 2 positive. Now what is B1, B1 is anti-symmetric linear combination of delta r 1, r 2 where one is positive and other is negative.

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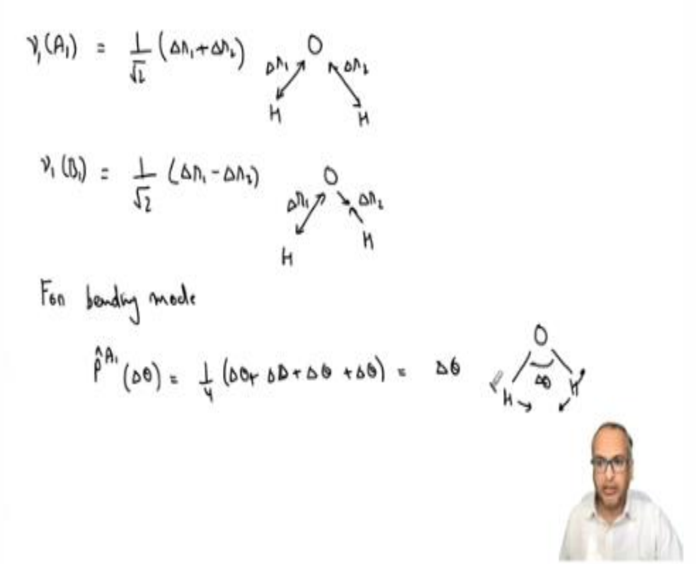

$$\nu_1(A_1) = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$$

$$\nu_1(B_1) = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

For bending mode

$$\hat{P}^{A_1}(\Delta\theta) = \frac{1}{4}(\Delta\theta + \Delta\theta + \Delta\theta + \Delta\theta) = \Delta\theta$$

So that means what I can write is, so I can say that my one of the vibrational modes mu1, mu1 is for the frequency. Which has A1 symmetry can be written as 1 over root 2 delta r 1 plus delta r 2. Now visually how does it look so if I try to draw it on water molecule I can say both the bonds are stretching. Because both of them are positive delta r 1 and delta r 2. Now similarly if I want to write the second stretching mode.

Then this will be mu 1, B 1, which will be equal to 1 over root 2, delta 1 minus delta r 2. And now I can say that one of the bonds is stretching and the other is compressing. This is my second vibrational mode. So similarly, we can find the we can visualize how it looks for bending modes. So let us do it for bending mode so if I apply projection with A1 symmetry onto delta theta we have only one basis vector in this case, delta theta.

So we will say what do we get is delta theta + delta theta + delta theta + delta theta, which gives you delta theta over all. So the only bending mode which is possible here is with the two protons will move like this, so there is a change in the angle like this increase or decrease. So that is the only bending mode which is possible. Now let us consider one more example;

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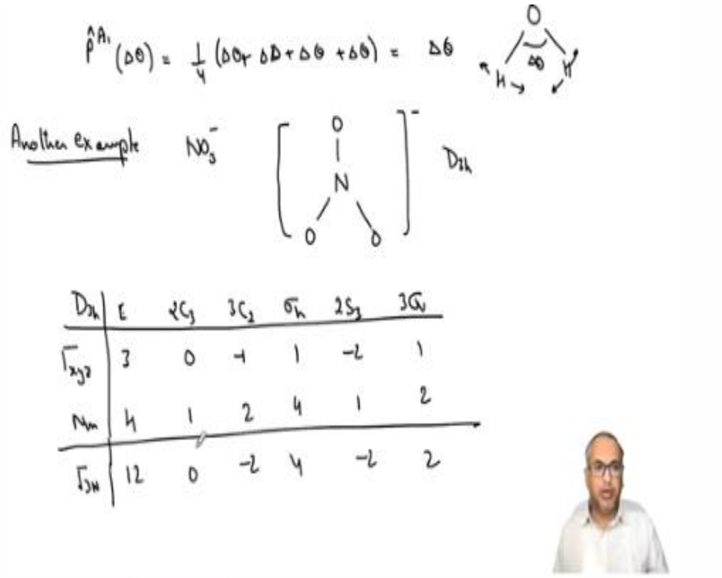

$$\hat{P}^{A_1}(\Delta\theta) = \frac{1}{4}(\Delta\theta + \Delta\theta + \Delta\theta + \Delta\theta) = \Delta\theta$$

Another example NO_3^- D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{xyz}	3	0	-1	1	-2	1
N_{um}	4	1	2	4	1	2
Γ_{3N}	12	0	-2	4	-2	2

So that the procedure is clear and then let us go to a little complex example then this. So another example, let us now consider NO3 Ion. So then NO3 ion looks like we have N over all negative charge onto this, the point loop is D3h here. So now let us start with finding the symmetry of vibration modes, so D3h you have E, 2C 3, 3C2, sigma h, and then 2S 3 and 3 sigma v. Now for this we get from x y z, so tau xyz, which is the summation of all IR representation x, y, and z is the basis.

So this we will get directly from character tables 3 0 minus 1, 1 - 2 1 and then number of unshifted atoms. So, this will be 4 here C3 will be 1 central atom will be unshifted C2 2 atoms will remain on shifted sigma h is also 4 will be unshifted, S3 1 atom will be in shifted and then sigma v, 2 atoms will be unshifted. So that gives me tau 3N, multiply these two so I will get 12, 0, - 2, 4, - 2, 2.

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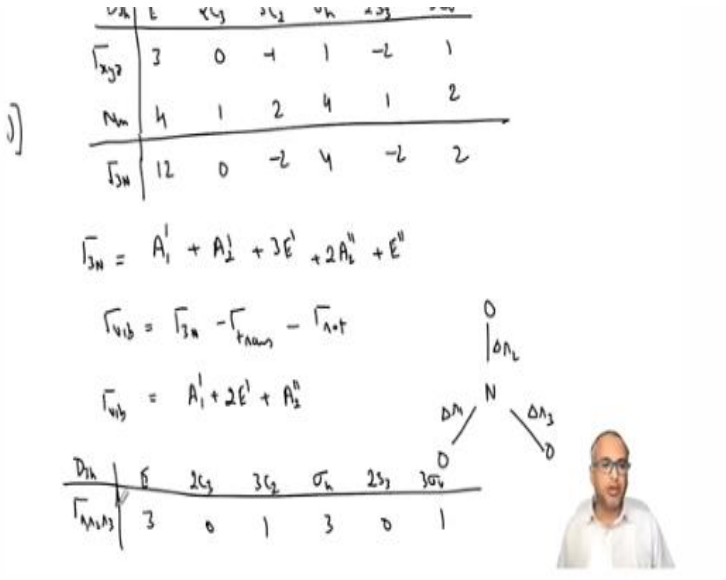

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{xyz}	3	0	-1	1	-2	1
N_{un}	4	1	2	4	1	2
Γ_{3N}	12	0	-2	4	-2	2

$$\Gamma_{3N} = A_1' + A_2' + 3E' + 2A_2'' + E''$$

$$\Gamma_{vib} = \Gamma_{3N} - \Gamma_{trans} - \Gamma_{rot}$$

$$\Gamma_{vib} = A_1' + 2E' + A_2''$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\Delta r_1 \Delta r_2 \Delta r_3}$	3	0	1	3	0	1

Now upon reduction of this tau 3N, can be broken into the component IRs using reduction formulas. So this will be A1 prime + A2 prime + 3 E prime + 2A2 double prime + E double prime. Now from here I can calculate tau vibrational which will be tau 3N - tau translational which will be all x, y, z and tau rotational all Rx, Ry, Rz. Now rotation so this gives, leaves A1 prime + 2 E prime + A 2 double prime.

So this is the procedure to obtain symmetry of all the normal modes of vibration. Now what we have to do is you have to use internal coordinates to find out, to help visualize this. So let us start with the change in bond length. So we have N O O O. So we have delta r 1, delta r 2, delta r 3. So if I create under D3h, tau r 1, r 2, r 3 and this will be the D3h. So, I will see that I will get a representation like 3, 0, 1, 3, 0, 1. And now I can reduce this to get the component IRs component irreducible representations.

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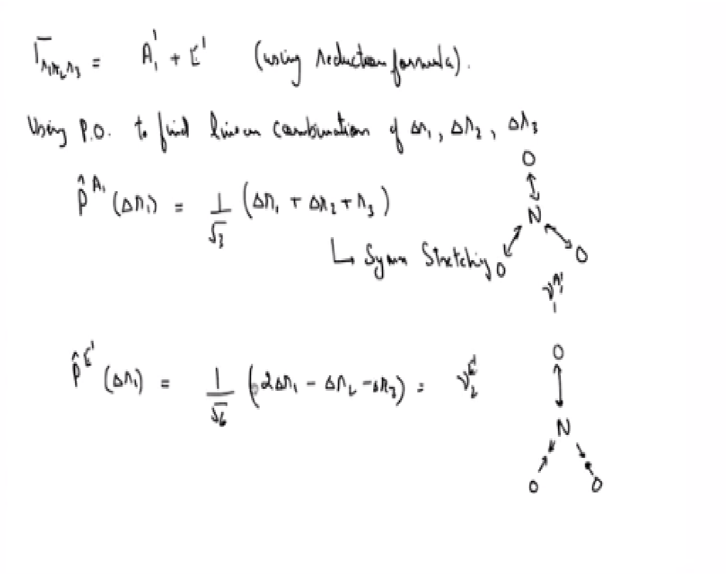

$\Gamma_{\Delta r_1 \Delta r_2 \Delta r_3} = A_1' + E'$ (using reduction formula).

Using P.O. to find linear combination of $\Delta r_1, \Delta r_2, \Delta r_3$

$$\hat{P}^{A_1'}(\Delta r_1) = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + r_3)$$

↳ Sym Stretching

$\nu_1^{A_1'}$

$$\hat{P}^{E'}(\Delta r_1) = \frac{1}{\sqrt{6}}(2\Delta r_1 - \Delta r_2 - \Delta r_3) = \nu_2^{E'}$$

So if I do that tau r1, r2, r3 is broken up into A1 prime + E prime, using reduction formula. Now we will use projection operator of this symmetry onto one of the basis sets. One of the functions in the basis set. Using projection operator to find linear combinations of delta r1, delta r2, delta r3. So first one is very simple if we do totally symmetric representation projection operator what you will get is for normalization.

So again, I am not going to go into details of how to apply projection operator that should be fairly simple by now, delta r 1 + delta r 2 + delta r 3. So that means all the bonds are increasing in length, this will be called as symmetric stretching. And you can draw it like that all the bonds are increasing in length symmetrically, this is can call it as nu1, with A1 symmetry, A1 prime symmetry, so this is nu1.

So this is nu1. so now similarly for other stretching vibrations E prime delta r 1 this if you do so you will get 1 over root 6, 2 times delta r 1, minus delta r 2 minus delta r 3. So this can be called as nu2 second mode stretching mode with E prime symmetry. And now you can draw it as one of the bonds is increasing in length and the other two bonds are compressing. So these are getting shortened this is getting increased so this will be second mode.

Now you should get two linear combinations here which are orthogonal to each other we have already got one so how do you get the second one? To get the second one, again it is not trivial and you need to use hit and trial.

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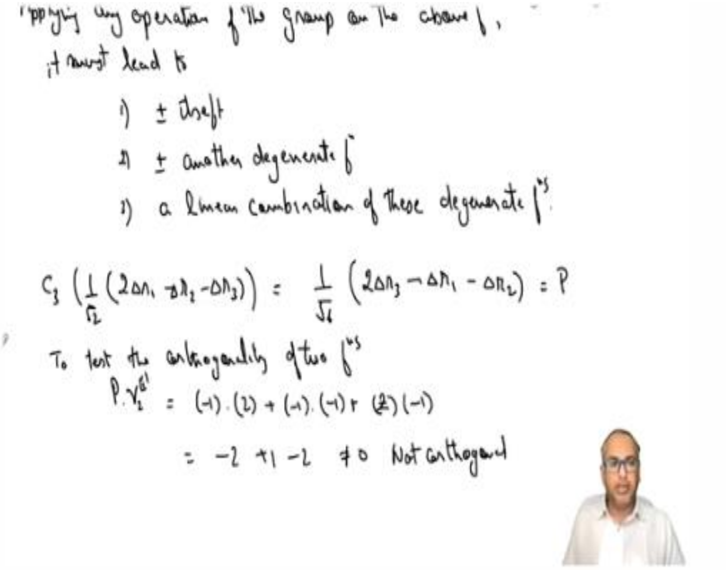

'pplying any operation of the group on the above f^n,
it must lead to
1) ± itself
2) ± another degenerate f^n
3) a linear combination of these degenerate f^{ns}.

$$C_3\left(\frac{1}{\sqrt{2}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)\right) = \frac{1}{\sqrt{6}}(2\Delta r_3 - \Delta r_1 - \Delta r_2) = P$$

To test the orthogonality of two f^{ns}

$$P.\nu_2^{E'} = (-1).(2) + (-1).(-1) + (2)(-1)$$

$$= -2 + 1 - 2 \neq 0 \text{ Not orthogonal}$$

So one of the methods is to apply so there are if you remember there are three rules, so if we apply any operation applying any operation, symmetry operation of the group, on the above function it must lead to, there are three options; plus or minus, of itself, you will get the function back with plus or minus sign, the second will be plus or minus, another, you may get lucky and you will get a degenerate function.

The second function which you are looking for, or third is a linear combination of these degenerate functions. So let us do it let us try to do a symmetry operation onto this function and see what we get. So let us see let us pick up C3 out of D3h point group, and apply it on this particular function. 2 delta r1 - delta r2 - delta r3. So, if you apply this what you will get is 2 delta r3, r1 goes to r 3, r2 goes to r1, delta r1, delta r2 and let us call it as function P.

Now we have to test whether P and nu2 which we got earlier are these orthogonal. So to test the orthogonality of two functions. Whether they are degenerate or non, will get to know if they are orthogonal or not, so let us do that now, how do you do that, so we will have to multiply the coefficients of different functions in thism different basis vectors so delta r 1 coefficients multiplies with the delta r 1 coefficient here and delta r 2, delta r 2, delta r 3, delta r 3.

And then take summation over all, and see if you are getting 0 or not. Som for delta r 1, I have minus 1, you have and 2 here + minus 1 here and minus 1 here + 2 here and minus 1 here. So, this becomes minus 2 + 1 minus 2 so this is not equal to 0, so it is not orthogonal.

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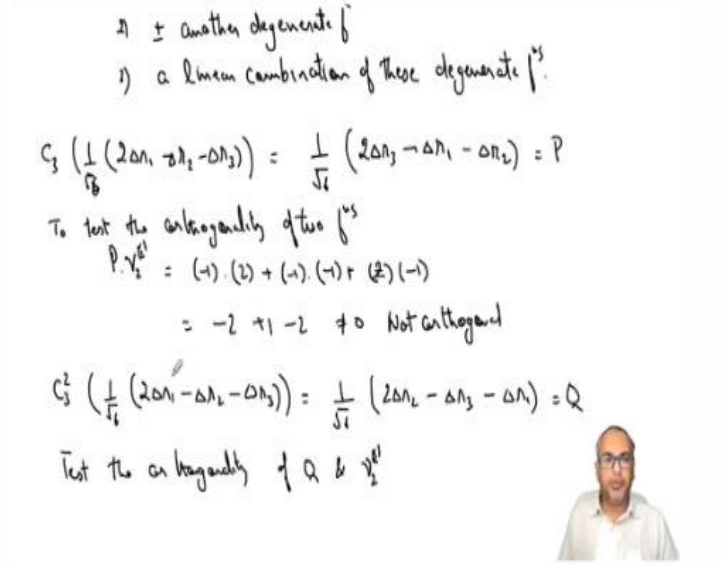

i) ± another degenerate f^{n}

ii) a linear combination of these degenerate f^{ns}.

$$C_3\left(\frac{1}{\sqrt{6}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)\right) = \frac{1}{\sqrt{6}}(2\Delta r_3 - \Delta r_1 - \Delta r_2) = P$$

To test the orthogonality of two f^{ns}

$$P.\nu_2^{E'} = (-1).(2) + (-1).(-1) + (2)(-1)$$

$$= -2 + 1 - 2 \neq 0 \quad \text{Not orthogonal}$$

$$C_3^2\left(\frac{1}{\sqrt{6}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)\right) = \frac{1}{\sqrt{6}}(2\Delta r_2 - \Delta r_3 - \Delta r_1) = Q$$

Test the orthogonality of Q & $\nu_2^{E'}$

I am just giving you another way of finding these orthogonal functions, in case of degenerate IR representation, so let us now do a C3 square operation onto the same. This was 6, 1 over root 6 on to 2 delta r 1 minus delta r 2 minus delta r 3. Now what do I get here. I will get 2 delta r 2 - delta r 3 - delta r 1, let us call this Q. Again, let us test the orthogonality, whether we are getting any orthogonal function or not, of Q and nu2 E prime.

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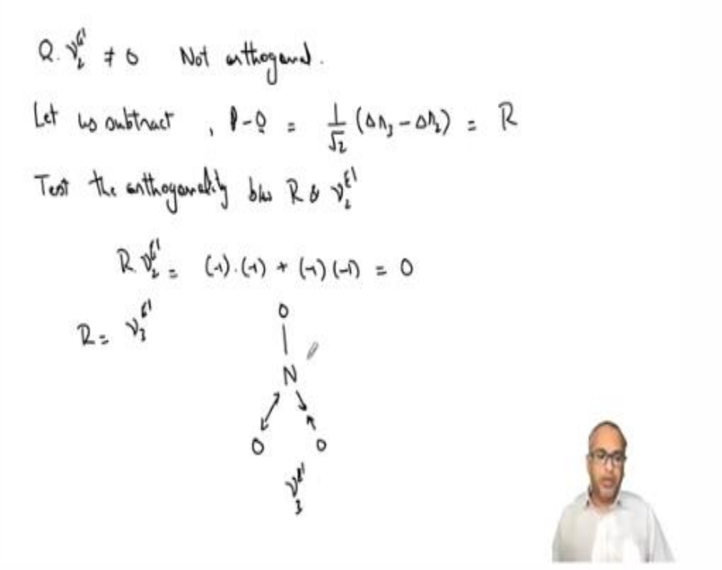

$Q.\nu_2^{E'} \neq 0$ Not orthogonal.

Let us subtract, $P - Q = \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r_2) = R$

Test the orthogonality b/w R & $\nu_2^{E'}$

$R.\nu_2^{E'} = (-1).(-1) + (1)(-1) = 0$

$R = \nu_3^{E'}$

So what do we get here. So we will see that Q dot nu2 E prime is not equal to 0, so again this will be not orthogonal. So now what do I do? So let us do a hit and trial, let us subtract P - Q and what do we get here, we will get after normalization 1 over root 2, delta r 3 - delta r 2. Now let us call it as R, so now let us test the orthogonality between R and nu2 E prime. So that will give you R nu2 E prime this will give you delta 2, delta r 2 has minus 1 here;

And it had minus 1 there plus 1 into minus 1and this goes to 0. So that means R can be treated as nu3, so that means R is equal to nu3, so the third vibrational mode which we are looking for. This means that you can say that my N, one of the bond is not changing another bond is increasing and other bond is compressing. So, this is my and this has symmetry as E prime this is my third stretching vibration mode.

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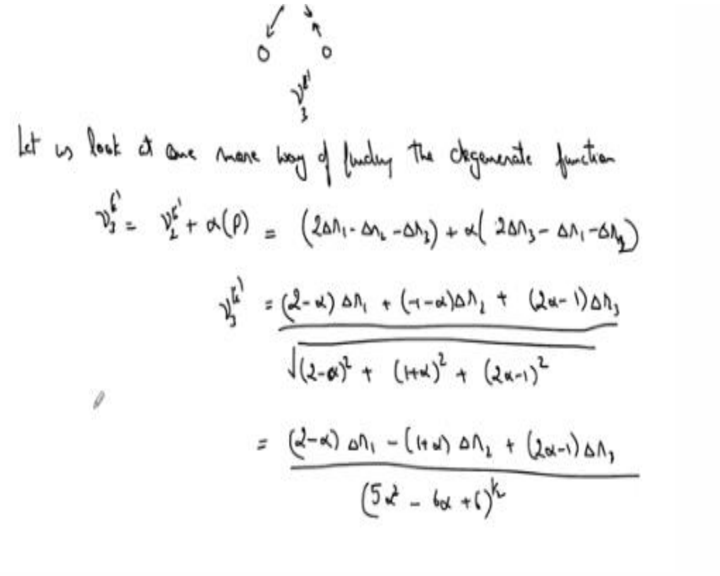

$\nu_3^{E'}$

Let us look at one more way of finding the degenerate function

$$\nu_3^{E'} = \nu_2^{E'} + \alpha(P) = (2\Delta r_1 - \Delta r_2 - \Delta r_3) + \alpha(2\Delta r_3 - \Delta r_1 - \Delta r_2)$$

$$\nu_3^{E'} = \frac{(2-\alpha)\Delta r_1 + (-1-\alpha)\Delta r_2 + (2\alpha-1)\Delta r_3}{\sqrt{(2-\alpha)^2 + (1+\alpha)^2 + (2\alpha-1)^2}}$$

$$= \frac{(2-\alpha)\Delta r_1 - (1+\alpha)\Delta r_2 + (2\alpha-1)\Delta r_3}{(5\alpha^2 - 6\alpha + 6)^{1/2}}$$

So but this is a cumbersome method to find out, as we have discussed earlier there is no definite way of finding one. So let us try to do it in a different way, let us look at one more way of finding the degenerate function. So now let us consider that upon so let us say nu3 E prime, can be written as linear combination of nu2 E prime and some alpha times P which we have obtained earlier.

Then we applied C3 onto this we obtained linear combination which was termed as P, so now if you consider this, then it is possible like that the 2 can be a linear combination. This can be a linear combination of any linear combination and we can find out alpha. So let us do that delta r 1 - delta r 2 - delta r 3 + alpha times 2 delta r 3 - delta r 1 - delta r 2. Now this gives me 2 - alpha let us now separate the variables.

So 2 minus alpha, delta r 1 + minus 1 - alpha delta r 2 + 2 alpha - 1 delta r 3, now this is my mu 3 E prime. And the normalization coefficient can be written as because these were not normalized so we need to normalize it so the square root of sum of squares of the individual coefficients. So we can write 2 - alpha square + 1 + alpha square + 2 alpha - 1 square. Now if we can simplify this what do we get 2 minus alpha delta r 1 - 1 plus alpha delta 2 + 2 alpha minus 1 delta 3, divided by 5 alpha square - 6 alpha + 6 square root there is only one variable here.

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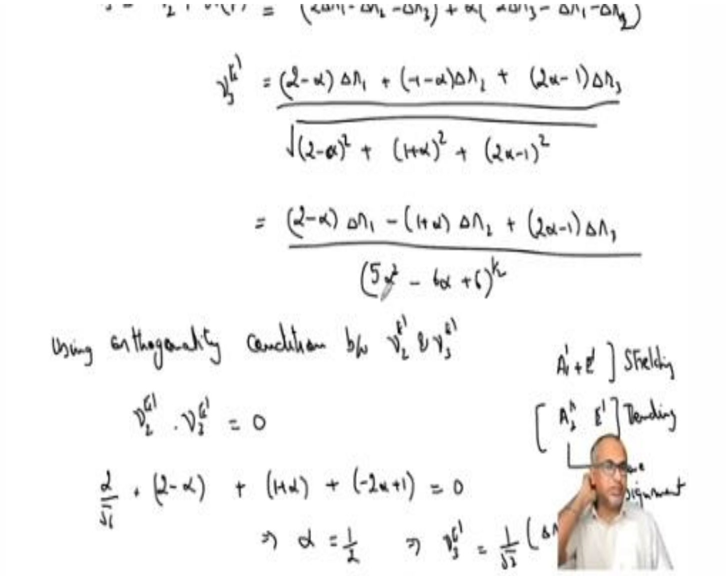

$= (2\Delta r_1 - \Delta r_2 - \Delta r_3) + \alpha(2\Delta r_3 - \Delta r_1 - \Delta r_2)$

$$\nu_3^{E'} = \frac{(2-\alpha)\Delta r_1 + (-1-\alpha)\Delta r_2 + (2\alpha-1)\Delta r_3}{\sqrt{(2-\alpha)^2 + (1+\alpha)^2 + (2\alpha-1)^2}}$$

$$= \frac{(2-\alpha)\Delta r_1 - (1+\alpha)\Delta r_2 + (2\alpha-1)\Delta r_3}{(5\alpha^2 - 6\alpha + 6)^{1/2}}$$

Using orthogonality condition b/w $\nu_2^{E'}$ & $\nu_3^{E'}$

$\nu_2^{E'} \cdot \nu_3^{E'} = 0$

$\frac{2}{\sqrt{6}} \cdot (2-\alpha) + (1+\alpha) + (-2\alpha+1) = 0$

$\Rightarrow \alpha = \frac{1}{2} \Rightarrow \nu_3^{E'} = \frac{1}{\sqrt{2}}($

$A_1' + E'$] Stretching

[A_2'' E'] Bending

signment

So now and I know that using orthogonality condition between nu2 and nu3, so both are E prime symmetry. So nu2 E prime dot nu3 E prime, should be equal to 0. So now I can equate the coefficients multiply the coefficients and equate it to 0 and what do I get? So, I will get 2 by root 6 into 2 minus alpha, so actually this normalization is not required so we can directly put it to because this will be a common factor in all 3, so this will go to 0 any ways;

So it is not required to put it here plus 1 + alpha plus minus 2 alpha plus 1 equal to 0, and this gives me alpha is equal to half. So now substituting this value of alpha in here, I will get a normalized nu3 which is nothing but nu3 E prime, just nothing but 1 by root 2, delta r1 minus delta r2. So I am getting different form here but r 1, r 2, r 3 are interchangeable. So it does not really matter whether I am getting r 2 - r 3, r 3 - r 2 or r 1 - r 3.

So the point is that one of the bonds is increasing in bond length, and another bond is decreasing in bond length. So that finishes up stretching mode, visualizing stretching mode, now the next part here is the bending mode. So, in case of a planar molecule like this there is also a possibility of out of plane bending and in-plane bending. So, I will leave up to you that what kind of internal coordinates would you choose to devise a tau reducible, which can define the in-plane bending as well as out of plane bending.

So you already know that you have already covered out of tau vibrational modes, A1 prime and

E1 prime. So you have defined it for this. Now what you are left with is A2 double prime and another E prime. So this is stretching that we have already seen now this portion is left for bending. bending modes. Now bending modes, I leave it as home assignment so try to do it for yourself, otherwise we will discuss in the interaction session.

So, this finishes up. I am deliberately leaving it for you to do it so that you get some idea of what angles to be chosen as internal coordinates and what angles will define the bending mode there is a possibility of in-plane bending and out of plane bending and all. So, this finishes up visualization of the vibrational modes and we have seen that how group theory is helpful in doing that and the last lecture now is on spectral transition probabilities that will be coming up later that is all.