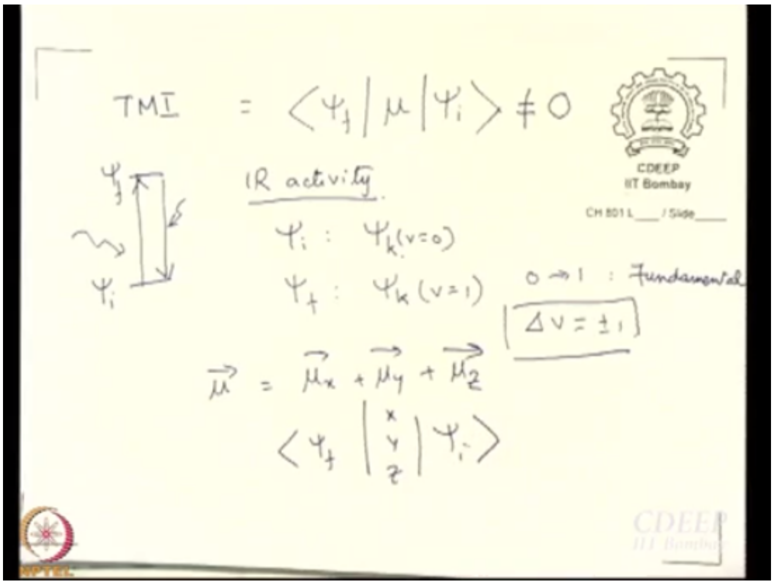
Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture - 41
IR and Raman Activity

Change in dipole moment yes, but do you all know about transition moment integral? Transition moment integral is just this.

(Refer Slide Time: 00:35)



$$\mathrm{TMI} = \langle \psi_f | \mu | \psi_i \rangle \neq 0$$

IR activity

$\psi_i : \psi_k(v=0)$

$\psi_f : \psi_k(v=1)$

$0 \rightarrow 1$: Fundamental

$\boxed{\Delta v = \pm 1}$

$$\vec{\mu} = \vec{\mu}_x + \vec{\mu}_y + \vec{\mu}_z$$

$$\left\langle \psi_f \middle| \begin{matrix} x \\ y \\ z \end{matrix} \middle| \psi_i \right\rangle$$

Are we familiar with this notation? So what does this mean? So what is (()) (00:52) and suppose I write only this, what does this mean? psi of star, integral? Is there an integral? When you write (()) (01:10) together then only the integral comes. How you will write integral without dx. So this just means the complex conjugate. When you write them together of course this line is only to ensure that it is nice symmetry looking thing. The second line is not even required, one line would have been enough.

Okay, this is just to make it symmetry, nature love symmetry, we are natural creatures, we also love symmetry, okay. So this is called transition moment integral and those who have not studied this spectroscopy course when you study it you learn that for any transition to take place this transition moment integral must be nonzero. If a transition is to take place suppose you have 2 levels okay.

This is level i, this is level f, psi i and psi f. Now some light comes and causes a transition from psi i to psi f, just because you have the levels it is not necessary that the transitions will take place, okay. So what you are going to do if you have not done it already in some course is called a semi empirical treatment of interaction of radiation with matter. There you are going to use time dependent perturbation theory.

You are going to model light as a wave and you are going to model the molecule as a 2 level system to start with and then using time dependent pertubation theory you are going to see that this is the all-important quantity alright. You learn that this transition or this transition for that matter induced by light can only take place when integral psi f star mu psi i d tau is nonzero, okay, if you have not studied it let us take this axiomatically until you study it in some other course.

Most of the people have studied this somewhere right, whoever is M. Sc., here studied it I hope. If you have not studied it just believe me for now that this is the essential condition for IR activity. How does a microwave oven work? It heats up the water molecule right. Any food that you eat unless you are a stone eater or something, any food that you eat contains a lot of water alright.

So what happens is this entire food item behaves like an oven, all the water molecule inside start rotating, but they cannot rotate for ever, so they have to give up the excess energy that they have acquired and there is some mechanism called dielectric friction by which this rotation energy gets converted to heat energy that is why food heats up very fast. Okay it is the water inside.

The problem is, what is the formula of oil? Chemical formula? I also do not know what it is, all I know is that it is nonpolar, right. I do not know what is the formula of the oil that we eat, it must be a mixture of so many things, but then it is nonpolar that is for sure. Oil is not polar. So if you keep a bowl of oil inside the microwave oven even for 15 years and keep the oven on it is not going to heat up, okay.

Why because these oil molecules are not microwave active, okay. So that it the condition for microwave activity. For vibrational transitions what will happen, you consider this kind of a transition. If it is a dipolar molecule, then dipole moment is going to change right. So you should consider the dipole moment to be mu 0, dipole moment at mean position + x * delta mu del x okay. So that goes into the transition moment integral.

Right now for the simplicity we will just write mu and be happy about it. Now so for IR activity what is the essential condition let us see. What is psi i, psi i will be psi v = 0 right, and what I will do is I will use a subscript K also because any poly atomic molecule is going to have 3n -6 number of normal modes of vibration. Let us say this is the Kth normal mode. The ground state has to be the v = 0 state agreed.

I think we all have studied quantum harmonic oscillator. We know that v = 0 is the only vibrational level that is populated at room temperature okay. So that has to be the initial state and most generally this also if you have not studied molecular spectroscopy learn it that course, psi f is generally psi k v = 1. This 0 to 1 transition is called a fundamental transition. Alright and for a simple harmonic oscillator the selection rule that is there is delta v = +/-1.

How do you derive this selection rule, that also you can derive from here actually but that is the story for another course, we will not go into that now, it is not very difficult to derive it, okay? So what we want to do is we want to replace psi k v = 0 here, we want to replace psi k v = 1 here and mu, mu is, what is mu, mu is you can write mu x + mu y + mu z vector sum, right. Mu can have 3 components x, y and z.

So essentially what we need to see is whether this psi f, x y z, psi i is this nonzero or not and that is something that we can do. Basically I have written 3 integrals here right, psi f, x, psi i; psi f, y psi i; psi f z psi i and we are going to see by symmetry when these are going to be, this integral is going to be nonzero and when it is going to be 0, alright. What is the condition for an integral to be nonzero?

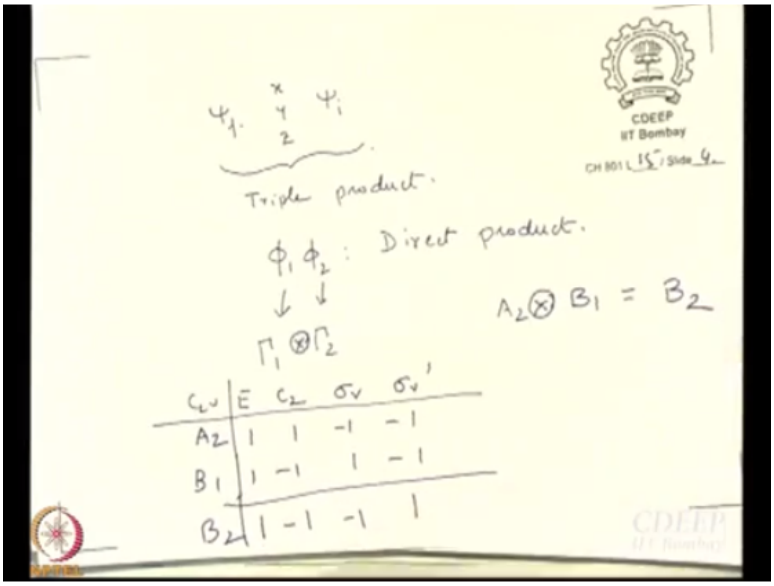
Now think in terms of symmetry, what I am saying is instead of writing mu, I can write x or y or z, mu x or mu y or mu z and these are just aligned towards x y and z right. So whatever symmetry property x and y and z will have. Mu x, mu y, mu z will have the same property. So I have to consider 3 integrals one is psi f, x, psi i; second is psi f, y, psi i; third is psi f, z, psi i. Not only do I have to keep my pen that way, his head also has to be in a particular way, otherwise it is eclipsing.

So any of these 3 integrals if you find then it is nonzero then the transition will be allowed alright, okay. Now you tell me, this is an integral right, what is the condition that an integrant has to satisfy so that the integral is nonzero from the point of view of symmetry. So if I put it in a very general term, can I say that this integrant has to remain invariant under any symmetry operation for the integral to the nonzero, apparently will give you the same thing provided you are working only with your one dimensional representations it becomes +/-.

See if the integrant changes okay, suppose there is a transition in a molecule going on. You apply a symmetry operation; you get back a molecule in equivalent configuration right indistinguishable configuration. Is there any reason why a transition that was taking place earlier should not take place now? Is there any reason? if I perform a symmetry operation, now if I perform a distortion which is not a symmetry operation then something that was not taking place earlier might take place now.

But if I perform a symmetry operation then this integral should remain nonzero right. So the integrant should remain unchanged upon symmetry operation alright, so I should work only with the integrant to start with.

(Refer Slide Time: 10:55)



CDEEP
IIT Bombay
CH 801 L 15 / Slide 4

$$\underbrace{\psi_f \quad \begin{matrix} x \\ y \\ z \end{matrix} \quad \psi_i}_{\text{Triple product.}}$$

$$\begin{matrix} \phi_1 & \phi_2 \\ \downarrow & \downarrow \\ \Gamma_1 & \otimes \Gamma_2 \end{matrix} \quad : \text{Direct product.}$$

$$A_2 \otimes B_1 = B_2$$

C_{2v}	E	C_2	σ_v	σ_v'
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Psi f then x or y or z, I am writing this in short do not get confused x or y or z, psi i, what I am saying is that this must contain apart that is totally symmetric. Totally symmetric means does not change when any symmetry operation is applied, okay. So this thing is called a triple product. When you multiply 3 functions together it is called a triple product. When you multiply 2 functions together some phi 1 phi 2 this is called a direct product.

A triple product is just an extended direct product, nothing to be scared off. Right so first you take this direct product you get some function, then you take a direct product of that function and this one that is all. So the question that we want to ask is when does this triple product contain a totally symmetric representation. When does a triple product contain at least a part that is totally symmetric.

Forget about (()) (12:18) now we have a better answer now. So what we really want to do then is that we want to know when does a direct product contain the totally symmetric representation, okay, see this belongs to some symmetry species gamma 1, this belong to some other symmetry species say gamma 2. If you take a direct product, this is written a direct product okay, convolution sign.

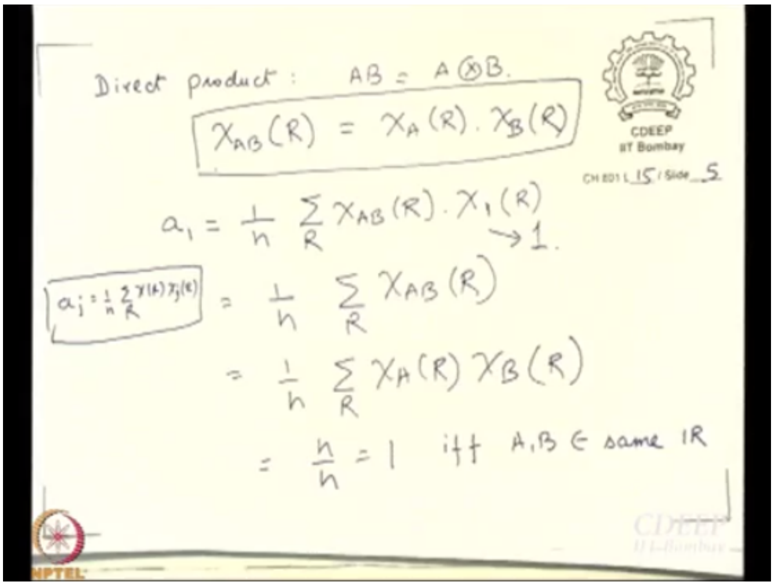
If you take a direct product what do you get, should you not get a reducible representation? Gamma 1 is an irreducible representation, gamma 2 is another irreducible representation. When you multiply them by each other you should get a reducible representation unless gamma 1 and gamma 2 are one dimensional. If gamma 1 and gamma 2 are one dimensional then what happens all characters are either +1 or -1.

When I say direct product what do I mean? This is what I mean, let us say C2v, what are the symmetry species? E, C2, sigma V, sigma V dash and let me take any 2 representations 1 1 -1 -1, 1 -1 1 -1. What is the name of the first one? 1 1 -1-1 A2 and what is the second one B1 very good. I want to know what is A2 cross B1. Actually it is B2. Let us see, you just multiply these characters together 1 * 1 is 1, 1 * -1 is -1, -1 * 1 is -1, -1 * -1 is +1 what is it now?

And once you have done on few of these, it becomes very simple. It is like multiplying by 1 and all, 1 multiplied by any number is that number right. Similarly, A multiplied by B is always B. B multiplied by B is always A why because if both were Bs then what would happen, this character is -1 so -1 * -1 is +1, see multiply 2B representations you get an A representation. Similarly, 1 multiplied by 2 subscript is always 2 and 2 multiplied by 2 is always 1.

So you can work out the symmetries of these direct products this way, alright. Okay, direct product.

(Refer Slide Time: 15:33)



Direct product : $AB = A \otimes B$.

$$\boxed{\chi_{AB}(R) = \chi_A(R) \cdot \chi_B(R)}$$

CDEEP
IIT Bombay
CH 201 L 15 / Slide 5

$$a_1 = \frac{1}{h} \sum_R \chi_{AB}(R) \cdot \underset{\to 1.}{\chi_1(R)}$$

$$\boxed{a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)}$$

$$= \frac{1}{h} \sum_R \chi_{AB}(R)$$

$$= \frac{1}{h} \sum_R \chi_A(R) \chi_B(R)$$

$$= \frac{h}{h} = 1 \quad \text{iff } A, B \in \text{same IR}$$

So for a direct product one thing that we can take axiomatically I thought I will prove it, but you know time is running out, so instead of doing that I would rather like to finish this discussion of IR activity and all. For direct product say AB which is = A cross B, chi AB for any symmetry operation R is given by chi A for that R multiplied by chi B of that R that is what we just did is not it, alright.

What is the question that we have asked, the question we asked is does our direct product contain the totally symmetric representation, okay? How will you answer that question, we answer that question by using our by now very familiar friendly neighbourhood relationship, a1 = 1/h sum over R chi AB R * chi, it is a little difficult to write because it can be A1, A1G and so on and so forth.

I will just write chi 1 R, now what is chi 1 R. For every R for a totally symmetric representation 1 right. So this is just 1, so you are left with 1/h sum over R chi AB R, alright, okay and what is chi AB of R. Chi R multiplied by chi BR, so write it like this 1/h sum over R chi A R chi B R and what is the sum, when is it equal to h? when A and B belong to the same symmetry species, know.

Remember one of the consequences of great orthogonality theorem, sum over R chi 1 R chi 2 R = 0 if gamma 1 is not equal to gamma 2 and = h if gamma 1 = gamma 2. So what we are saying is that this functions A and B must belong to the same symmetry species, same irreversible representation if this A1 is to be nonzero right. So = h/h = 1 if and only if A and B belong to the same symmetry species, same irreversible representation, alright.

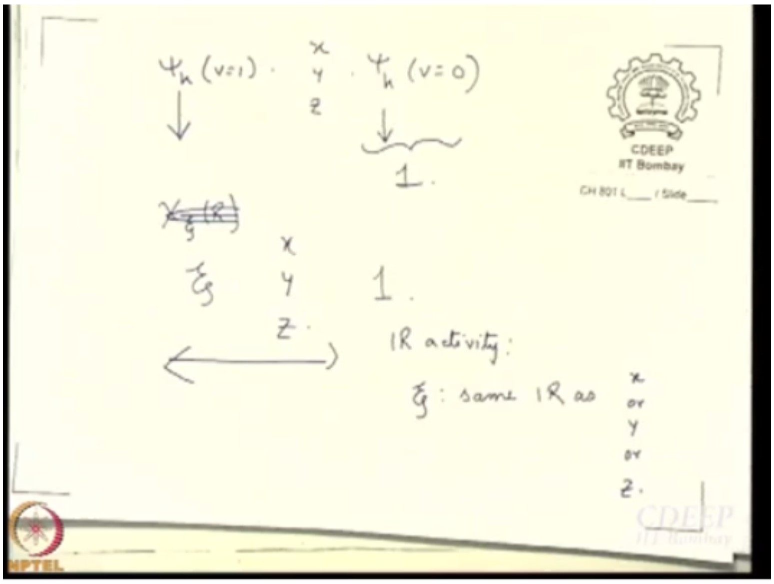
So we have now reached an important conclusion here. For a direct product you are going to have the symmetry species occurring in the direct product if and only if the 2 functions belong to the same symmetry species and then also A1 will occur only 1, is it okay or not. So this is something that we had worked out remember, aj = 1/h sum over R chi R chi i chi j R. I do not remember whether I used i or j as a subscript does not matter right.

So now what I am saying is that what am I looking for, I am looking for the totally symmetric representation. So for totally symmetric representation this chi of R has to be 1, no matter what R is, is not it and no matter what the character table is. No matter what symmetry point group it is. All characters are equal to +1 for the totally symmetric representation, so this becomes 1. You are left with sum over R chi AB R and here what you have written is chi AB R = chi AR * chi BR.

Now substitute that this is what you get and then again we know that this is going to be equal to 0 unless A and B belong to the same symmetry species and if they belong to the same symmetry species then that sum is going to be h, h/h = 1. So this is an essential condition for a direct product to be to contain the totally symmetric representation that the 2 function must belong to the same symmetry species, okay.

But why are we saying so many things. We are saying so many things because we want to ascertain whether psi k v = 1 * x or y or z * psi k v = 0. This triple product does it contain the totally symmetric species or not okay.

(Refer Slide Time: 21:30)



$\psi_h(v=1)\cdot \begin{matrix} x \\ y \\ z \end{matrix} \cdot \psi_h(v=0)$

$\downarrow \qquad\qquad \underbrace{\downarrow}_{1.}$

~~$\chi_\xi(R)$~~

$\xi \quad \begin{matrix} x \\ y \\ z. \end{matrix} \quad 1.$

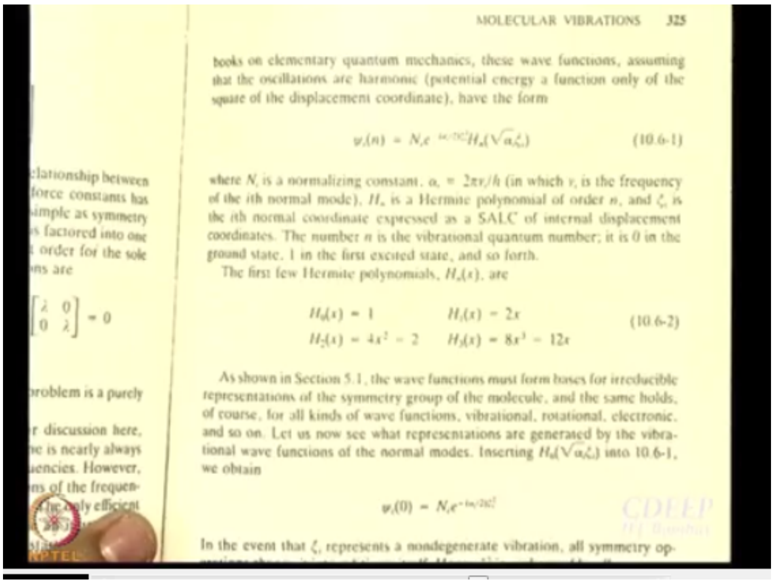
$\longleftarrow\!\!\longrightarrow$

IR activity:

ξ : same IR as x or y or z.

It is very simple, first I take this right product then that with this and life is made a little more simpler when you look at the forms of this wave functions okay, who remembers the v = 0 wave function for the simple harmonic oscillator? (()) (22:06) show you.

(Refer Slide Time: 22:38)



lationship between
force constants has
imple as symmetry
s factored into one
order for the sole
ns are

$\begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix} = 0$

roblem is a purely

r discussion here,
ne is nearly always
iencies. However,
ns of the frequen-

MOLECULAR VIBRATIONS 325

books on elementary quantum mechanics, these wave functions, assuming that the oscillations are harmonic (potential energy a function only of the square of the displacement coordinate), have the form

$$\psi_i(n) = N_i e^{-\alpha_i \zeta_i^2/2} H_n(\sqrt{\alpha_i}\,\zeta_i) \qquad (10.6\text{-}1)$$

where N_i is a normalizing constant, $\alpha_i = 2\pi\nu_i/h$ (in which ν_i is the frequency of the ith normal mode), H_n is a Hermite polynomial of order n, and ζ_i is the ith normal coordinate expressed as a SALC of internal displacement coordinates. The number n is the vibrational quantum number; it is 0 in the ground state, 1 in the first excited state, and so forth.

The first few Hermite polynomials, $H_n(x)$, are

$$H_0(x) = 1 \qquad H_1(x) = 2x$$
$$H_2(x) = 4x^2 - 2 \qquad H_3(x) = 8x^3 - 12x \qquad (10.6\text{-}2)$$

As shown in Section 5.1, the wave functions must form bases for irreducible representations of the symmetry group of the molecule, and the same holds, of course, for all kinds of wave functions, vibrational, rotational, electronic, and so on. Let us now see what representations are generated by the vibrational wave functions of the normal modes. Inserting $H_0(\sqrt{\alpha_i}\,\zeta_i)$ into 10.6-1, we obtain

$$\psi_i(0) = N_i e^{-\alpha_i \zeta_i^2/2}$$

In the event that ζ_i represents a nondegenerate vibration, all symmetry op-

Here for some reason the quantum number is written n instead of v, but then what can you do, can you read, I mean that is not a general question can you read this page. So see this is what it is n should be substituted by v actually, okay. What is this Hn, Hermite polynomial and here we have some examples of Hermite polynomials in x what is H0 x = 1. So for v = 0 you substitute 1 here, what are we left with, we are left with Ni then e to the power –alpha i/2 then xi i square.

What kind of a function is this, this is an Gaussian function is not it, it is a Gaussian function. So it is totally symmetric. It is symmetric. Gaussian function is totally symmetric, no matter whether xi is symmetric or anti-symmetric okay, xi square is there and what about H1, H1 x = 2x right. So you substitute 2x here, the initial part is symmetric anyway, does it not mean that the wave function for v = 1 has the same symmetry as the normal mode of vibration itself because this will get multiplied by xi.

Except for xi everything is either a number or symmetric quantity, understand. What we are saying is that for 0th vibrational quantum number for v = 0 the function is symmetric always. So character = 1 is totally symmetric and for v = 1 what do you have is you have something multiplied by xi in the wave function. So whatever is the symmetry of xi should also be the symmetry of the wave function for v = 1 right, are we okay with this.

Now so here the good thing is we can just write 1. Now you want to work with characters. Now I played Arjuna, I am only looking at the deflection of the fish, okay, you agree. So what do I need to do now. I need to work with chi, xi R, okay forget chi for now. So this I can replace by xi right, the normal mode and we know already how to determine the symmetry of normal mode that is what we have been talking about for the last 2-3 days, right.

Symmetry of xyz is provided in the character table and in fact we now know character tables well enough so that even if it not provided we can work it out right and then this thing is very nice, this turns out to be totally symmetric right. So this is always 1 so your triple product now boils down to a direct product. It is not a triple product anymore when you talk about IR activity is not it, right.

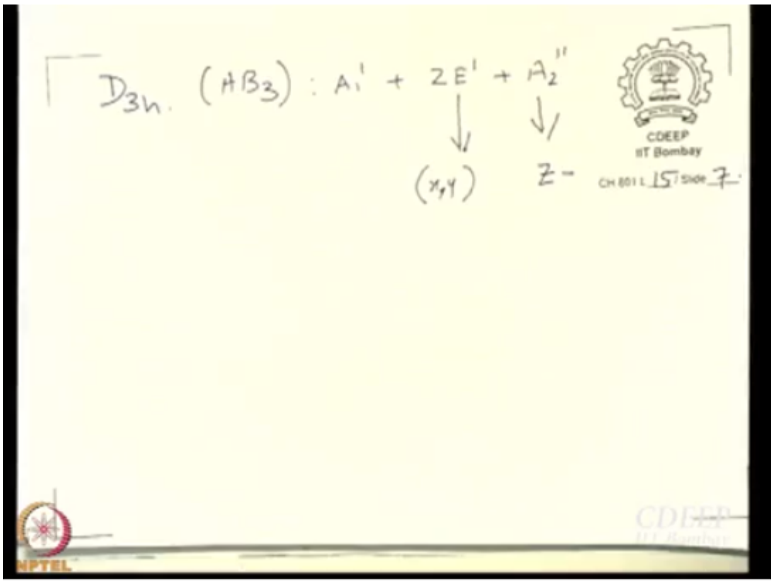
So I only need to worry about these 2, and what is it that we learned a little while ago, we learned that a direct product would contain the totally symmetric representation if and only if the 2 functions which make up the direct product belong to the same irreducible representation. So now see what is the condition for IR activity, now it is done. So condition for IR activity. IR activity means the possibility of absorption of IR light right to excite a certain kind of normal mode of vibration.

The essential condition was down to be that the normal mode of vibration xi should belong to the same symmetry, same irreducible representation, same symmetry species as x or y or z.

Now everything is hunky-dory. You would already know how to find the symmetries of the normal modes. You even know how to say to some extent, which internal motions contribute to which normal mode.

Now what you have learnt is that knowing the symmetry of the normal mode you can say whether this normal mode is IR active or not right, any question, is there question please ask. If there is no question, then we proceed with an example. So what is the condition for IR activity, okay, what did we work out yesterday which molecule, AB3. We worked out 2 kinds of AB3 actually.

(Refer Slide Time: 29:00)



D_{3h}. (AB_3) : $A_1' + 2E' + A_2''$

$2E' \downarrow (x,y)$

$A_2'' \downarrow z$ -

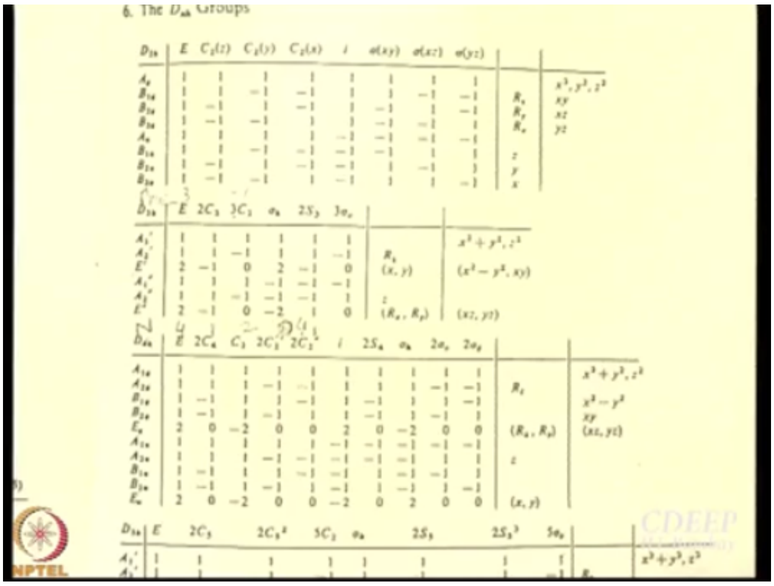
CH 801 L 15 Slide 7

First what was the (()) (28:28) or the first AB3 we worked on, wave 3, carbonate and so on and so forth, D3h molecule was AB3. What was the symmetry of the normal modes? we worked it out yesterday, tell me. A1 dash + 2 E dash + A2 double dash. Do you remember which is which, I remember A2 double dash because A2 double dash is our very favorite out of plane dome motion.

What about A1 dash, it is symmetric stretch and no bend, only symmetric stretch is not it, only symmetric stretch because here only we learnt that even if you use the angles you get A1 A1 dash but that is a redundant coordinate you have to throw it away okay. So A1 dash is pure symmetric stretch and what about this 2 E dash, how many normal modes are there in the 2 E dash, 4 normal modes what are they? Yes, so there is mixture, okay.

What is the percentage of mixture? we cannot really tell unless we go a little further which we would not. So we should be happy with that. Now I want to know which of these are IR active, which of these are IR inactive, alright B3h.

(Refer Slide Time: 30:35)



6. The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		x^2+y^2, z^2

What are the vibrations? you cannot see any more A1 dash, E dash, A2 double dash okay? What are the symmetry species of x y and z? can you read, very nicely, z is A2 double dash, what about x and y, E dash right, remember that. So this should be IR active. These should also be IR active. Moreover, do not forget something that this A2 double dash gives you a totally symmetric representation in the triple product only with z, not with x or y right.

So what it is going to do is that it is only going to absorb the z component of the light. So this is called z polarised transition and what about E dash, it is going to absorb the x component of polarization, y component of polarization and we all know what polarization is right, linear polarization. What is polarization, means oscillation right. So the plane of oscillation is only one that is plane polarized light.

When you mix x and y then you get circularly polarized light or elliptically polarized light depending on the coefficients okay. So this is a z polarized transition this is the x y polarized transition, alright. So using polarization resolved IR spectroscopy you can actually identify the bands a little better. You can say which is which little better. What about A1 dash, A1 dash does not show up in IR spectrum.

(()) (32:31) A1 dash is there no way of seeing it, actually there is, you see it in Raman, okay. How do you see it in Raman spectroscopy? let us see. I will keep this aside we will come back to it a little later.