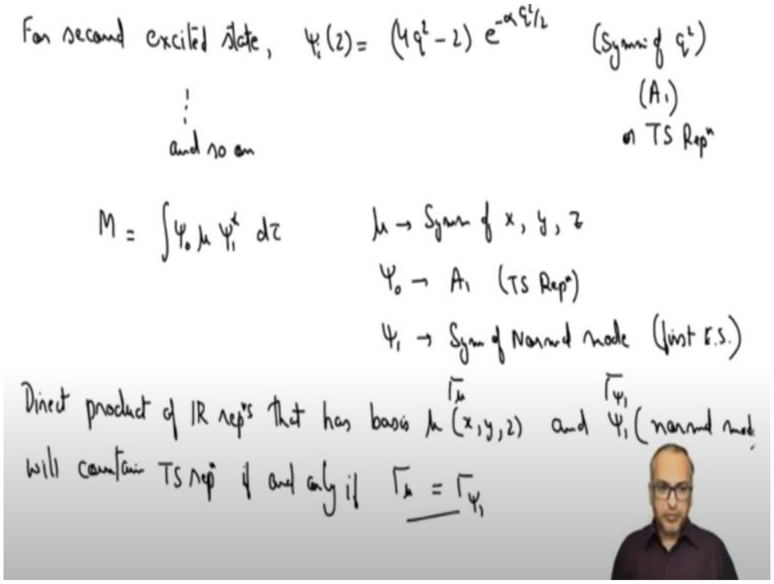
Symmetry and Group Theory
Dr. Jeetender Chugh
Department of Chemistry and Biology
Indian Institute of Science Education and Research, Pune

Lecture -64
Spectral Transition Probabilities Part- II

(Refer Slide Time: 00:22)



For second excited state, $\psi_i(2) = (4q^2 - 2)\, e^{-\alpha q^2/2}$ (Symm of q^2)

(A₁)

or TS Repⁿ

⋮

and so on

$$M = \int \psi_0 \mu \psi_1^* \, d\tau$$

$\mu \rightarrow$ Symm of x, y, z

$\psi_0 \rightarrow A_1$ (TS Repⁿ)

$\psi_1 \rightarrow$ Sym of Normal mode (first E.S.)

Direct product of IR repⁿs that has basis $\overset{\Gamma_\mu}{\mu\,(x, y, z)}$ and $\overset{\Gamma_{\psi_1}}{\psi_1}$ (normal mode) will contain TS repⁿ if and only if $\underline{\Gamma_\mu = \Gamma_{\psi_1}}$

So, now let us look at what happens to second excited state. So, let us calculate for second excited state psi i 2, now we have 4 q square minus 2, this is coming from Hermite polynomial and the initial component is minus alpha q square by 2. Now this means that now this is symmetry of q square is totally symmetric representation. So, that means this becomes, so for second excited set, it becomes symmetry becomes totally symmetric representation.

So, that means A1 or totally symmetric representation. Similarly, if you go to third excited state, you will again see that it will be forming symmetry of q alone. So, symmetry of q will be again equal to symmetry of the normal coordinate or normal mode. So, I can say and so on. So, every alternate excited state will have symmetry of totally symmetric representation and every other alternate will have symmetry of q that we can say;

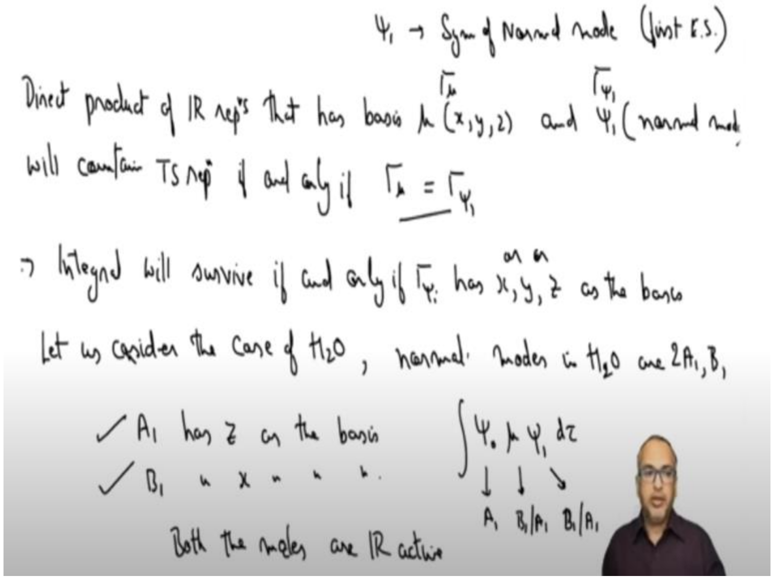
So, because it is for following symmetry of Hermite polynomials, which are even odd, even odd and so on. So, now we know the symmetry of ground state we know the symmetry of excited state. Now, let us go back and look at the integral, so our integral is of the form psi 0 mu psi 1 star d tau. Now mu has symmetry of x, y, z; psi 0 A 1 or totally symmetric representation; and psi 1.

Let us say if it is first excited symmetry of normal mode or if it is second excited state. Let us only talk about first excited state. So, now what will be the direct product of these three? So, direct product of these three will not depend on this one because this is A1. So, we have to consider the direct product of mu or the symmetry of x, y, z and psi 1. These will contain totally symmetrical presentation the direct product or I will write it down.

So, direct product of IR representations that has basis mu, which is x, y and z and psi 1 which is normal mode will contain totally symmetric representation, now this is again coming from direct product application. If and only if, let us call this as tau mu, let us call this as tau psi 1. Tau mu is equal to tau psi 1, then only it will contain totally symmetric representation the direct product will contain totally symmetric representation.

And the integral will survive, integral will not go to 0. Only if tau mu is equal to tau psi 1. now symmetry of mu is fixed symmetry of psi 1 we know what is the symmetry of psi 1.

(Refer Slide Time: 04:41)



$\psi_1 \rightarrow$ Sym of Normal mode (first E.S.)

Direct product of IR rep's that has basis $\overset{\Gamma_\mu}{\mu}$ (x, y, z) and $\overset{\Gamma_{\psi_1}}{\psi_1}$ (normal mode) will contain TS rep if and only if $\underline{\Gamma_\mu = \Gamma_{\psi_1}}$

$\Rightarrow$ Integral will survive if and only if Γ_{ψ_1} has $x, \overset{\text{or}}{,} y, \overset{\text{or}}{,} z$ as the basis

Let us consider the case of H_2O, normal modes in H_2O are $2A_1, B_1$

✓ A_1 has z as the basis

✓ B_1 " x " " "

Both the modes are IR active

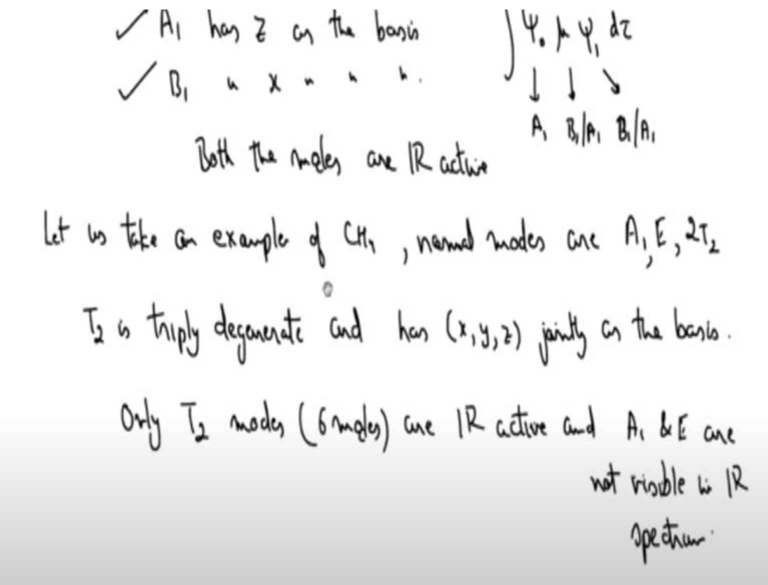
$$\int \underset{\underset{A_1}{\downarrow}}{\psi_0} \; \underset{\underset{B_1/A_1}{\downarrow}}{\mu} \; \underset{\underset{B_1/A_1}{\searrow}}{\psi_1} \, d\tau$$

So, that means the integral will survive, so, this implies that integral will survive if and only if, tau psi has x, y, z as the basis, either of the 3, x, y or z; x or y or z as the basis because then their irreducible representations will be same as tau mu and then the integral will survive. So, now let us see what happens in case of water, so let us consider the case of water. So, we have seen that the normal modes in water are 2A1 and B1.

So, 2 A1 modes are there and one B1 is there. Now, let us try to find out the symmetry of A1 the basis of A1, so A1 has z as the basis. And B1 has x as the basis. So, that means if I am now calculating the direct product of psi 0 mu psi 1. So, I can say that psi 0 mu psi 1 integral d tau. So, psi 0 has A 1 symmetry. This will have B 1 or A 1, whether your taking x or z component and psi 1 has again B 1 and A 1.

Whether you are taking which mode depends on which mode you are taking. So, now in this case both the integrals will survive that means this will also IR active. This is also IR active. So, both the modes are IR active.

(Refer Slide Time: 07:25)



✓ A_1 has z as the basis

✓ B_1 " x " " ".

$$\int \underset{\substack{\downarrow \\ A_1}}{\psi_0} \; \underset{\substack{\downarrow \\ B_1/A_1}}{\mu} \; \underset{\substack{\searrow \\ B_1/A_1}}{\psi_1} \, d\tau$$

Both the modes are IR active

Let us take an example of CH_4, normal modes are A_1, E, $2T_2$

T_2 is triply degenerate and has (x, y, z) jointly as the basis.

Only T_2 modes (6 modes) are IR active and A_1 & E are not visible in IR spectrum.

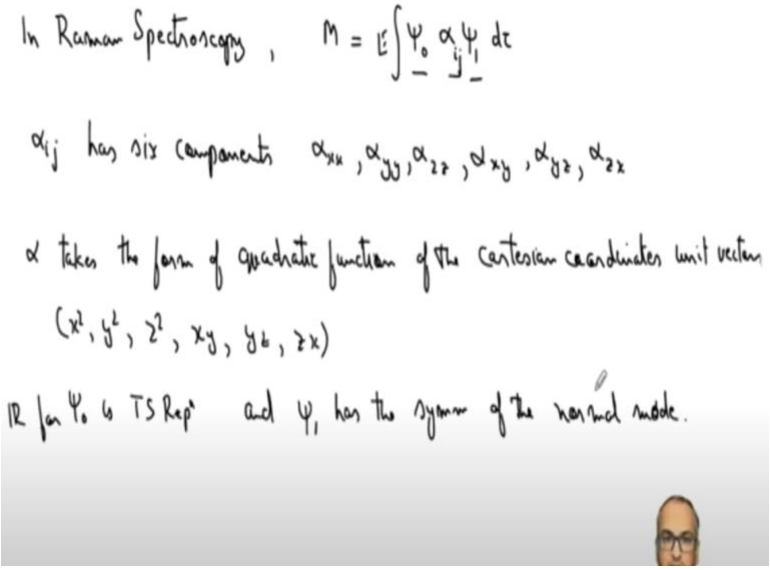
So, again, I want to emphasize that although we have determined there, the vibrational modes the normal modes of vibration using symmetry and group theory, not all modes will be active under IR or Raman spectroscopy and we will have to set up this integral and find out using direct product whether the integration will survive or not and that will define whether IR will be active or not.

So, basically here you will see all three modes in IR spectrum. Now, let us take another example quickly. So, let us take an example of CH4 in this. So, the normal modes we have not done this case, we have not calculated in this class, but I would suggest you do it as a home assignment. So, normal modes are A1, E, and 2T2. So, these are the normal modes which we got. Now out of this T2 is triply degenerate.

And has x, y, and z jointly as the basis. So, that means the only T2 mode will survive here, other modes will not survive. So, that means only T2 modes. So, how many total modes are there then, that means six modes are IR active. And A1 and E are not visible in IR spectrum. So, this should be very clear now, so this is for IR spectroscopy, so now we have learned how to identify which modes which are observed?

Which normal modes of vibration will be actually observed in IR spectroscopy based on symmetry rules? Now, let us in the same lines, let us also continue this discussion for Raman spectroscopy.

(Refer Slide Time: 10:11)



In Raman Spectroscopy, $M = E\int \underline{\psi_0}\, \alpha_{\underline{ij}}\, \underline{\psi_1}\, d\tau$

α_{ij} has six components $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}, \alpha_{zx}$

α takes the form of quadratic function of the Cartesian coordinates unit vectors
$(x^2, y^2, z^2, xy, yz, zx)$

IR for ψ_0 is TS Rep^n and ψ_1 has the symm of the normal mode.

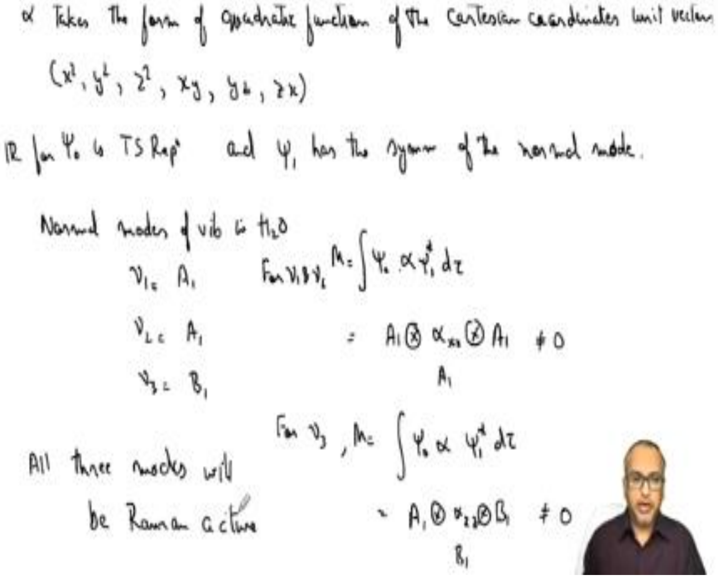
So, in Raman spectroscopy the only difference is that the integral instead of now dipole moment now you have polarizability. In Raman spectroscopy the transition moment integral, that is M changes to psi 0, alpha, psi 1 d tau, so you can still write it as mu and then mu can be written as alpha e so you have e outside. So, basically you are interested in the symmetry of psi 0 alpha and psi 1. So, alpha can say alpha ij here, alpha ij has six components.

Remember the tensor which is alpha xx, alpha yy, alpha yz, sorry, we will write zz first alpha zz, alpha xy, alpha yz, alpha zx. So, alpha ij has six components and if any of this component survives in this integral the whole M will be non-zero and the mode will be Raman active. Now, what is the symmetry of alpha? Symmetry of alpha is basically the direct product of x and y and z. I mean xy, yy, yz any of these direct products.

So, alpha takes the form of quadratic function of the Cartesian coordinates unit vectors. Which is in the form of x square, y square we can write down x square, y square, z square, xy, yz, zx. Now here also, psi 0 is totally symmetric representation. So, the IR for psi 0 is totally symmetric representation, IR is irreducible representation here. Do not get confused with infrared spectroscopy.

So, IR for psi 0 is totally symmetric representation and psi 1 has the symmetry of the normal mode. That we have already seen and we are talking about only first excited state, you can of course you can talk about the second or third excited state if you want to but let us keep our discussion to first excited state.

(Refer Slide Time: 13:35)



α Takes the form of quadratic function of the Cartesian coordinates unit vectors

$(x^2, y^2, z^2, xy, yz, zx)$

IR for Ψ_0 is TS Repⁿ and ψ_1 has the symm of the normal mode.

Normal modes of vib in H_2O

$\nu_1 = A_1$ For ν_1 & ν_2 $M = \int \Psi_0\, \alpha\, \Psi_1^*\, d\tau$

$\nu_2 = A_1$ $= A_1 \otimes \alpha_{xx} \otimes A_1 \neq 0$

A_1

$\nu_3 = B_1$

For ν_3, $M = \int \Psi_0\, \alpha\, \Psi_1^*\, d\tau$

All three modes will be Raman active

$= A_1 \otimes \alpha_{zz} \otimes B_1 \neq 0$

B_1

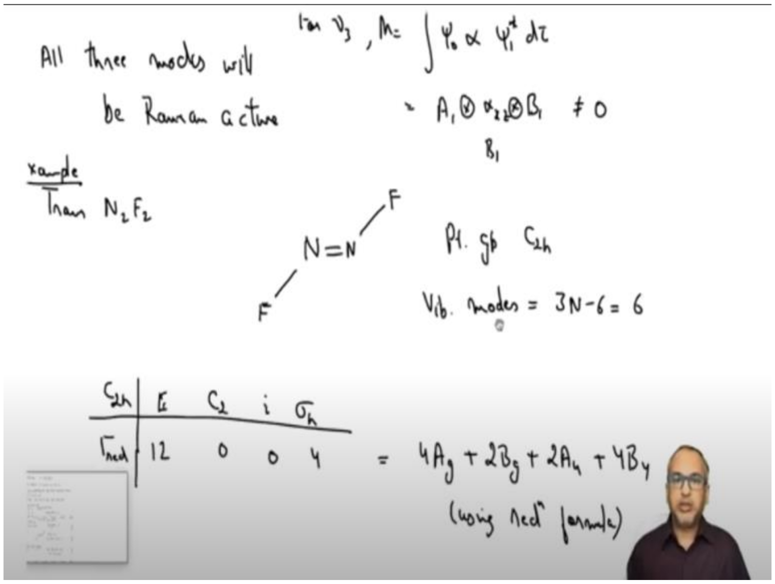
So, now we know the symmetry of all three so now we have to see whether the integration will survive or not in a particular case. So, now let us see the normal modes of vibration in H2O are, let us write it systematically, so you have A1, mu 2 will be A1, mu 3 will be B 1. Now for this one the transition, so for mu 1 and mu 2 the integration or M will be equal to psi 0 alpha psi 1, d tau star is assumed.

Now psi 0 is A 1 direct product alpha will have direct product as so you have to find which of the alpha will form direct product as psi 1. So, now if i take alpha xx here, that is basically A 1. So, you can have different alpha components from character table but you have to choose which alpha which has symmetry as psi 1 star. So, psi 1 star has the symmetry as we know that it is symmetry of the normal mode, symmetry of the normal mode is A1.

So, that means this integration will not go to zero, because it contains totally symmetric representation. Now for mu 3, M is equal to psi 0, alpha psi1 star, d tau; psi 0 is always A1, alpha not you have to find if there is any binary product of Cartesian coordinate unit vectors, which has symmetry of B 1. So, now direct product with I think this has alpha xz has the symmetry of B1 psi 1 star has the symmetry of normal mode, which is B1.

So, again, this will not go to 0 that means all the 3 modes will be Raman active. So, all 3 modes will be active in Raman as well as in IR spectrum.

(Refer Slide Time: 16:27)



All three modes will be Raman active

for ν_3, $M = \int \psi_0 \alpha \psi_1^* d\tau$

$= A_1 \otimes \alpha_{zz} \otimes B_1 \neq 0$

B_1

xample

Trans N_2F_2

Pt. gp C_{2h}

Vib. modes = 3N-6 = 6

C_{2h}	E	C_2	i	σ_h
Γ_{red}	12	0	0	4

$= 4A_g + 2B_g + 2A_u + 4B_u$

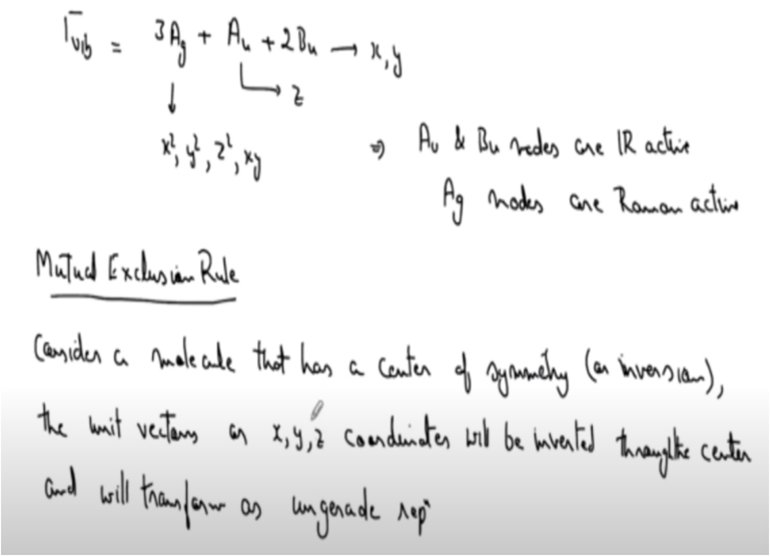
(using red^n formula)

So, now there is one very important role, let us take one more example if we have time let us say, let us consider trans N2F2 example. In this case, I will tell you why we are discussing this example. So, let us draw the structure, now the point group here is C2h, you should be able to calculate that by now. So, and the number of vibrational modes if you calculate, this will be this is a non-linear molecule.

So, 3N minus 6 this will be 6. N is 4 so 4 3 is are 12 and then out of 12 you have 3 translational 3 rotational, so you are left with 6 vibrational modes. Let us try to find out what are those 6 vibrational modes, C2h, so, you have E, C2, i, sigma h, tau reducible I am directly writing tau reducible so that will give you 12, 0, 0, 4 and this will be equal to 4Ag, + 2Bg. I am skipping all the maths and I expect you to solve it by yourself, four before.

So this is using reduction formula. So, we have now obtained what are the symmetries of different vibrational modes. Now which of these vibrational modes will be IR active and which of these will be Raman active, how would we tell that?

(Refer Slide Time: 18:35)



$$\Gamma_{vib} = 3A_g + A_u + 2B_u \rightarrow x, y$$

$3A_g \downarrow x^2, y^2, z^2, xy$; $A_u \rightarrow z$

$\Rightarrow$ A_u & B_u modes are IR active

A_g modes are Raman active

Mutual Exclusion Rule

Consider a molecule that has a center of symmetry (or inversion), the unit vectors or x, y, z coordinates will be inverted through the center and will transform as ungerade rep

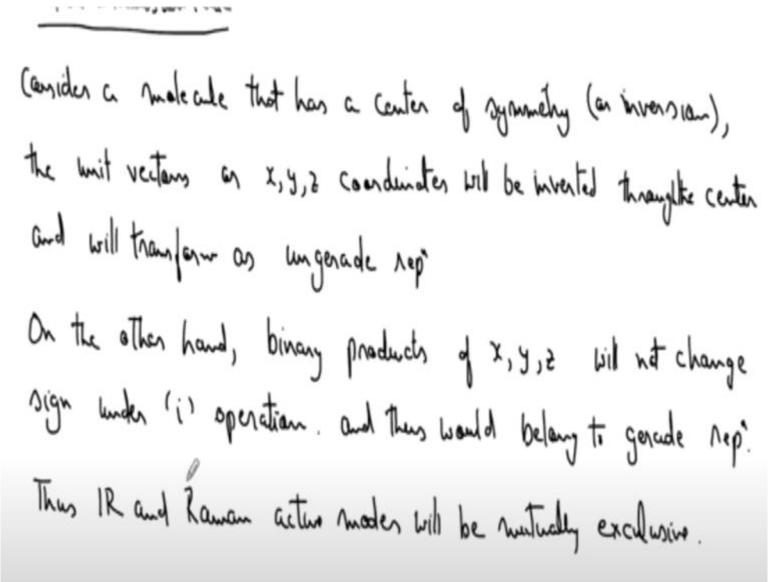
So, we know that tau vibrational is equal to 3Ag + A u + 2Bu. So, this is the total vibrational modes and then we have to actually find out the symmetry of vibrational modes from here by subtracting the translational and rotational components. So, out of Ag, Bg, Au, Bu. So, you can remove the symmetry of translational modes and rotational modes. So, let us not do that and I am directly writing tau vibrational as this.

Now Ag, what is the symmetry of Ag? So, let us quickly get the character table of C2h. So, we are not even setting up the integration. I am just opening a book and looking at the character table of C2h. So, now C2h if I see this has the basis as Ag has the basis as x square, y square, z square, xy. Au has the basis as z, and Bu has the basis as x and y. So, now you can see that this implies that Au and Bu modes are IR active, and Ag modes are Raman active.

So, now there is a mutual exclusion between IR and Raman. So, whatever modes are IR active those are not Raman active and whatever modes are Raman active are not IR active. So, this is very important in spectroscopy in IR, Raman spectroscopy. So, what is this mutual exclusion rule? This is the last principle and then will wind up this course. So, I will say consider a molecule that has a center of symmetry.

So, if you notice the molecule which we discussed N2F2 has center of symmetry i, or we can say inversion center. Now in this molecule the unit vectors or x, y, z coordinates will be inverted through the center and will transform as ungerade representation. So, their IR representation would always have u as the subscript, because i under symmetry operation i, x, y and z will always have minus sign. So, for minus sign under i, that means ungerade representation.

(Refer Slide Time: 22:33)



Consider a molecule that has a center of symmetry (or inversion),
the unit vectors on x, y, z coordinates will be inverted through the center
and will transform as ungerade rep^n
On the other hand, binary products of x, y, z will not change
sign under 'i' operation. and thus would belong to gerade rep^n.
Thus IR and Raman active modes will be mutually exclusive.

Whereas we can say, on the other hand binary products of x, y, z will not change sign under i operation. And thus, would belong to gerade representation. So, the IR representation corresponding to binary products of x, y, z, any binary product, will always have plus 1 sign because this will be essentially the direct product of the two component IR representation which will have minus 1, minus 1.

So, this will always form a gerade representation, x, y, z will always form a basis to ungerade representation and thus whenever there is a center of symmetry in the molecule, the IR and Raman spectrum will be mutually exclusive to each other. So, thus IR and Raman active modes will be mutually exclusive. So, basically you can, so whatever lines we observed in IR spectrum will not be observable in Raman spectrum and vice versa.

So, that means, let us say if you are doing some synthesis and you want to know whether your synthesized molecule has center of symmetry or not. Let us say if you want to synthesis a trans compound and you end it up, in cis compound or a mixture, so it is not a pure trans component. Let us say the pure trans compound only had the center of symmetry. So, now that can be easily tested by recording a simple IR and Raman spectrum of the same compound.

Let us say if you find some lines which are common to both the spectrum that means the molecule does not have a i or it has a contamination from a non i compound. So, that explains the mutual exclusion rule and with this we come to the end of symmetry and group theory course. And I really enjoyed teaching you all and I hope you have learned to the extent I wanted and you have enjoyed the course as well.

That is all and see you guys in the interaction sessions or in exams if you have any difficulties during interaction sessions, please do ask and see you guys in exams and otherwise, thank you that is all for today.