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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture no. – 53
Vibronic Coupling

So in the discussion of benzene so far we have arrived at a situation where we have learnt that out of the three possible transitions that has spin allowed, one is orbitally allowed as well, two are orbitally forbidden.

Now we asked the question, is there any mechanism by which the orbitally forbidden transitions can have some kind of allowedness, and the answer is yes, so it is always a bypass, there is a main road and there is a bypass, it is just that in our case the bypass is much much narrower than the main road, so something that is fully allowed will have, if you remember we had said something right, what is the kind of extinction coefficient that we can expect for a fully allowed transition, 5,000? No, 5 is right, but not thousand, 10 to the power 5, 5,000 is 5 into 10 to the power 3, so 10 to the power 3 to 10 to the power 5 there is a range on this, right, fully allowed transitions typically are associated with epsilon values of 10 to the power 3 to 10 to the power 5, orbitally forbidden spin allowed transitions are typically associated with the value of 10 to the power 3 to 10 to the power 1 which means that there is some way in which orbitally forbidden spin out transitions can take place, cool as an extent fine but it can take place.

Spin forbidden transitions have much lower epsilon values and when we look at benzene I think this will be manifested very nicely, but the question is how is it that orbitally forbidden transitions are also associated with non-negligible epsilon values of 10 to the power 1 to 10 to the power 3, and the answer is by vibronic coupling.

So now we'll see quickly what vibronic coupling is and what effect it has on the spectrum, electronic spectrum of benzene. See vibronic coupling means once again we are not really going to get in to the quantum mechanics of it because it involves a little higher level discussion of perturbation theory, let me just write the transition moment integral, transition moment integral that we have written is something like this, now I'll write using integrals for the change sai S dash sai S D tau S then we had written integral sai V dash sai E dash mu sai V sai E D tau, this d tau is EV right, it contains electronic and vibronic coordinates, when we work under Born Oppenheimer approximation we said that this can be written as D tau E multiplied by D tau V, right, and then this single integral we gave a double integral and we happily separated this integral into a product of an integral in vibrational coordinates and another in electronic coordinates, right, but more often than not what happens is Born Oppenheimer approximation may not hold, it's called an approximation right it is not a firm rule, any approximation works within some limit and then it breaks down.

And as you have seen earlier in case of, our discussion of rho vibrational spectrum Born Oppenheimer approximation does break down, right, so in this case if Born Oppenheimer approximation breaks down then you cannot really separate this integral anymore, so what you do is you write this transition moment integral as, you expand it as a Taylor series that's what I'm not going to do in detail, you write it as a Taylor series and then the first term suppose it is orbitally not allowed first term will vanish, but in the second term and all what you will have is you have to consider this entire thing,

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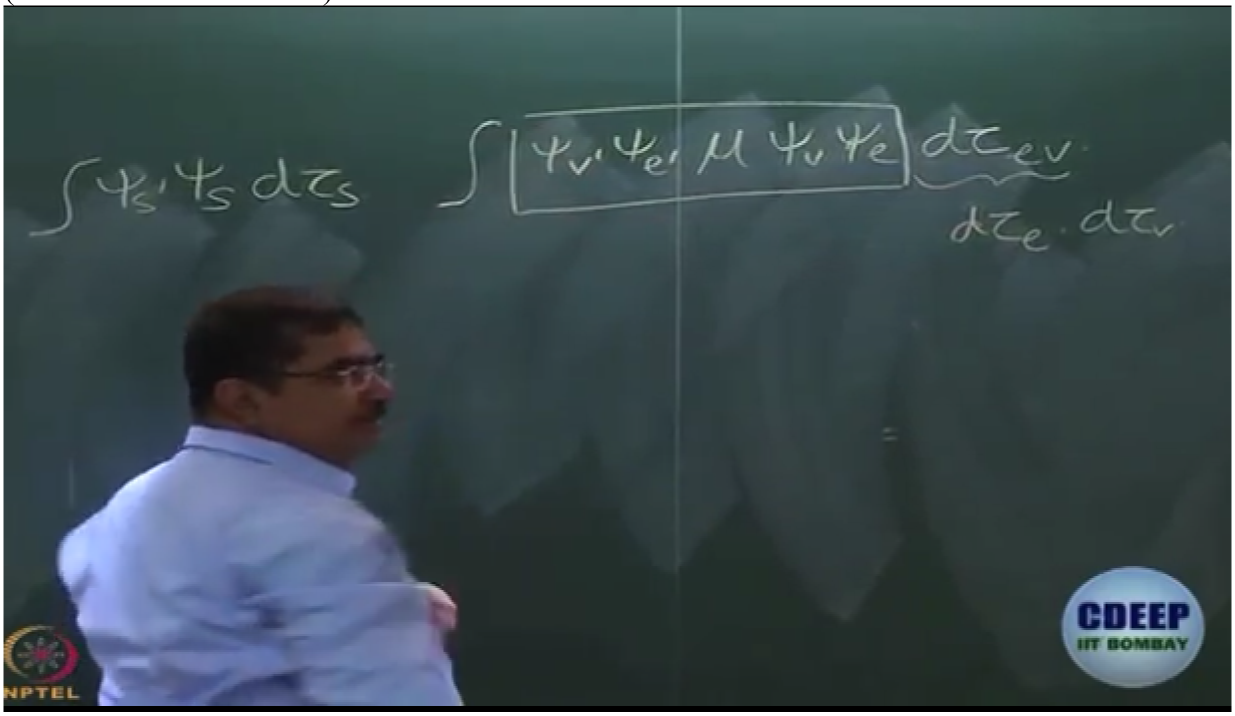

so you might remember that transitions that are not dipole allowed can still be same by using the quadrupole, right.

But when does the quadrupole effect show up? Only when it is dipole forbidden, when the strong effect is not there then sometimes you see the weak effects, what we are talking about now is also weak effect, you see only when the strong effect is not there that is the transition is orbitally forbidden, alright.

So when it's orbitally forbidden now it is not enough to look at the triple product, we've to look at the product of all these 5 functions,

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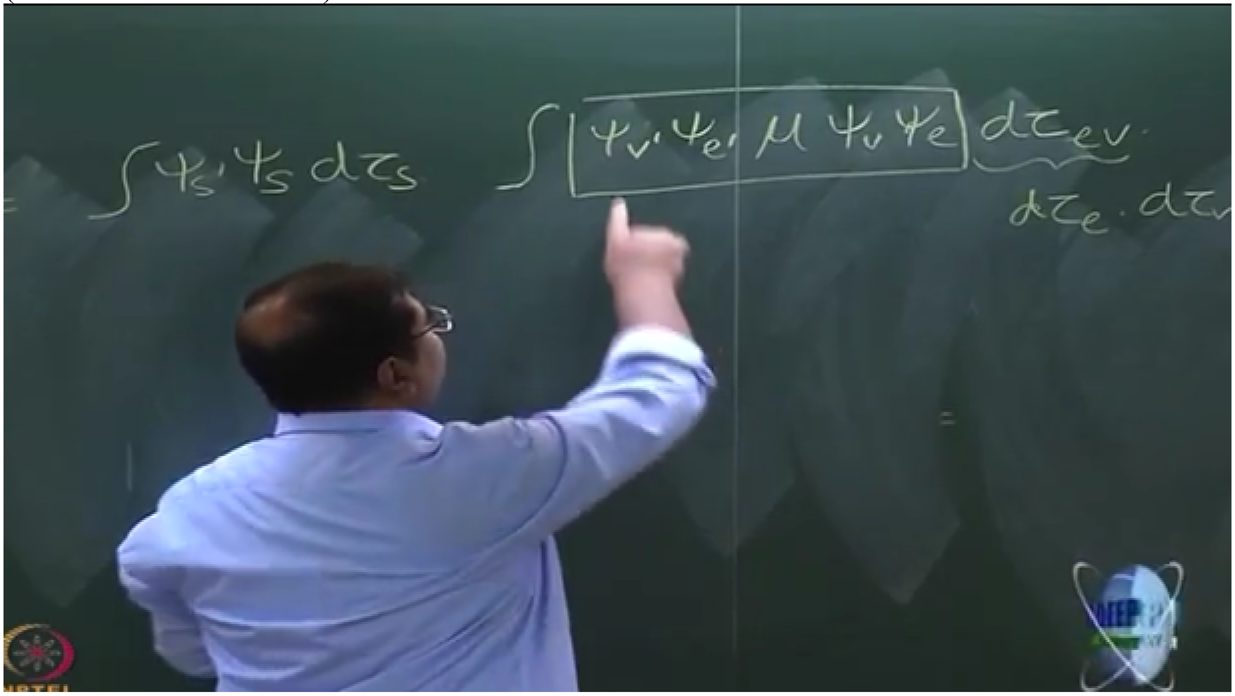

this of course conveniently breaks down into X, Y, Z, alright.

In case of benzene at least this sai E is A1G don't really have to worry about it, alright,

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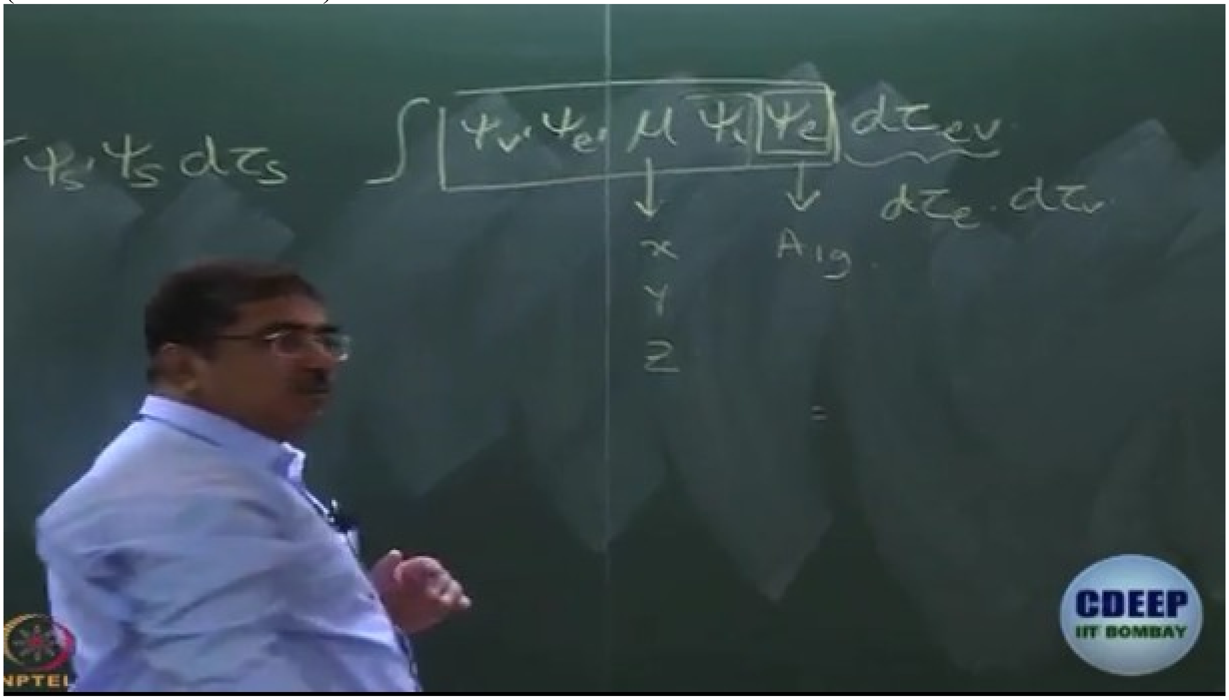

so what we do have to worry about is this sai V mu sai E dash sai V dash, product of this 4 functions, we're making sense, have you understood? Right, now in fact we can make it a little easier, what have we considered already? We have considered this already right, when we are talking about your allowedness, orbital allowedness we have already consider this direct product, okay, and we have arrived at some symmetry gamma, let us say gamma I, okay, or it can even be sum over I, AI gamma I, right.

So if you remember, yeah, so this is what it is, right, we have seen that when we took this direct product for example we had A1G + A2G + E2G, when we took this direct product A2U and B1U we had B2G and so on so forth, so each of these I can write as sum over AI gamma I where gamma I is an irreducible representation, right, of course it can be possible that only one AI has an nonzero value, everything else is 0 that’s fine.

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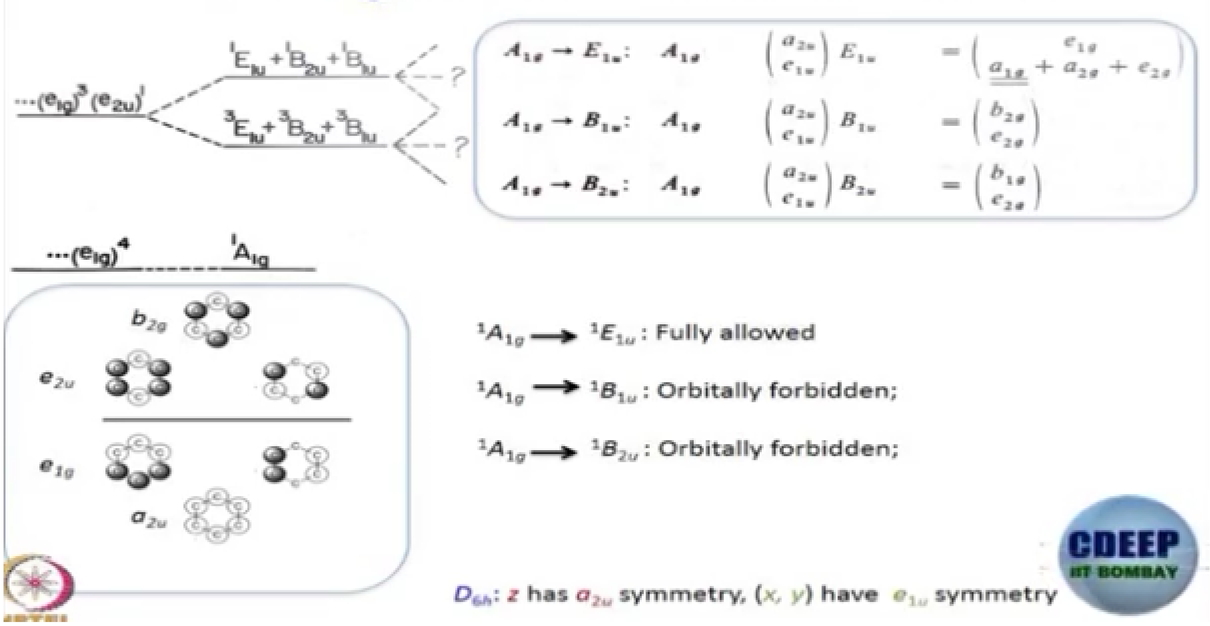

State Diagram and Electronic Transitions

$$A_{1g} \rightarrow E_{1u}: \quad A_{1g} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} E_{1u} = \begin{pmatrix} e_{1g} \\ \underline{\underline{a_{1g}}} + a_{2g} + e_{2g} \end{pmatrix}$$

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$^1A_{1g} \longrightarrow {}^1E_{1u}$: Fully allowed

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D_{6h}: z has a_{2u} symmetry, (x, y) have e_{1u} symmetry

Now what are we worried about now? This is the symmetry sum over I, AI gamma I, we have sai V dash x sum over I AI gamma I x sai gamma, what am I doing? Sai V, okay,

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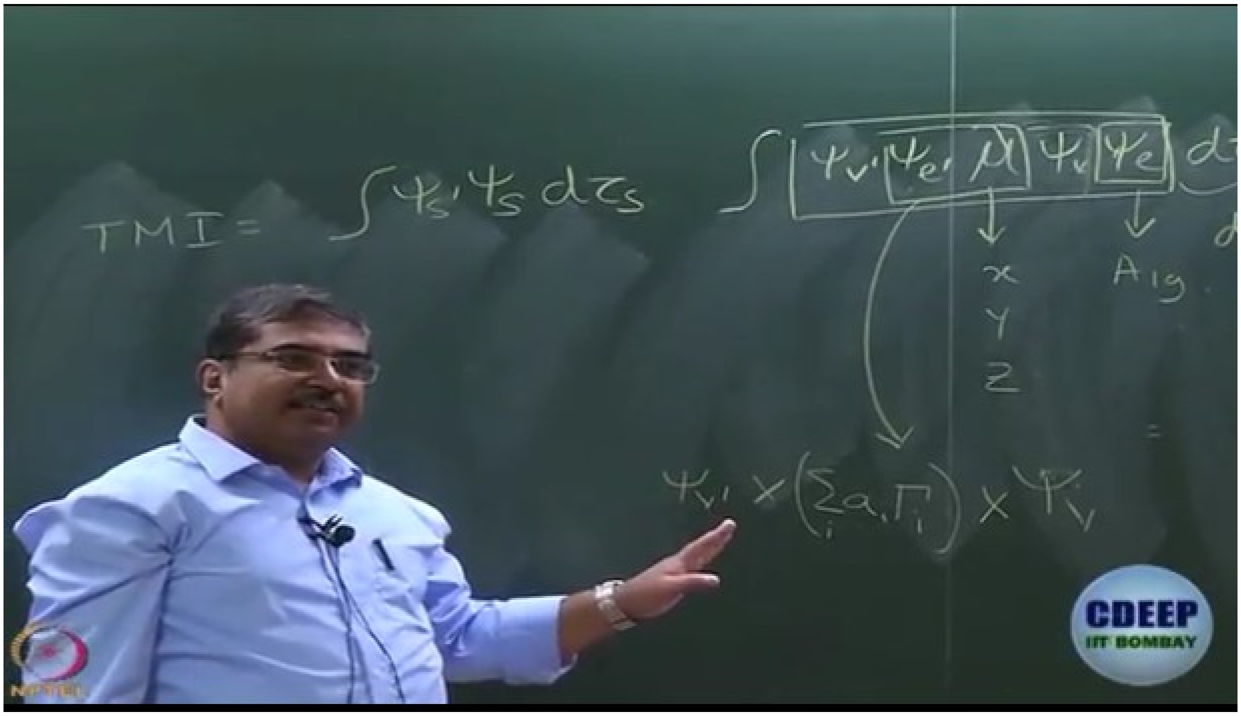

if this triple product contains the totally symmetric representation, then we are done, okay, to keep things simple let me just write gamma I, alright, is there any harm if I write this as sai V dash x sai V x gamma I, is it same right? Doesn't matter in which I take the product.

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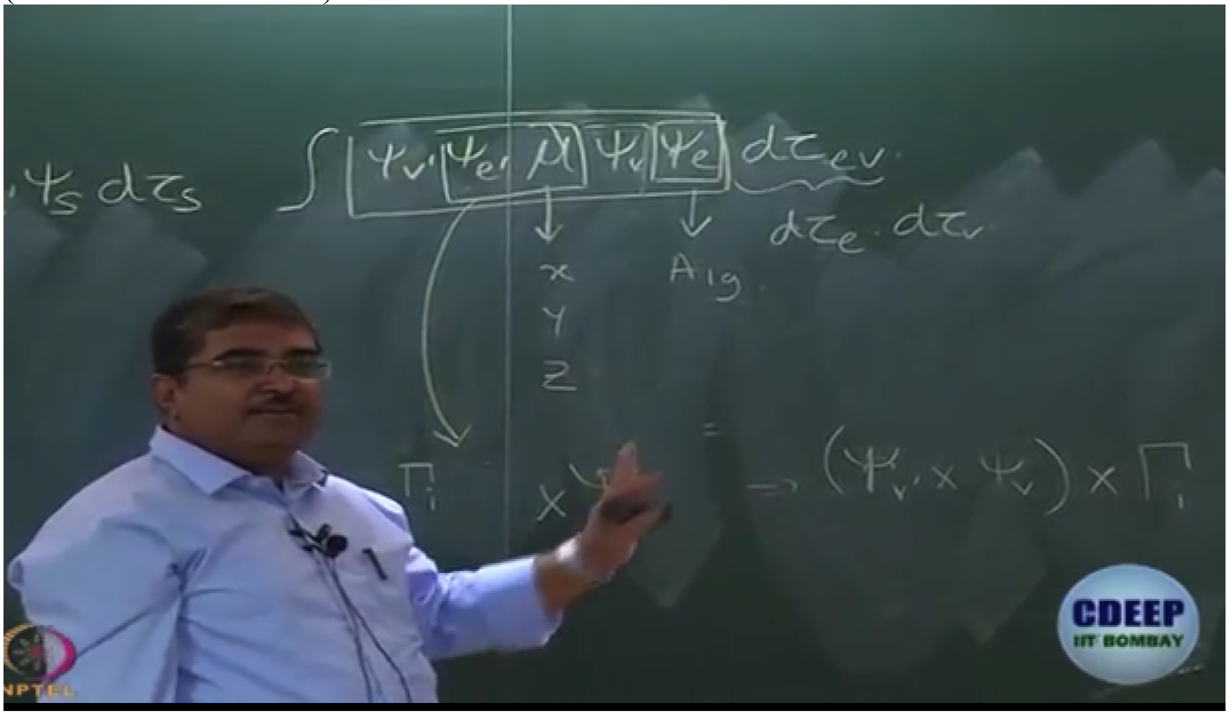

When will this contain the totally symmetric representation? Yes, when sai V prime x sai V have the same symmetry as gamma I, right, so the condition for these to contain let me stick to A1G for the moment since we are talking about benzene, the condition for these to contain A1G is that this direct product of the symmetry

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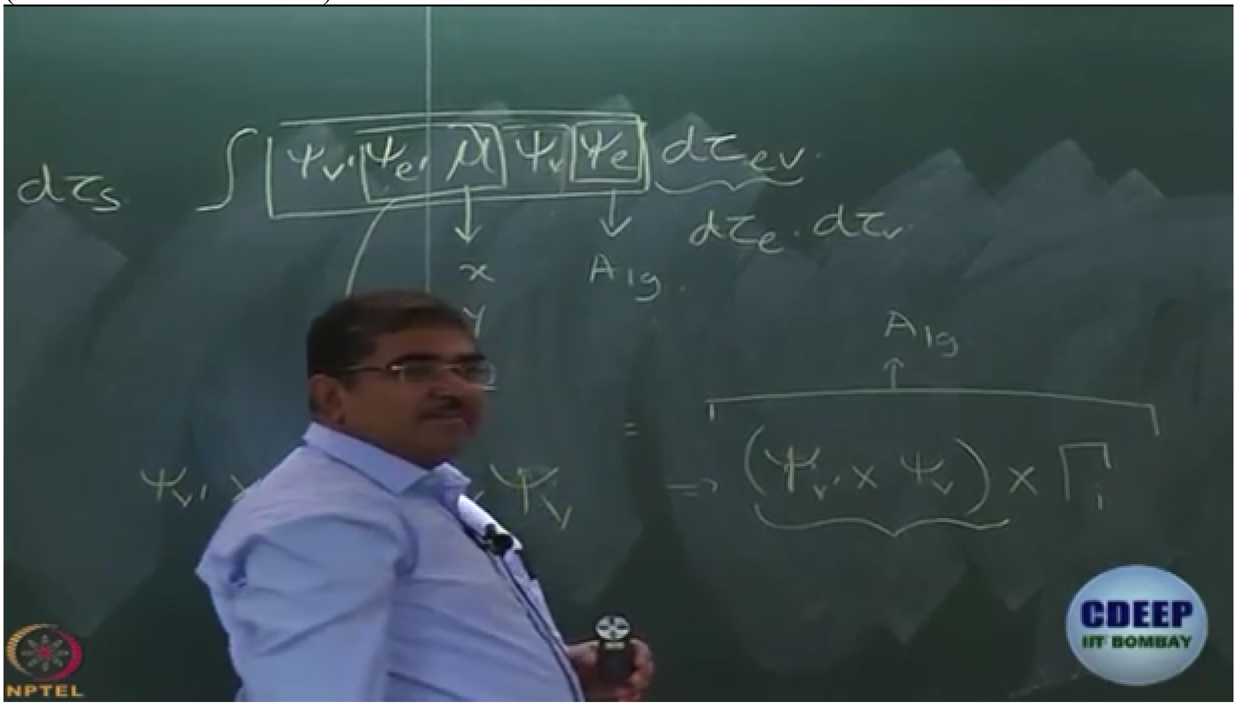

is of vibrational wave functions of origin and destination must contain gamma I, understood? See so far what we were saying or rather what are we saying now? We have this kind of, anyway it’s fine,

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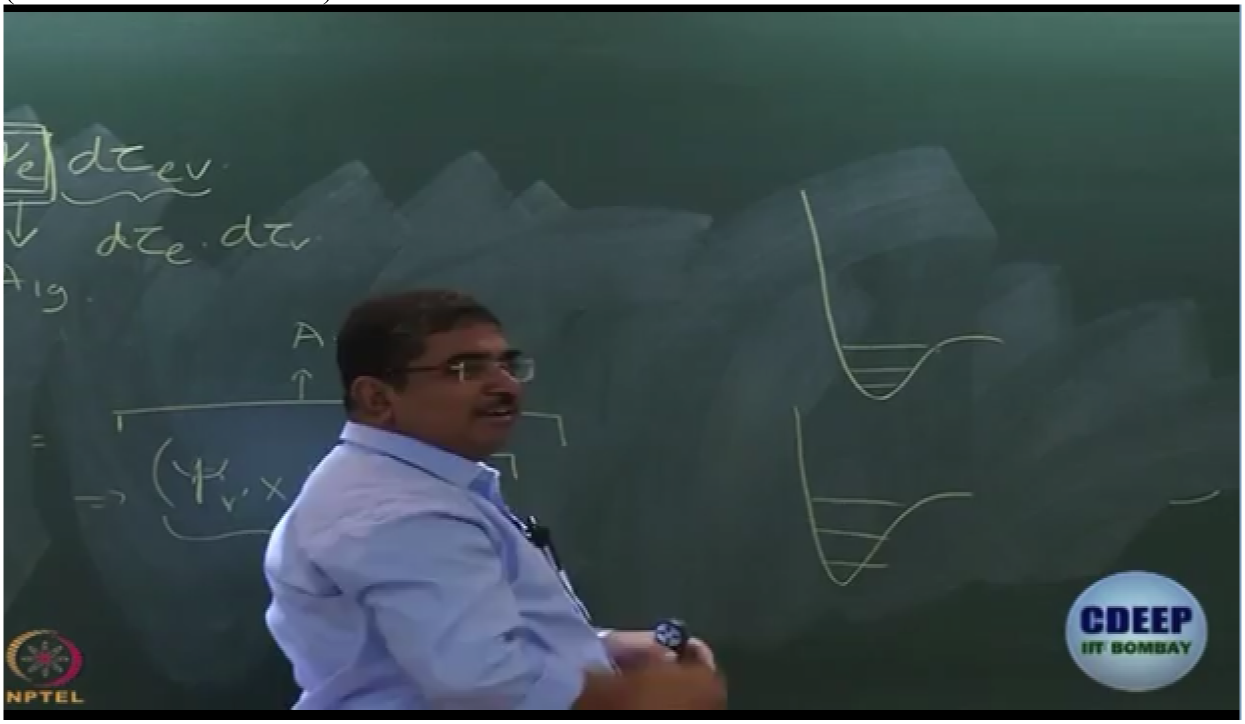

it will better if I draw this a little higher up but it's okay, suppose I go from here to here 0 to 1 dash, or suppose I go from here to here 1 to 0 dash, this 1 to 0 dash will that take place at room temperature usually? Not unless it's a very very low frequency vibration for normal frequencies that we have, this 1 dash to 0 will be seen only at high temperature right, it will be a hot bend, 0 to 1 dash it is possible, okay.

Let us restrict out this discussion to 0 to 1 dash and 1 to 0 dash because in any case 0 to 2 dash and all are always little less probable than 0 1 dash or 1 0 dash. So what we are trying to say is this suppose by origin, vibrational level of origin is V = 0 and suppose the vibrational level in the destination is V dash = 1, then the direct product of these two vibrational levels must contain the same symmetry as the symmetry that I got using the pure electronic wave functions and the dipole moment. Do you understand?

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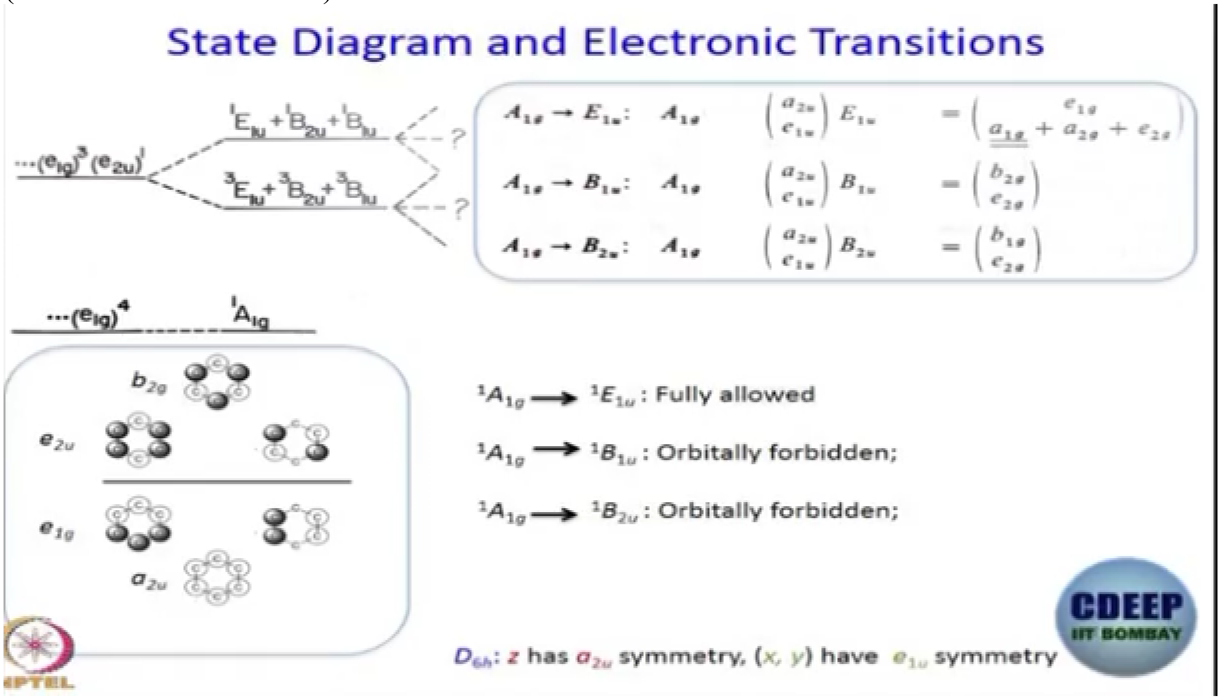

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So if I can have a direct product which has a symmetry of B2G, then B2G x B2G will give me A1G, right, then this will become vibronically allowed, if I have a direct product of vibrational levels which is E2G then E2G x E2G again will give me a some which will contain A1G, it will become vibronically allowed, if it has B1G then this one will become vibronically allowed E2G again this cingulate A1G to cingulate B2U will become vibronically allowed, right, so we are trying to understand conditions in which an orbitally forbidden transition becomes vibronically allowed and the conclusion that we have reached is that, that can happen when the direct product of the vibrational wave functions that are involved has the same symmetry as the direct product of the electronic states involved and a component of the dipole moment, that is too long a sentence, may not be easy to understand, but perhaps this is easy to understand.

Will you agree with me if I say that, if I have a direct product of vibration of wave functions that is B2G or E2G then this cingulate A1G to cingulate B1U should become vibronically allowed or if I have a direct product that is B1G or E2G than cingulate A1G to cingulate B2U will become vibronically allowed, right, right. I think we'll come back to this once again tomorrow because this part will require maybe half an hour to get absorb, but it will get absorbed only if you go back and study.

But before we close let me ask you one more thing, we are saying that this sai V and sai V dash are either 0 or 1, what do we already know about the symmetries of V = 0 wave function and V = 1 wave function, V = 0 wave function is totally symmetric, V = 1 wave function has the same symmetry as the normal mode, alright, and if I say that in our discussion of vibronic coupling we restrict ourselves to V = 0 and V = 1 wave function, see we are talking, when we talk about vibronic coupling we are saying that V = 0 to V dash = 0 this is a pure electronic transition, we want to work with situations where this pure electronic transition is not allowed, so we are saying that now we talk about 0 to 1 dash or 1 to 0 dash transitions, vibronic transitions, okay.

Since we restrict ourselves to V = 0, V = 1 wave function which means that now we don't even have to worry about the V = 0 wave function because that is A1G, right, so see I can simplify this discussion a little further, since one of them is A1G anyway, all I have to say is sai V = 1 should have the same symmetry as gamma I, right, and that has the same symmetry as the normal mode itself, okay, so the way to look at it is this from the orbital part only you generate the direct product, if it contains A1G like it does in the first case then fine it is orbitally allowed, we don't have to worry about it anymore, but if it is not orbitally allowed you don't throw away the direct product, you see what the product is B2G, E2G, B1G, E2G, but we are saying is in these cases if I have a normal mode who symmetry is B2G then that normal mode can couple with these electronic levels and can make this orbitally forbidden transition vibronically allowed. If I have a normal mode that has E2G symmetry than the same thing happens, in case of A1G to B2U transition I need normal modes of B1G or E2G symmetry, okay, so that is what we are saying, the first one can be vibronically allowed by B2G and E2G vibrations, the second one is vibronically allowed by B1G and E2G vibrations.

Do we have such vibrations? Do we have such vibronic coupling? That is what we'll learn tomorrow and that is what will, let us explain the electronic spectrum of benzene.

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