INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture no. – 54
Electronic Spectrum of Benzene

We are in the last phase of discussion of electronic spectroscopy, and right now we are doing a case study. Yesterday we have talked about the electronic states and transitions of benzene, and in doing that we have talked about something called vibronic coupling.
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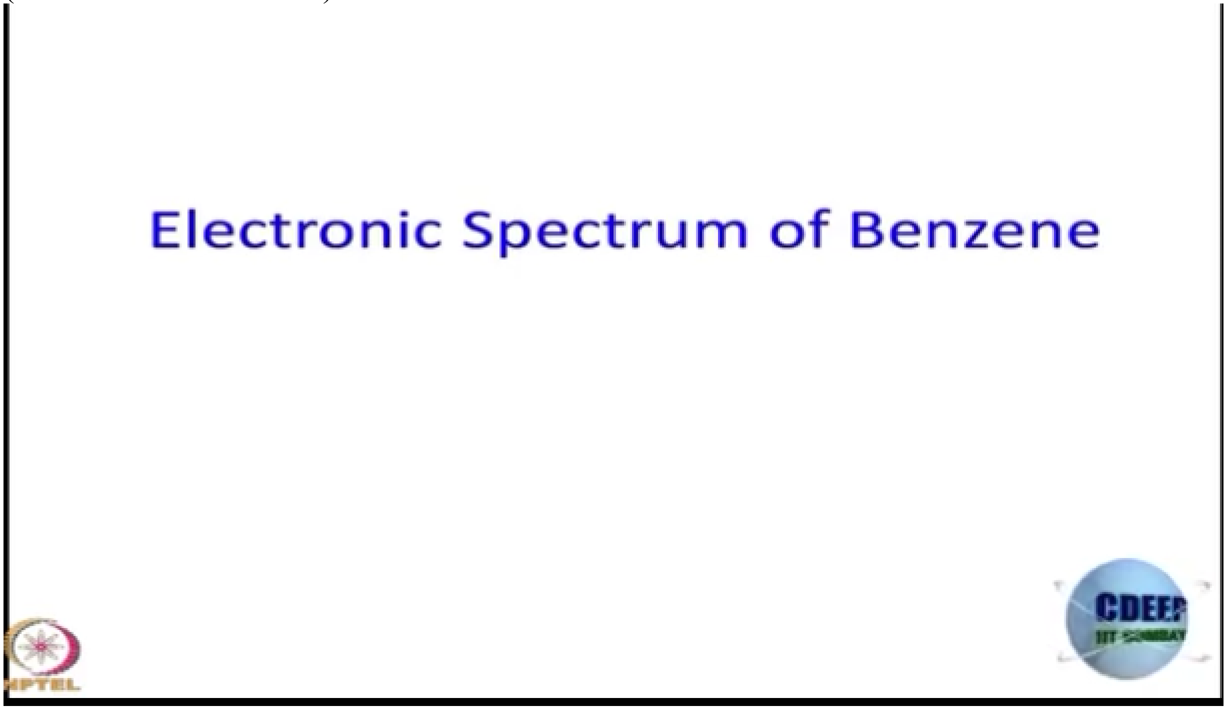

Electronic Spectrum of Benzene

Today we want to see what the spectrum actually looks like and how far we can go in interpreting what the bands are due to, how far we can go in assignment of the electronic absorption spectra bands of benzene, right.

But before that this is a summary of yesterday’s discussion,
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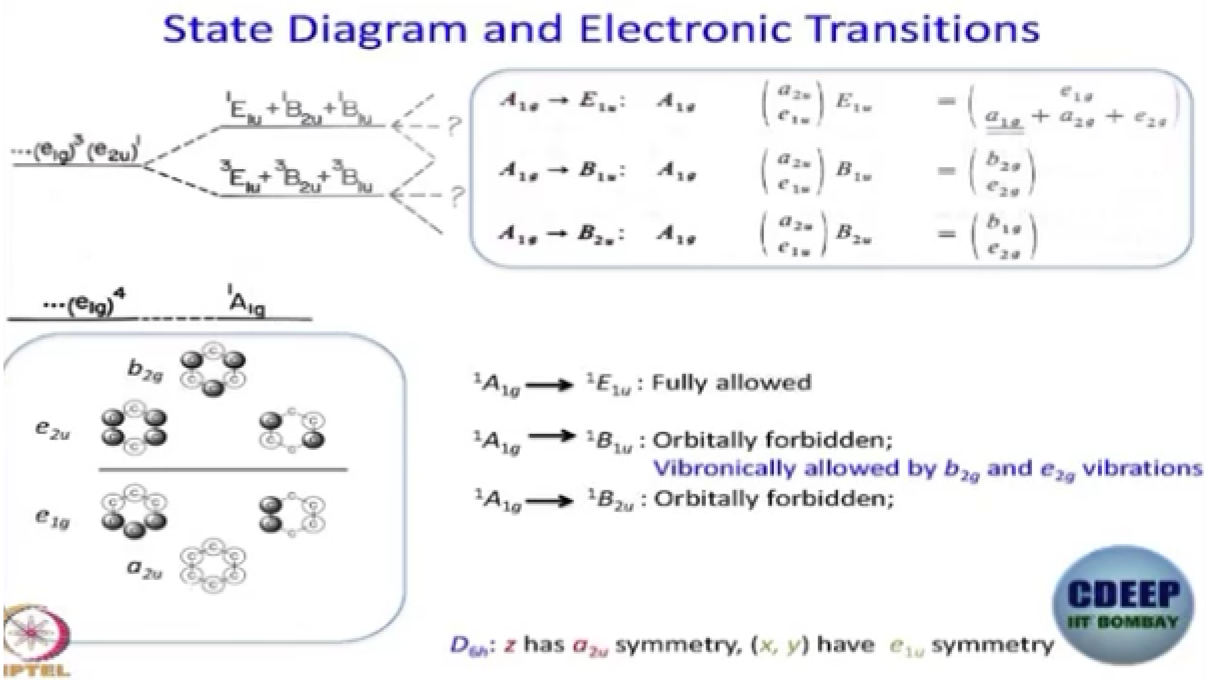

State Diagram and Electronic Transitions

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

$A_{1g} \rightarrow B_{1u}$: $A_{1g} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} B_{1u} = \begin{pmatrix} b_{2g} \\ e_{2g} \end{pmatrix}$

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

what we have said is this, we have understood the symmetry of the pi molecular orbitals of benzene, and from there we have said that the ground state of benzene, not very surprisingly a cingulate A1G, because all electrons, all occupied molecular orbitals at double occupied as we have learnt earlier that corresponds to a totally symmetric electronic state.

Then we talked about a homo to lumo transition, so one electron goes from the highest occupied pi bonding orbital to the lowest energy ash file unoccupied pi star bonding orbital, if you do that in the language of symmetry the transition is form an E1G orbital to an E2U orbital so the electron configuration now is E1G3, E2U1, so even out of this E1G orbitals one is double occupied, one is singlet occupied and one of the E2U orbitals is singlet occupied, and as we know when we have 2 orbitals that are singlet occupied the symmetry of the state is given by a direct product of the symmetry is of these singlet occupied orbitals, so we had done direct product of E1G and E2U, and we have seen using the product table of D6H point group we have seen that we get 3 states E1U, B2U and B1U, and of course this two electrons are now into non degenerate states, so you can have singlet as well as triplet combinations, so you end up generating 6 different states, but as of now we don’t know what the relative ordering of energies are, we have to do it as I said yesterday by a more rigorous quantum chemical calculation and by the time we are done with the discussion today, we will see that we have an experimental way of determining not only the order, but also the absolute values of this energies from the spectrum of benzene, okay.

Then we wanted to see what are the states, first of all we are talking about transitions that are spin allowed, we are going to encounter one transition that is spin forbidden, but as we know spin forbidden transitions have very small values of transition probability or molar absorption coefficient or extinction coefficient whatever you might want to call it, so for now we limit our discussion to cingulate cingulate transitions, the ground state as we agreed is A1G, excited states are E1U, B2U, B1U, so when we talk about cingulate A1G to cingulate E1U, cingulate A1G to cingulate B1U, cingulate A1G to cingulate B2U, we asked the question which of this transitions are allowed and which of this transitions are not allowed. And to understand that we go by the usual root, we need to know the symmetries of X, Y and Z coordinates because we have to work out the symmetry of the triple product, the three factors involved in this triple product are the wave function from which the transition originates, the destination wave function and one of the components of the dipole moment, so X or Y or Z that is what we did here, right, the initial suggest that in _4:55_ convention they don't write sai 2 mu sai 1, they write sai 1 mu sai 2, for the purpose of direct product it doesn't matter.

So A1G in all the three cases denote the symmetry of the ground state, E1U, B1U, B2U are the symmetries of the excited state form by homo to lumo transition and A2U denotes what? A2U is Z, right, and E1U contains X as well as Y, E1U as you know is a two dimensional representation, so X and Y jointly form the bases of this two dimensional representation, so what we did is we worked out these triple products in all the cases, and we saw that only in the case of A1G to E1U transition through XY we get something in A1G, so we said that only cingulate A1G to cingulate E1U is fully allowed and it's XY polarized.

The other two transitions cingulate A1G to cingulate B1U or cingulate A1G to cingulate B2U are orbitally forbidden. After this we embarked on the discussion on how it might be possible for orbitally forbidden transitions to becomes vibronically allowed, and this is what we had said. When we wrote the expression for the transition moment integral we wrote it like this, alright,
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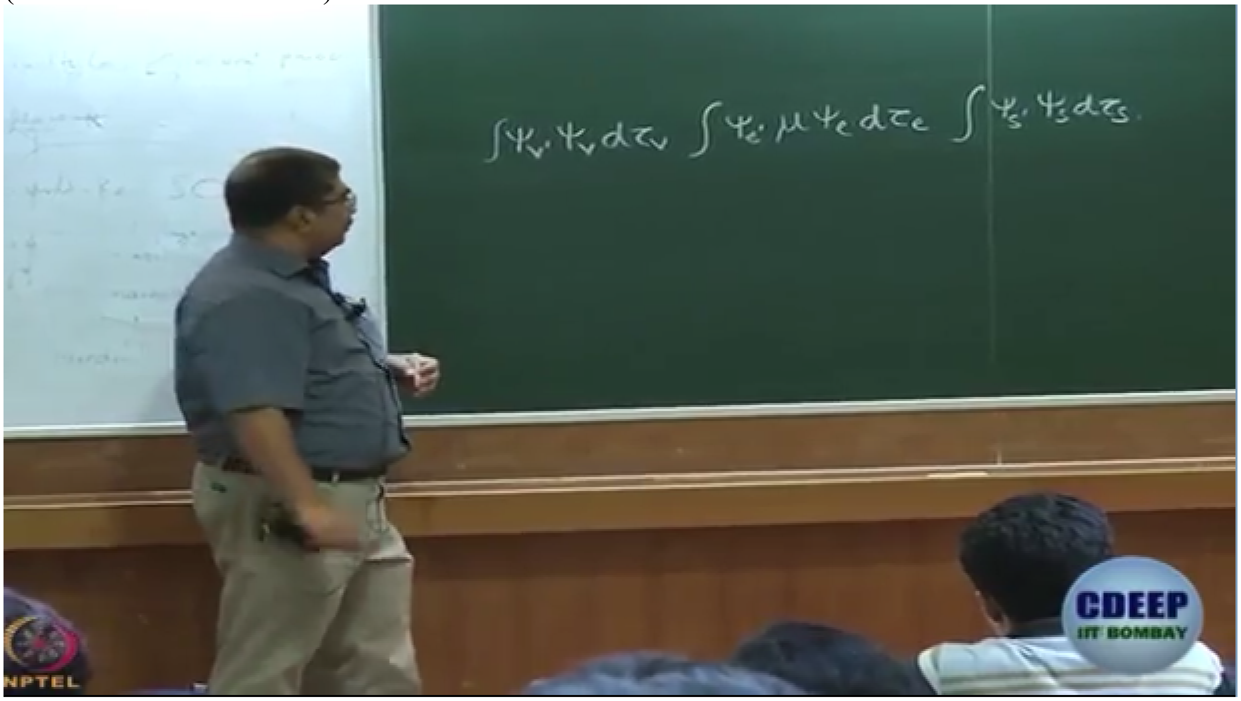

but suppose you cannot separate this two, then the integral you have to worry about is something like this, so we are talking about a situation where Born Oppenheimer approximation doesn't work anymore,

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$$\underbrace{\int \psi_{v'}\psi_v d\tau_v \int \psi_{e'} \mu \psi_e d\tau_e}_{\int \psi_{v'}\psi_{e'} \mu \psi_e \psi_v d\tau_{ev}} \int \psi_{s'}\psi_s d\tau_s.$$

you cannot separate the coordinates of electronic and vibrational motion they're entangled, of course what you should ask at this point is while will I even write this wave functions like that, I should ideally write something like sai V dash E dash and sai EV, alright, but then those of you who've studied perturbation theory will know the way we,

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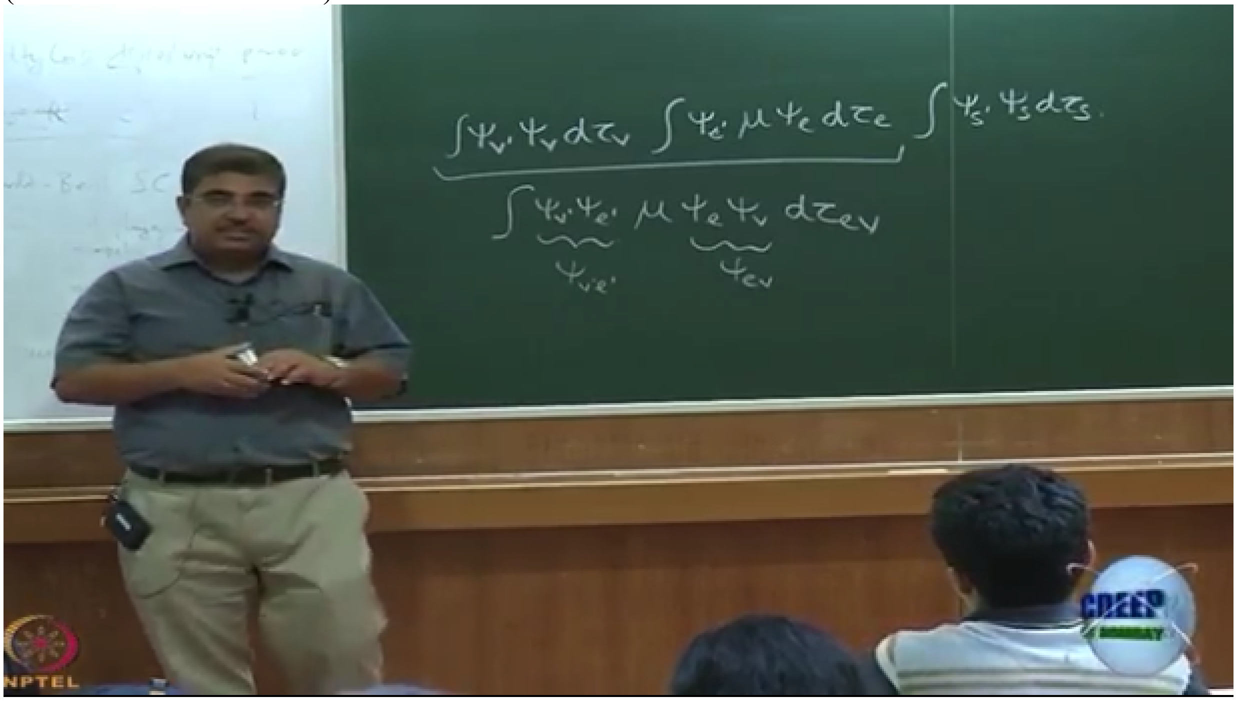

$$\underbrace{\int \psi_{v'}\psi_v d\tau_v \int \psi_{e'} \mu \psi_e d\tau_e} \int \psi_{s'}\psi_s d\tau_s.$$

$$\int \underbrace{\psi_{v'}\psi_{e'}}_{\psi_{ve'}} \mu \underbrace{\psi_e \psi_v}_{\psi_{ev}} d\tau_{ev}$$

I mean everybody has studied so everybody would know the way we handle this is that generally when we have a situation like this we expand it according to Taylor series, right, and then if you write this as a perturbation term then the product of the increments actually it's too small to be considered, so you can still get away by using a product of wave functions as long as you recognize that the coordinates are not separable anymore, so this is the integral that we have to work with if you want to talk about vibronic coupling.

Vibronic coupling means coupling of electronic and vibrational motion, coupling means you cannot consider them separately anymore, they talk to each other, so here vibrational and electronic coordinates actually talk to each other, they cannot be disentangle, so this is what it is.

Now if I want to work with this integral then essentially what I am saying is that I must worry about this product, product of all this wave functions and component of the dipole moment,
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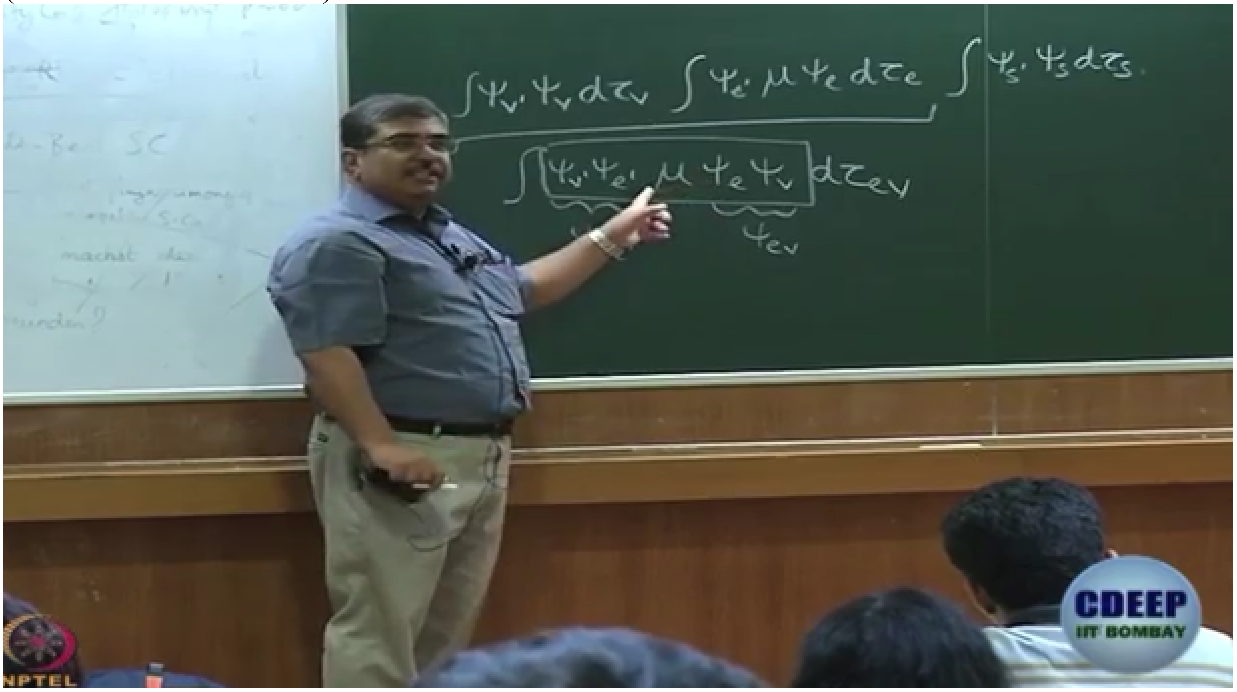

this product must contain the totally symmetric representation, if that is the case then the transition which is orbitally not allowed can be vibronically allowed, are we okay so far? Then let me take this and let me write like this, sai V dash sai E dash X, Y, Z sai E sai V, we need to determine the symmetry of this alright, don't we already know what is the symmetry of this triple product? Right, if we come back to us with specific example for A1G to E1U transition
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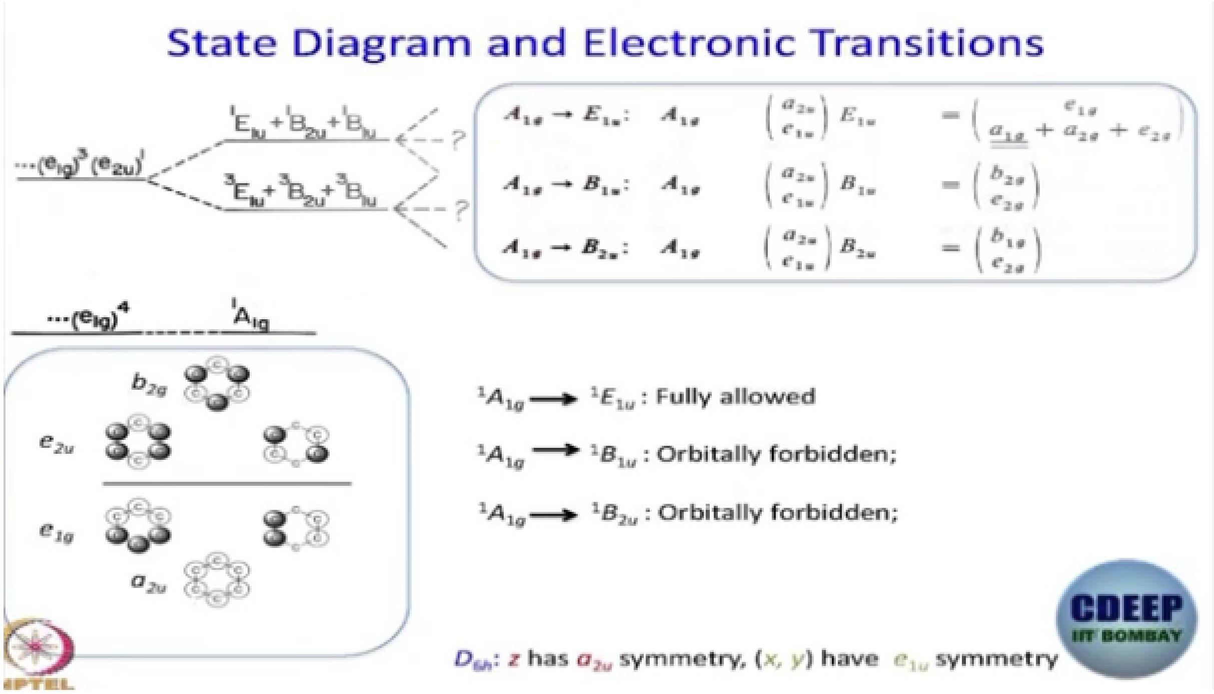

State Diagram and Electronic Transitions

$\cdots(e_{1g})^3(e_{2u})^1$

${}^1E_{1u} + {}^1B_{2u} + {}^1B_{1u}$

${}^3E_{1u} + {}^3B_{2u} + {}^3B_{1u}$

$\cdots(e_{1g})^4$ ${}^1A_{1g}$

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the triple product is A1G x A2U x E1U that gives you E1G or A1G x E1U x E1U that gives you A1G + A2G + E2G, right, so we already know what the symmetry of this triple products are for benzene that we have worked it out, so what we need to worry about is suppose this is something gamma I, we need to worry about sai V dash gamma I sai V this triple product.

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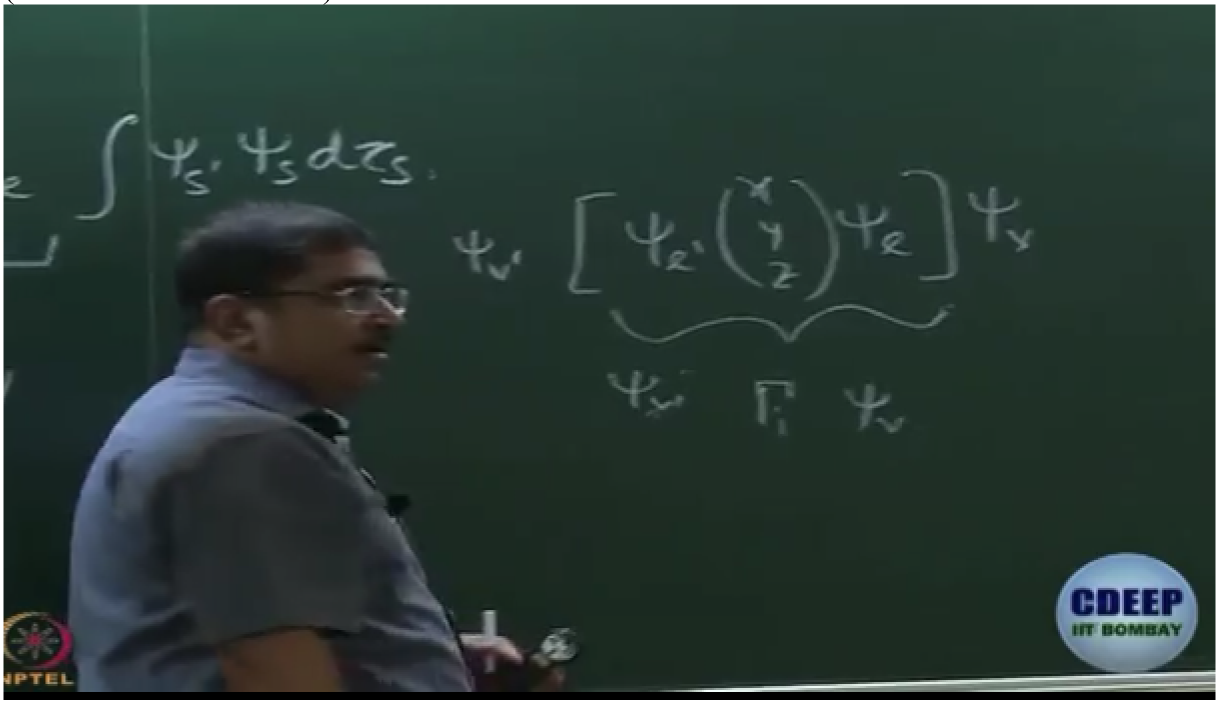

And then what we also said yesterday is that we are going to worry only about 0 1 dash transition, 0 1 dash means vibrational level for the lower electronic level is V = 0, vibrational level for the destination level is 1, the destination level is usually denoted by a dash, V dash to 1, so 0 to 1 dash this is the one that we'll see all the time, right, 0 is the only level that is populated at room temperature and if you work at higher temperature what will consider is 1 dash to 0, I'm not trying to say that 0 to 2 dash, 0 to 3 dash will not take place, they will take place, but for our discussion here, these two are enough, alright.

So if that is the case we know very well, suppose I work with this situation 0 1 dash, what is the symmetry of sai V in that case? It's totally symmetric, right, V=0 we have discussed this earlier when talking about normal modes of vibration this is the same symmetry, this is totally symmetric so in this case I'll just write A1G.

What is the symmetry of sai V dash? If V dash = 1, yeah, what is the symmetry of sai V dash? If V dash = 1, same as that of the normal mode, remember from our discussion of normal mode same symmetry as xi. Now the convenient thing is since we have A1G already, I don't even have to worry about this, my only concern is this xi and gamma I, understood.

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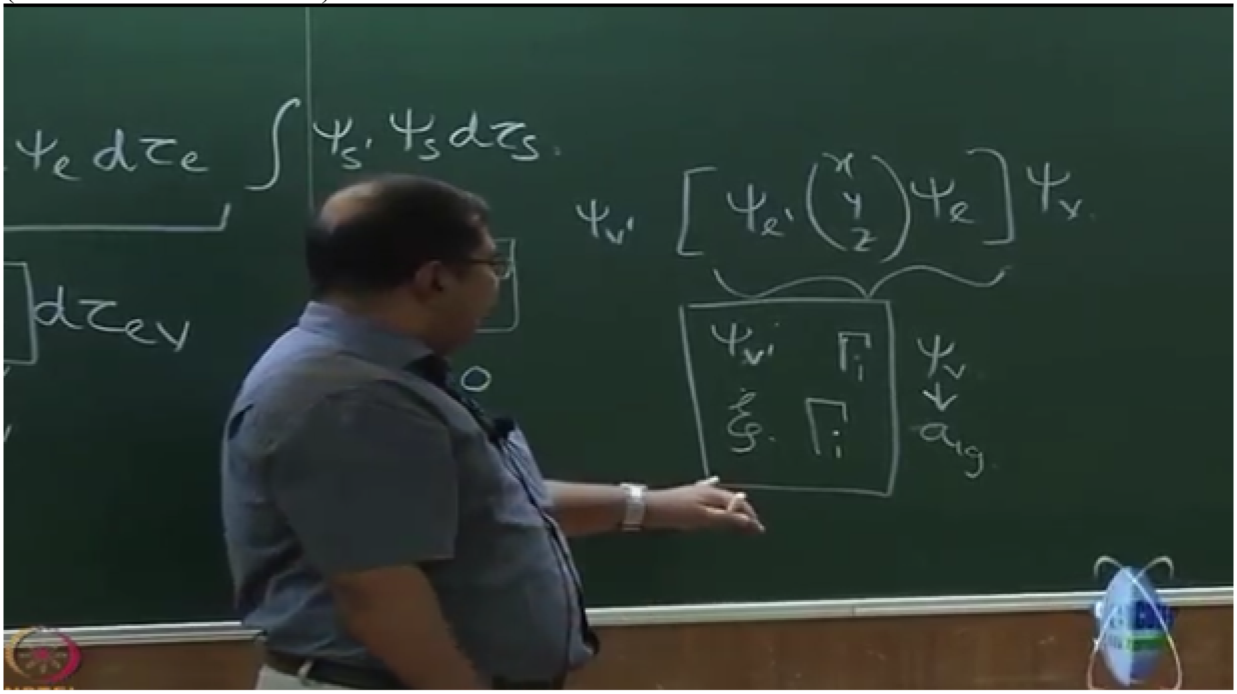

Now tell me when will the direct product of the symmetries of xi and this gamma I contain a totally symmetric representation, we have derived this small working formula earlier, when will they contain the totally symmetric representation, when they are at the same, right, if the symmetry of normal mode is the same as gamma I then your, then the direct product will contain a total symmetric representation and therefore the transition that is orbitally forbidden will become vibronically allowed, okay, this is what we've discussed yesterday.

So now you see with that background now we can talk about whether any transition in benzene that is orbitally disallowed can become vibronically allowed.

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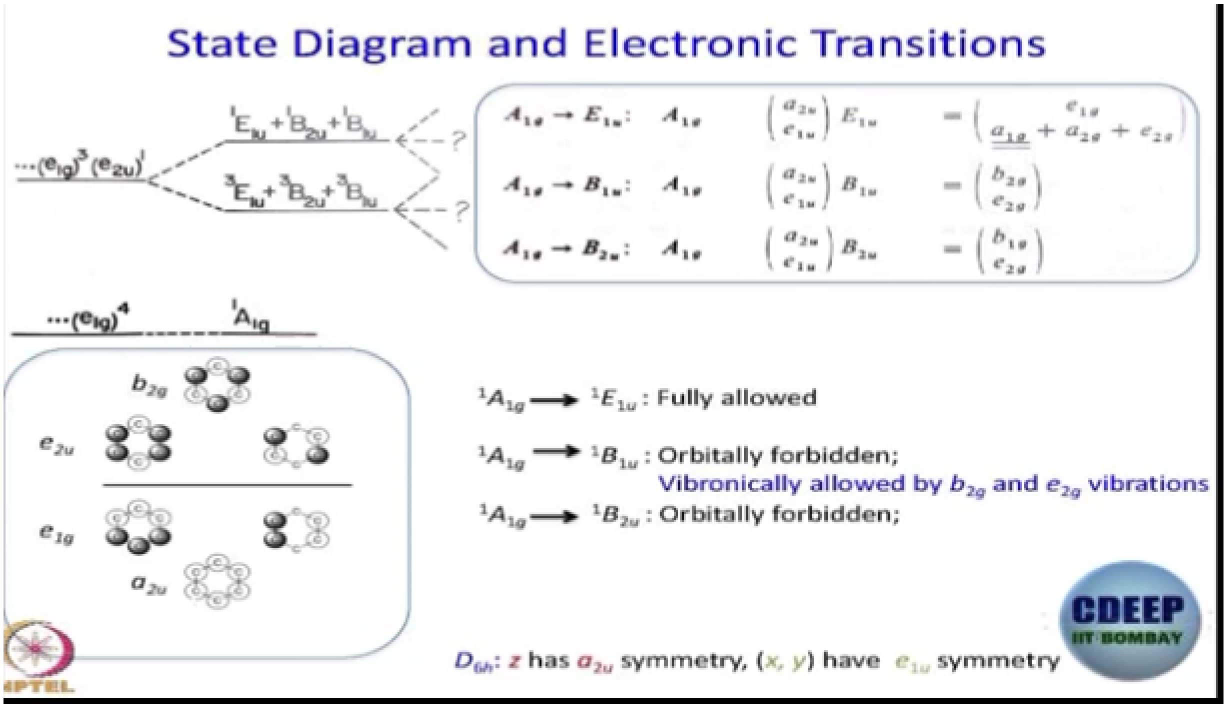

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What about the first one? We don't even have to worry about the second one right, cingulate A1G to cingulate E1U we don't even worry about that, actually we don't worry about the first one because already it is allowed.

Let's talk about the second one, cingulate A1G to cingulate B1U this has turned out to B2G and E2G, so what kind of vibrations are required to make this cingulate A1G to cingulate B1U vibronically allowed, vibrations of which symmetry? Either B2G or E2G, agreed, so this cingulate A1G to cingulate B1U which is orbitally forbidden can become vibronically allowed by coupling with V2G and E2G vibration.

Similarly the cingulate A1G to cingulate B2U can become vibronically allowed by coupling with B1G and E2G vibrations, simple, okay, so far so good I hope everybody is understood everything, any question? Any question? If not, what is the next question to ask here? What would the next question be? We've established the conditions for which these orbitally forbidden transitions can become vibronically allowed, you have to have vibrations, vibrational normal modes of certain symmetries, so of course the next question to be asked is does benzene have normal modes of vibrations of those particular symmetries, right, I hope we can all work it out, symmetries of normal mode we have learnt, right, how many normal modes of vibrations will be there for a benzene?

Yeah, okay 3N – 5 or 3N-6, and what is N for benzene? 12 or 6? Sure, not 6, so 3 x 12 – 6, how much is that? 30, in one of the questions in all the exams I forgotten whether it was 4 4 2 or 8 0 1, I had actually said this question, find out the symmetries of normal modes of vibration of benzene, okay, it's a valid question, but for now we don't have to do it, I'll just give you the answer, this is, so this is the question to ask, right, the answer is this, we'll come to that a little later, sorry,
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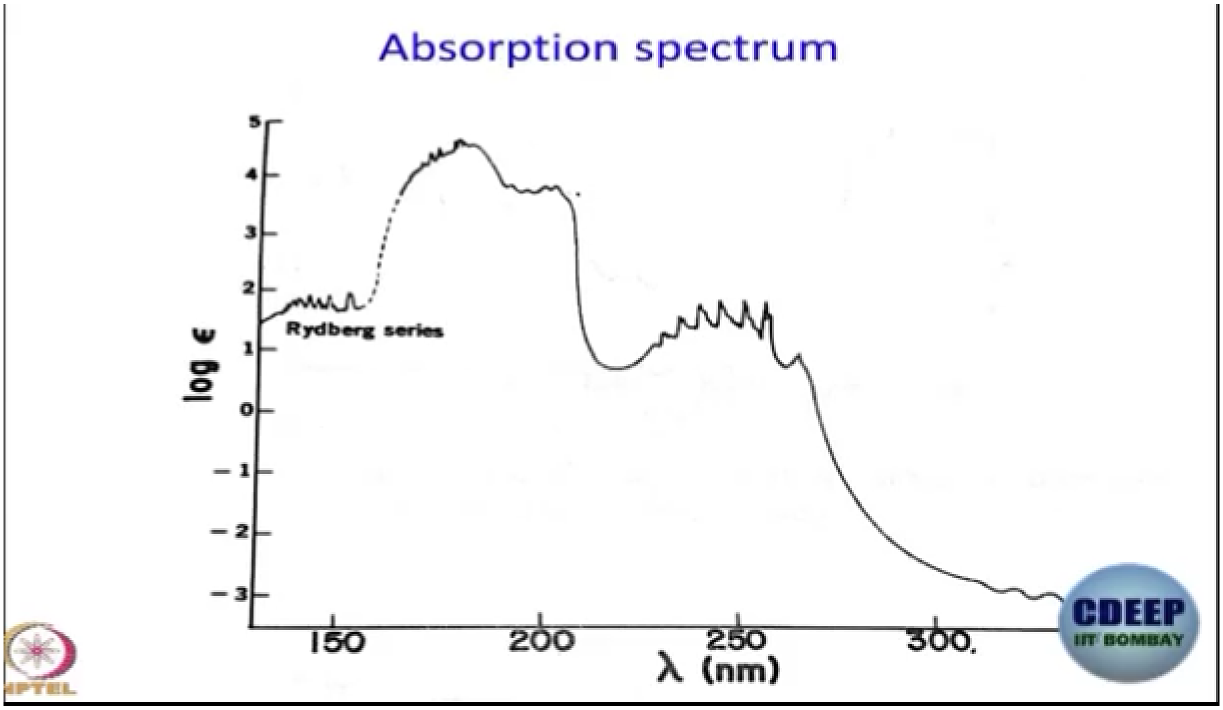

Absorption spectrum

so in a while I’ll show you what are the normal modes of vibration that are there for benzene, but before that this here is the absorption spectrum of benzene, does it look weird or not? It looks weird to me. Can you tell me why it looks weird? The answer is there, if you look at the spectrum you can figure out why it looks little weird, it doesn’t really look like the absorption spectrum that you are seeing, yes, it doesn’t look weird, does it save answer? Vishwaroop, why does it look weird? Y axis is in log, is it similar plot? Why is the Y axis in log? When do we draw semi log plots? When do we have a logarithmic scale? Yes, easier answer.

When do we draw log scale? When we want to show the small intervals and large intervals together in the same plot because the moment you take log what happens is the smaller numbers get amplified, see this is your 10 to the power -1, this is 10, no this is 1, this is 10, so this part is actually magnified and the upper ones are kind of shank, so if we want to see small numbers as well as large numbers together then you use a log scale and that is exactly the reason why this is plotted in log scale so that we can see strong transition, strong bands as well as weak bands, alright, the biggest one is this, and what is the value there? Almost 10 to the power 5, isn’t it? So 10 to the power 5 when epsilon is 10 to the power 5 what kind of a transition is it? 10 to the power 3 to 10 to the power 5 we have discussed earlier is a fully allowed transition, so we can assign that band directly to fully allowed transition.

What is the only fully allowed transition? Cingulate A1G to A1U? E1U, right, you are right, so cingulate A1G to cingulate E1U,
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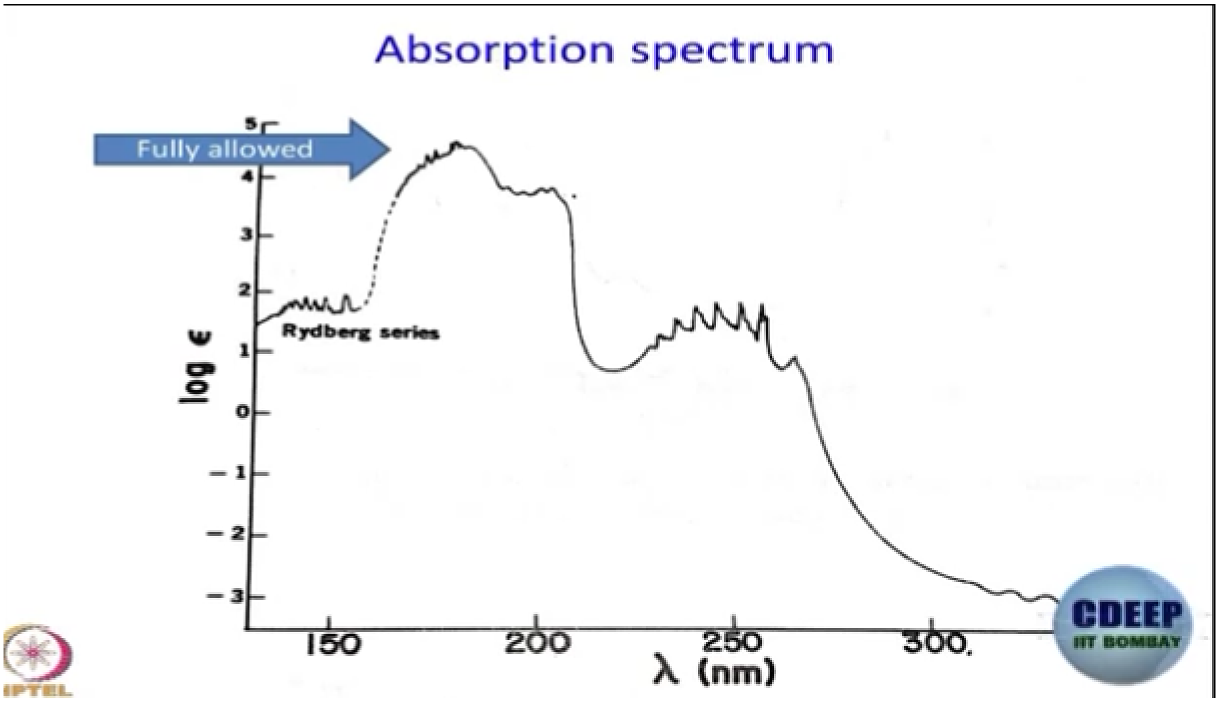

Absorption spectrum

Fully allowed

so already with whatever we have discussed so far we can assign the strongest band that is there in benzene,

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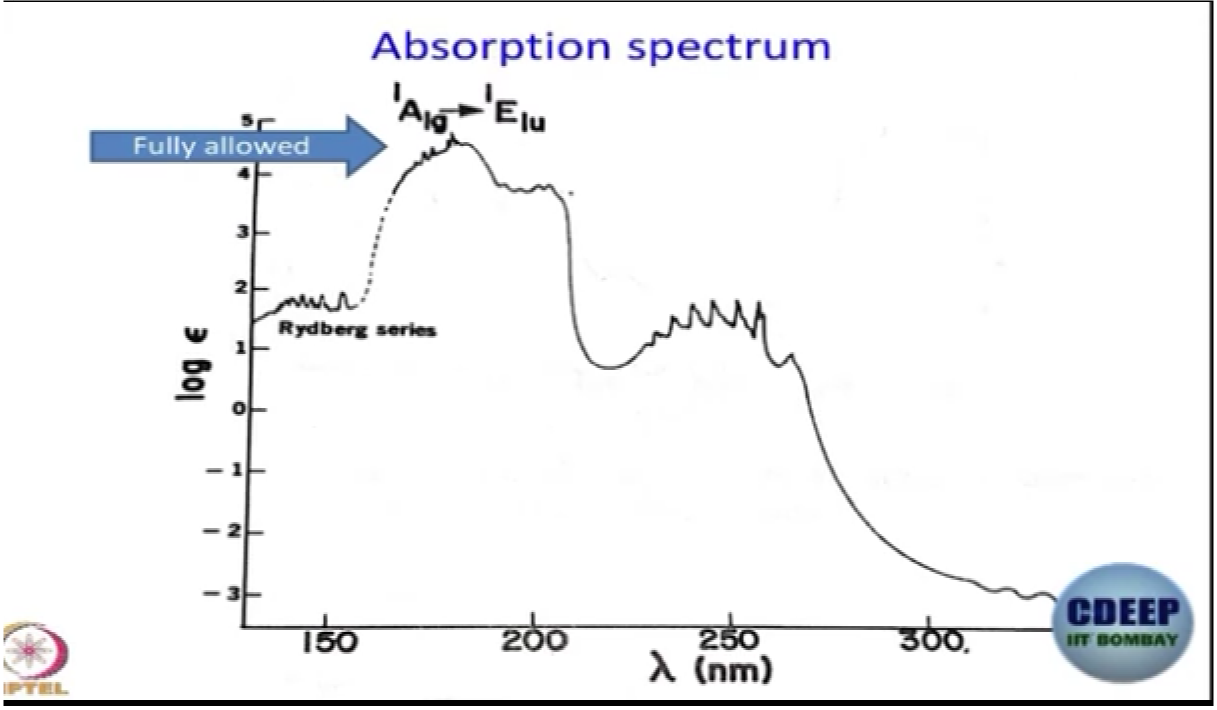

Absorption spectrum

${}^1A_{1g} \rightarrow {}^1E_{1u}$

Fully allowed

but usually that is not the most useful band, you know why because look at the wave length, it’s somewhere between 150 and 200 nanometer, usually we don’t even work at such wavelengths unless you can work in backroom and all that.

What is the next band? It's somewhere here around 200 nanometer, this is orbitally forbidden because it's a little smaller and this band is definitely orbitally forbidden because your epsilon is only 10 to the power 2, but then you know what? This is really the most important band in benzene, what is the region? 250, 260, 240 right, this is called the benzenoid band, in fact if you have any compound which has an aromatic compound, this is the band that you will always see, okay, it looks a little different in solution state, this is gas spectrum,

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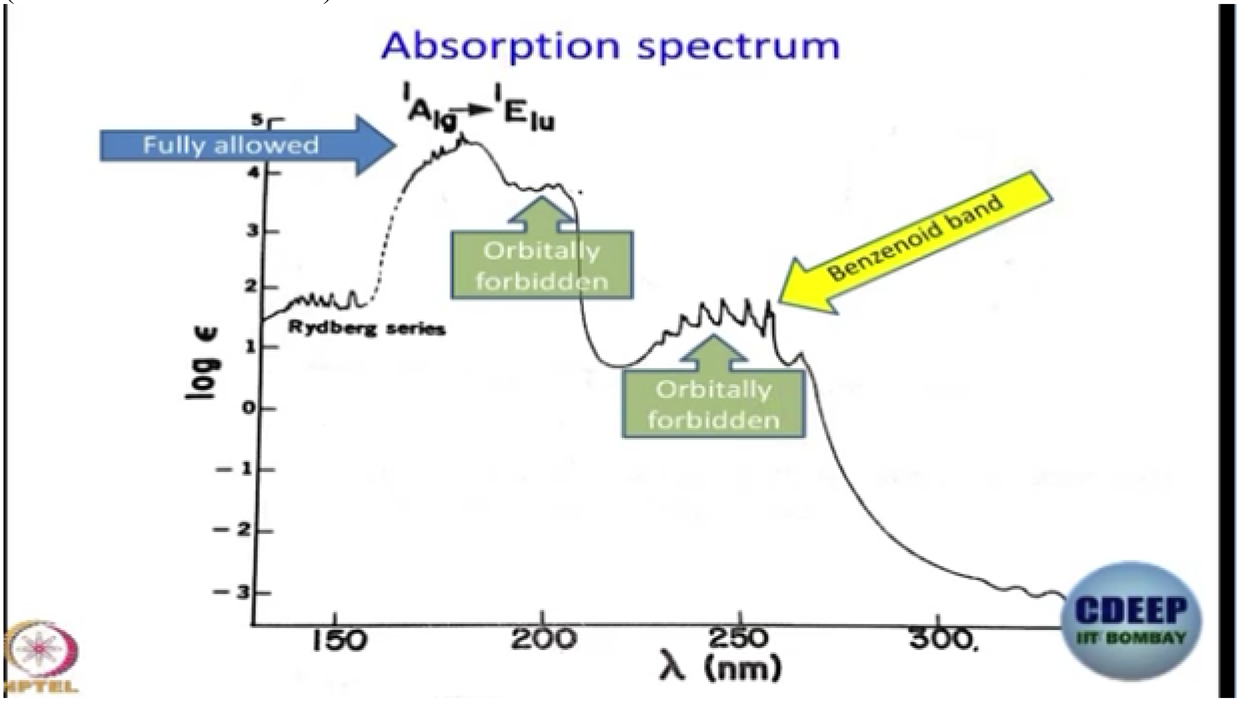

Absorption spectrum

but then and also it is semi log, but this 250, 260 nanometer is where all aromatic compounds have an absorption, so that band is Markov aromatic state, so it's most important, it's a benzenoid band and as you see it's an orbitally forbidden transition, so we want to find out which one it is, there are two candidates right, we want to know which one it is, and this one of course is really very small right, had we not made a similar plot we would have missed it, it's like 10 to the power -3,

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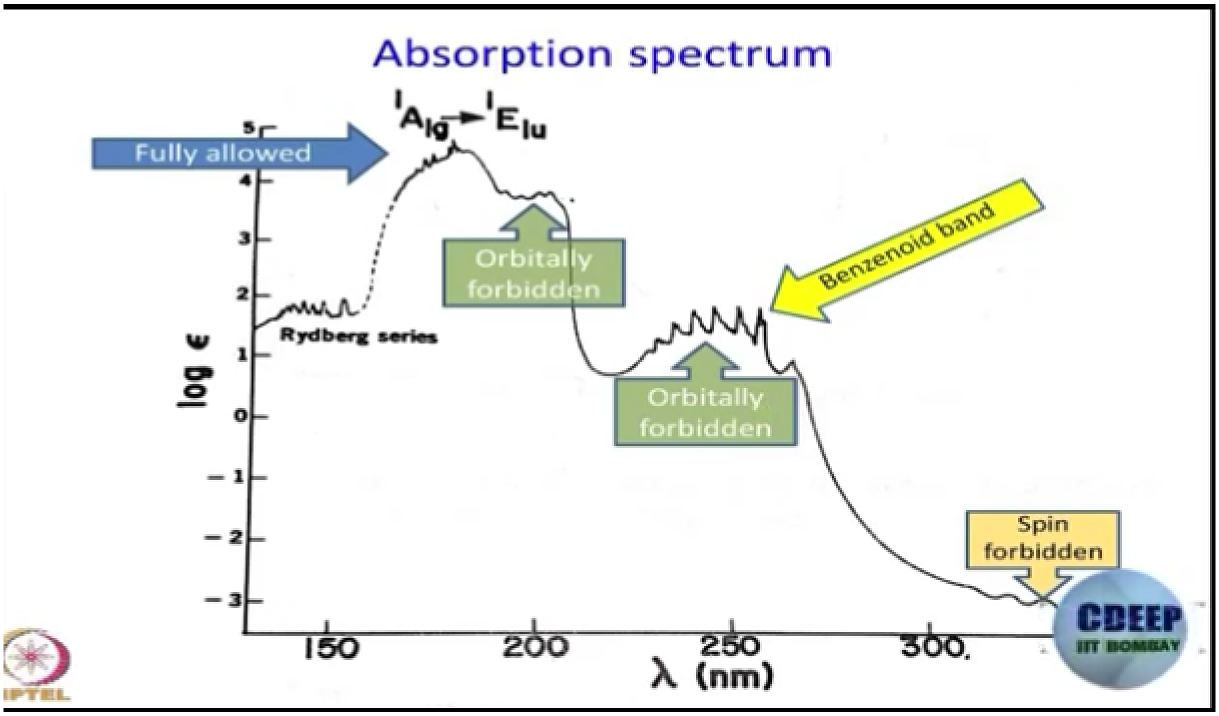

Absorption spectrum

that is obviously spin forbidden transition, alright, so this is the spectrum that we are trying to understand.

Now if I take a closer look at the benzenoid band this is what it looks like, now it is not semi log anymore, Y axis is now linear, so it looks a little better, so the question is what is the, where do I get this band from, which transition? As you know since it's an orbitally forbidden transition there are two candidates, one is cingulate A1G to cingulate B1U, the other is cingulate A1G to cingulate B2U, and we know that they would become vibronically allowed by different times of vibration.

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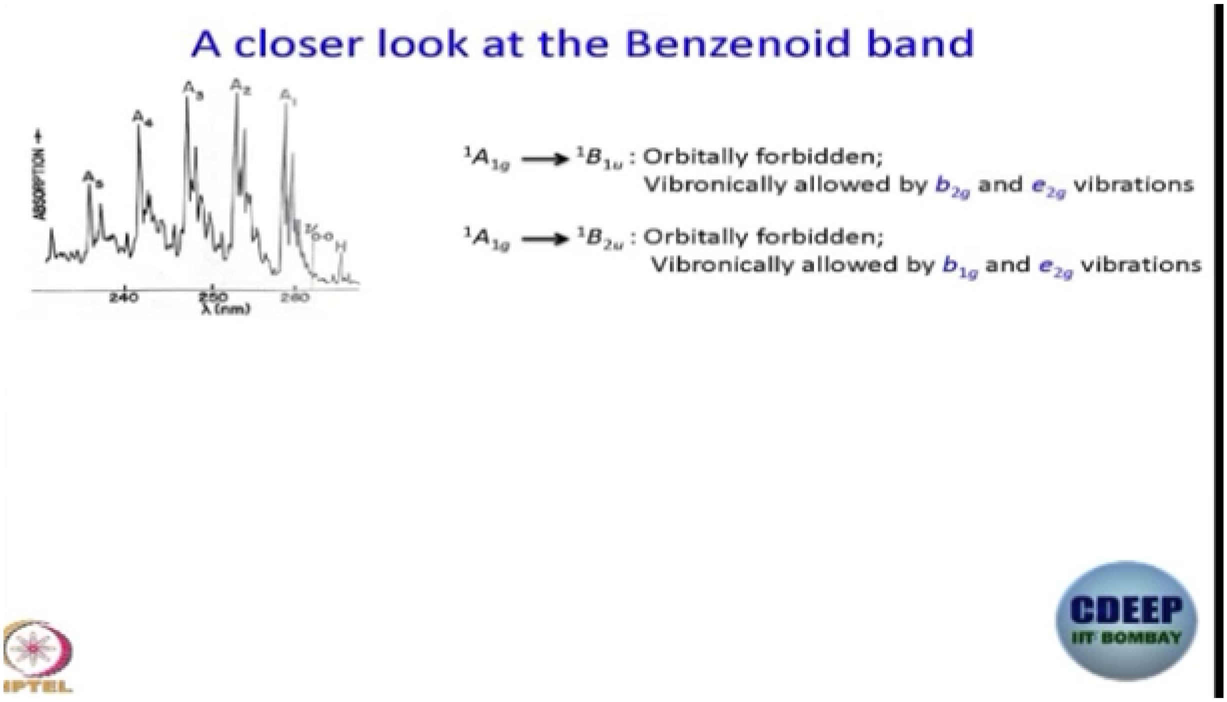

A closer look at the Benzenoid band

$^1A_{1g} \longrightarrow {}^1B_{1u}$: Orbitally forbidden;
Vibronically allowed by b_{2g} and e_{2g} vibrations

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Now this is what I had kind of jumped again and started talking about that is while ago, now I'll show you at least of normal modes of vibration of benzene, I'll show you symmetries as well as energy, anything in bracket is theoretically calculated energy, anything not in bracket is experimentally absorbed in it, here it goes, okay.

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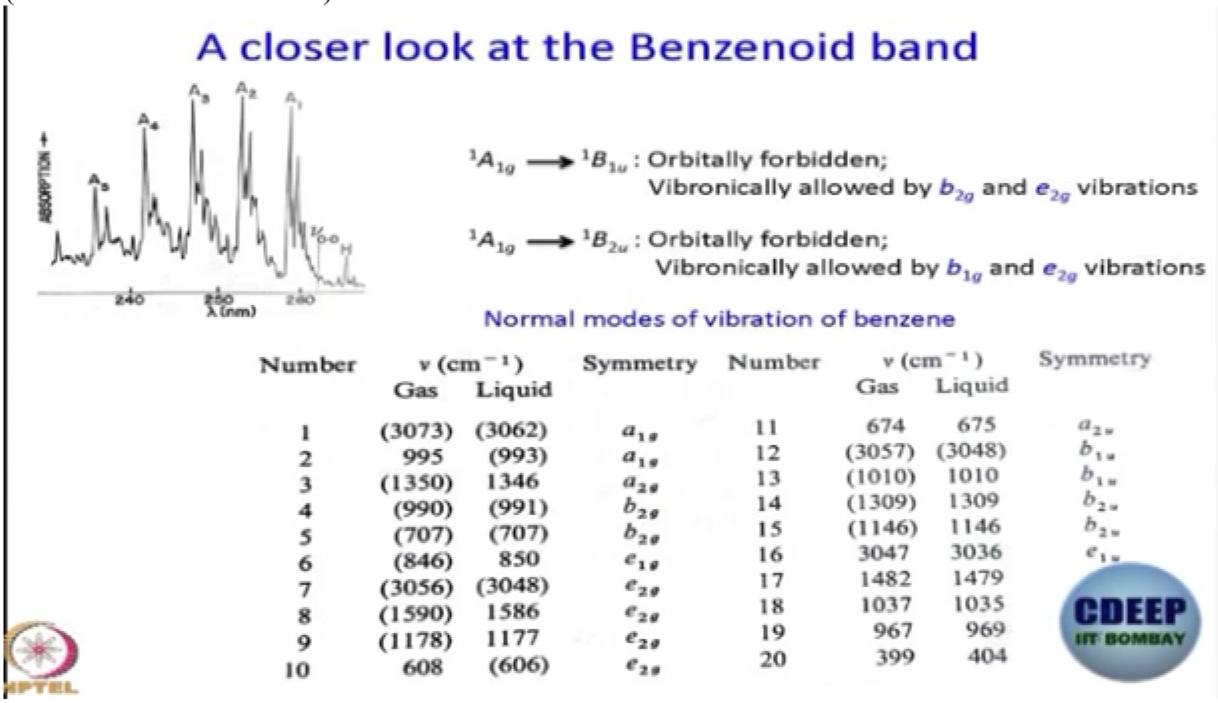

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Normal modes of vibration of benzene

Number	ν (cm^{-1})		Symmetry	Number	ν (cm^{-1})		Symmetry
	Gas	Liquid			Gas	Liquid	
1	(3073)	(3062)	a_{1g}	11	674	675	a_{2u}
2	995	(993)	a_{1g}	12	(3057)	(3048)	b_{1u}
3	(1350)	1346	a_{2g}	13	(1010)	1010	b_{1u}
4	(990)	(991)	b_{2g}	14	(1309)	1309	b_{2u}
5	(707)	(707)	b_{2g}	15	(1146)	1146	b_{2u}
6	(846)	850	e_{1g}	16	3047	3036	e_{1u}
7	(3056)	(3048)	e_{2g}	17	1482	1479	
8	(1590)	1586	e_{2g}	18	1037	1035	
9	(1178)	1177	e_{2g}	19	967	969	
10	608	(606)	e_{2g}	20	399	404	

So what are we asking? We are asking, do we have B2G vibration? Do we have E2G vibration? Do we have B1G vibration? Okay, what is the answer? There is no B1G right? Benzene does not have B1G vibration.

What about B2G, do we have B2G? Yes, where are they? Here, I'm using a long file anyway,
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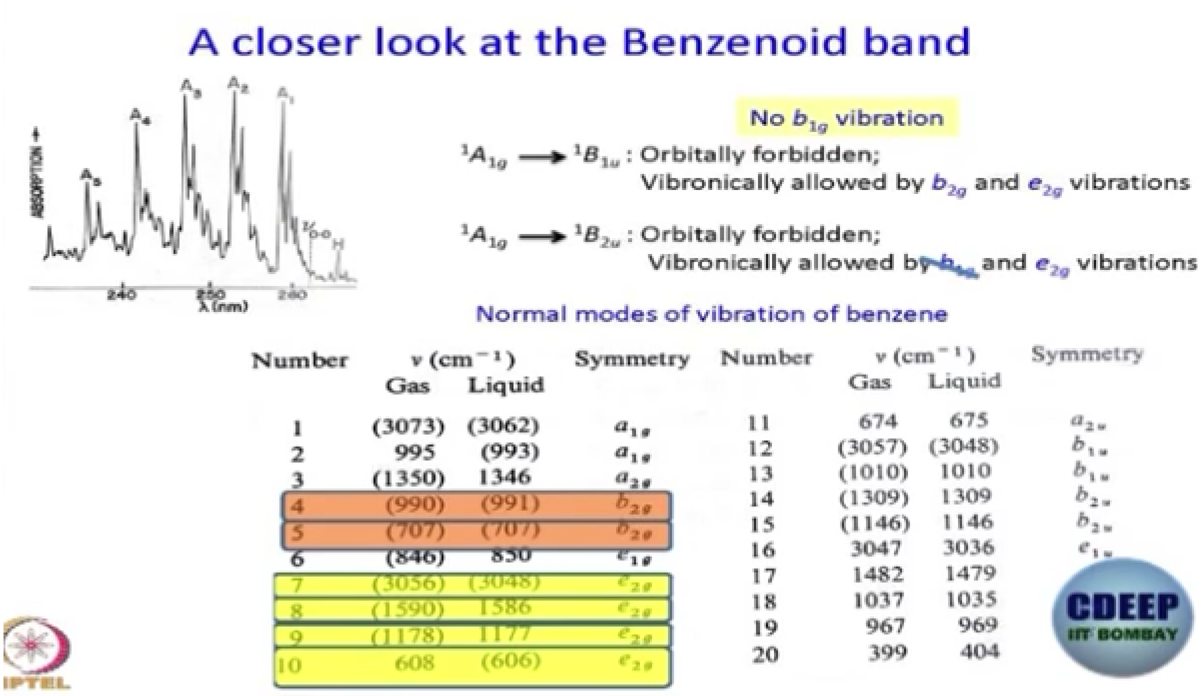

A closer look at the Benzenoid band

No b_{1g} vibration

$^1A_{1g} \rightarrow {}^1B_{1u}$: Orbitally forbidden;
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2	995	(993)	a_{1g}	12	(3057)	(3048)	b_{1u}
3	(1350)	1346	a_{2g}	13	(1010)	1010	b_{1u}
4	(990)	(991)	b_{2g}	14	(1309)	1309	b_{2u}
5	(707)	(707)	b_{2g}	15	(1146)	1146	b_{2u}
6	(846)	850	e_{1g}	16	3047	3036	e_{1u}
7	(3056)	(3048)	e_{2g}	17	1482	1479	
8	(1590)	1586	e_{2g}	18	1037	1035	
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10	608	(606)	e_{2g}	20	399	404	

these are the B2G vibrations and these are the E2G vibrations, okay, let me arrange it a little bit and this is what the situation is, this is the benzenoid band we are trying to understand, we have a couple of B2G vibrations,
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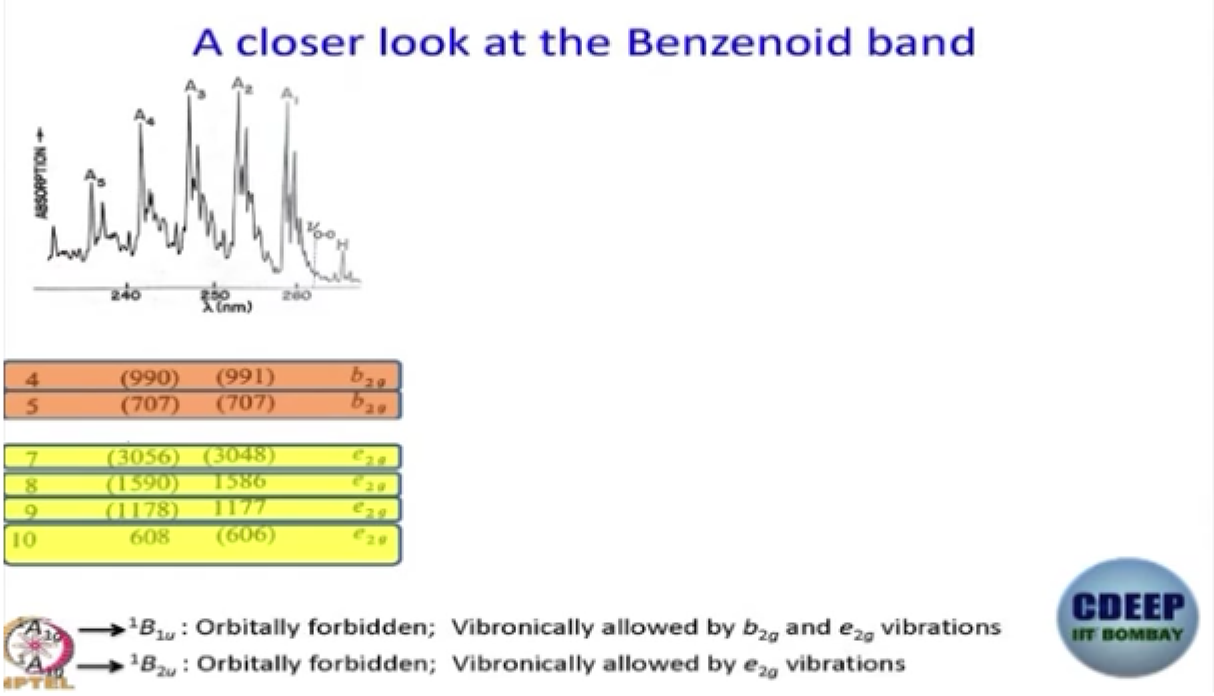

A closer look at the Benzenoid band

4	(990)	(991)	b_{2g}
5	(707)	(707)	b_{2g}
7	(3056)	(3048)	e_{2g}
8	(1590)	1586	e_{2g}
9	(1178)	1177	e_{2g}
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$^1A_{1g} \rightarrow {}^1B_{1u}$: Orbitally forbidden; Vibronically allowed by b_{2g} and e_{2g} vibrations

$^1A_{1g} \rightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations

we have actually 4 x 2, 8 E2G vibrations, and we are trying to understand which one is it. If it is cingulate A1G to cingulate B1U then it will be vibronically allowed by B2G and E2G vibration, if it is the other one cingulate A1G to cingulate B2U then it'll be vibronically allowed only by E2G vibration, okay.

So let us see how you can go about solving this riddle. To do that first question we ask is do you see which one is the lowest energy band here? Which is the lowest energy band? This one, the one where we have written H, right, that is the lowest energy band right because here you have lambda, 240, 250, 260 so longer lambda means smaller energy, that is your lowest energy band.

What is this lowest energy band? It cannot be 0 0 dash transition, can it? Because 0 0 dash transition is seen only for orbitally allowed transitions, as we have discussed earlier this is not an orbitally allowed transition, it is vibronically allowed, if it is vibronically allowed you cannot have a 0 0 dash transition, are we clear about that? It has to be 0 1 dash or something like that, so what is it?

Now I have to give you a little bit of additional information and that will explain why of all letters we have written H there, that information is this band shows significant temperature dependence, at higher temperature that band becomes stronger, at lower temperature the band becomes weaker,

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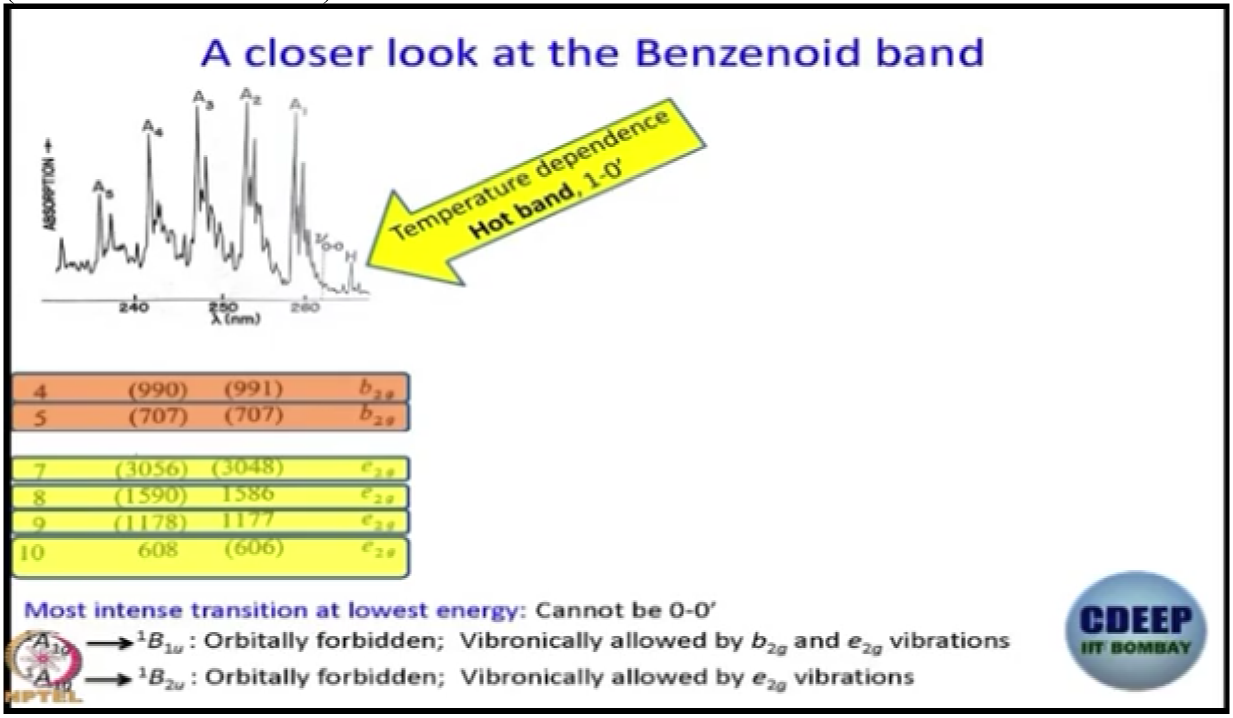

A closer look at the Benzenoid band

Temperature dependence
Hot band, 1-0′

4	(990)	(991)	b_{2g}
5	(707)	(707)	b_{2g}
7	(3056)	(3048)	e_{2g}
8	(1590)	1586	e_{2g}
9	(1178)	1177	e_{2g}
10	608	(606)	e_{2g}

Most intense transition at lowest energy: Cannot be 0-0′

$^1A_{1g} \rightarrow {}^1B_{1u}$: Orbitally forbidden; Vibronically allowed by b_{2g} and e_{2g} vibrations

$^1A_{1g} \rightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations

so it turns out to be a hot band.

So if it's a hot band then its origin is in 1 dash, so this is assigned as A1, not 1 dash 1, 1 0 dash transition, okay, it's a hot band. So if it is a hot band, if I try to draw the potential energy surfaces, I'll just draw two levels right, so that I don't goof up too much, this is the transition we are talking about, isn't it? This is a 1 0 dash transition, no this is a 1 1 dash transition, this is a 1 0 dash transition, okay.

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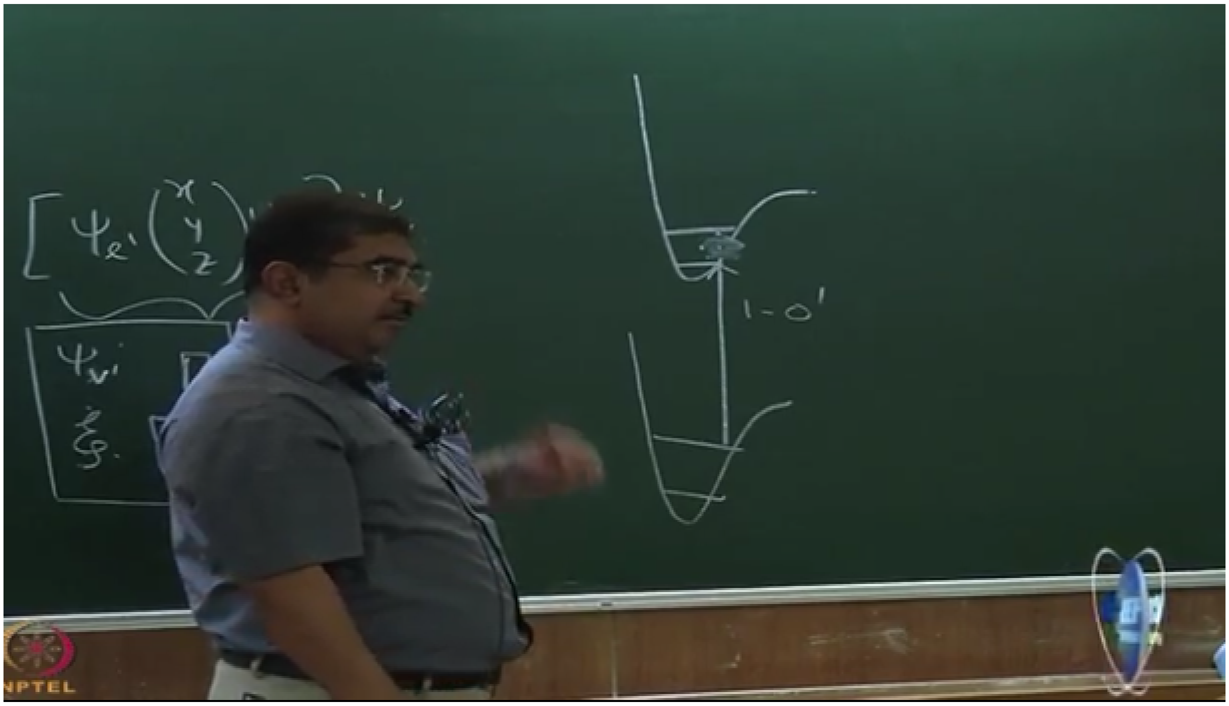

What will the energy be? This is E 0 0 dash, is that right? Energy difference between the 0th vibrational levels of the two potential energy surfaces that is called the band origin,

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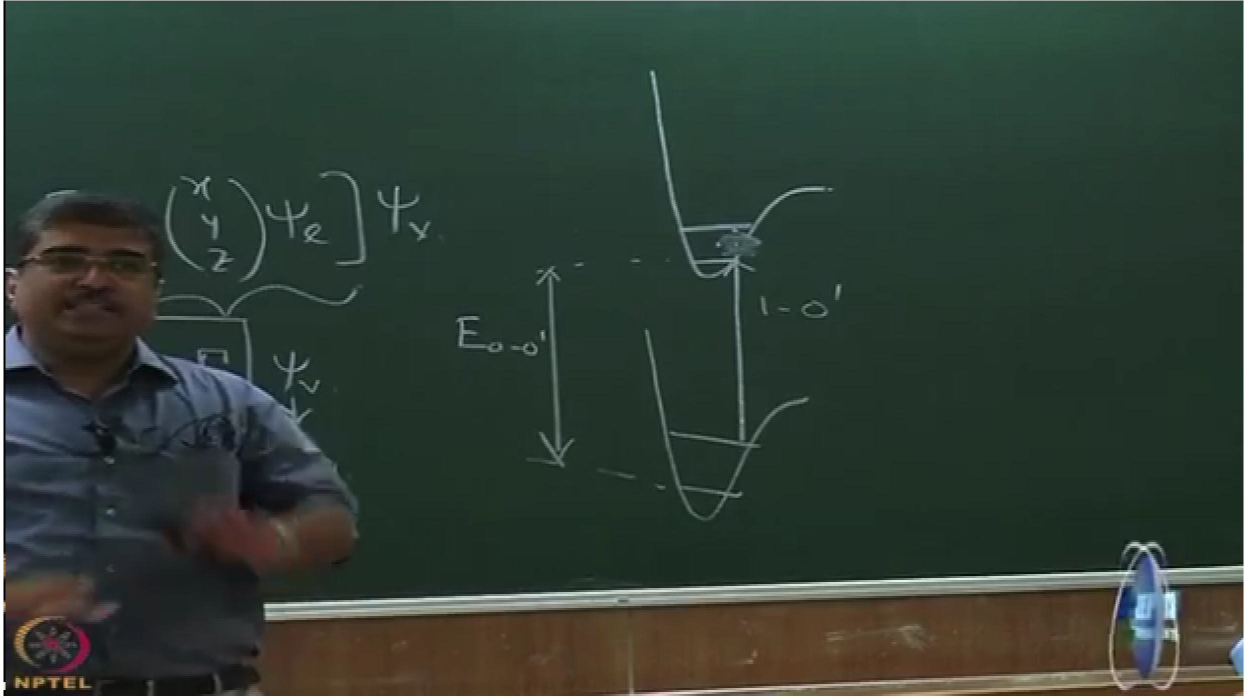

we have discussed band origin earlier while talking about this fortrat diagram and all this is your band origin, and so how do I get this? This band origin minus this energy, isn't it? Right, minus this so I can write this as nu bar, when nu bar is the nu bar for vibration, I've written something else there but that doesn't matter, okay, maybe I'll call it epsilon 0 0, so this epsilon 1 0 dash is epsilon 0 0 – nu bar V, alright.

Now look at the next band, the immediately next band here, so as you see it looks very much like this one right? The structure is the same, so that is described to 0 1 dash, do you agree with me that 0 1 dash should have higher energy than 1 0 dash? Right, what is 0 1 dash? This is 0 1 dash, right,

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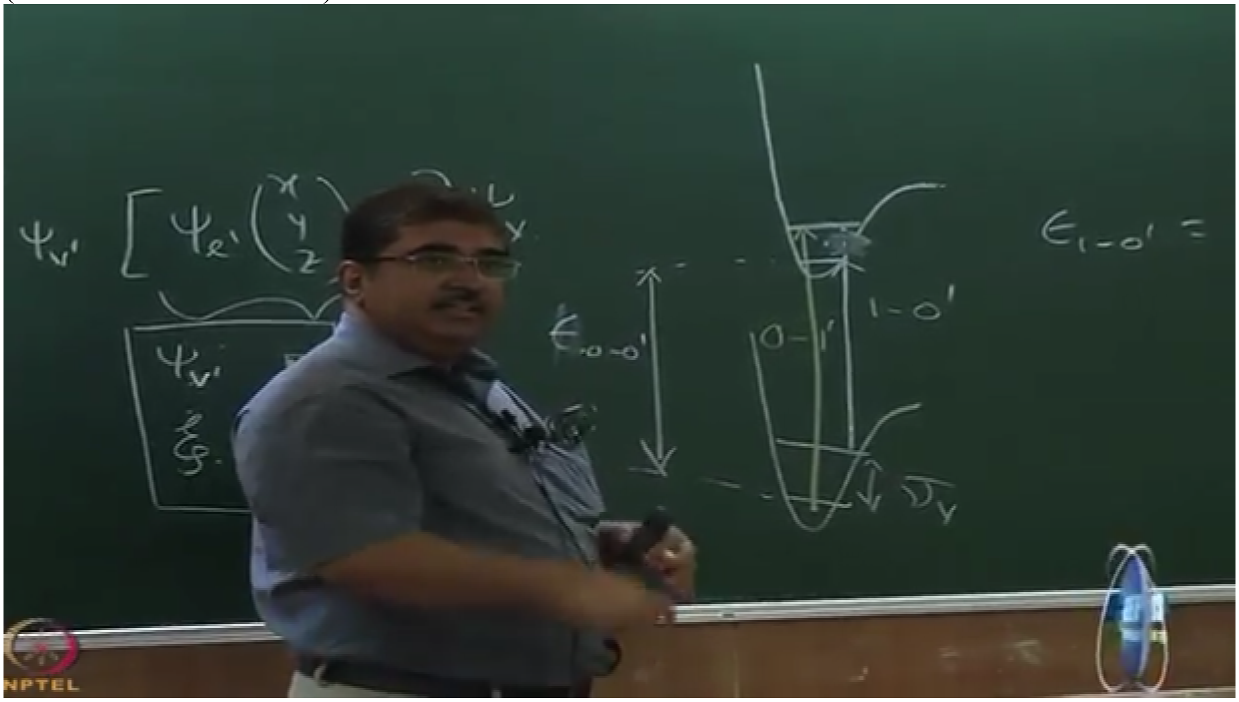

just immediately next higher energy, what is that? Epsilon 0 1 dash will be band origin, epsilon 0 0 dash + nu bar V, right? What is nu bar V? This, ideally I should write nu bar V dash because

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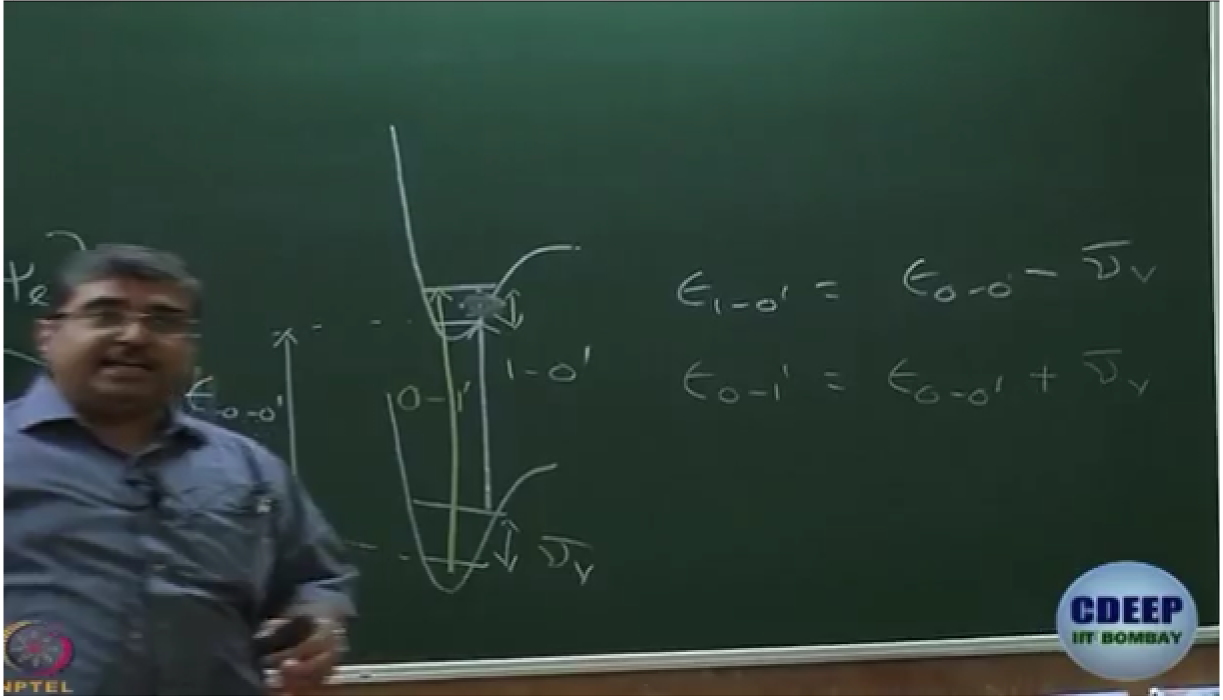

vibrational frequency is off the ground and excited states will not be the same, but as a first approximation and as you'll see in a while we are really doing a very approximately point of the problem, so as the first approximation I'll set nu bar V and nu bar V dash to be the same, alright, so far so good, now see what I can do? Do I know the values of epsilon 1 0 dash and epsilon 0 1 dash.

Do I know these values by some way? How? How do we know the values? Well, we have the spectrum, don't we?
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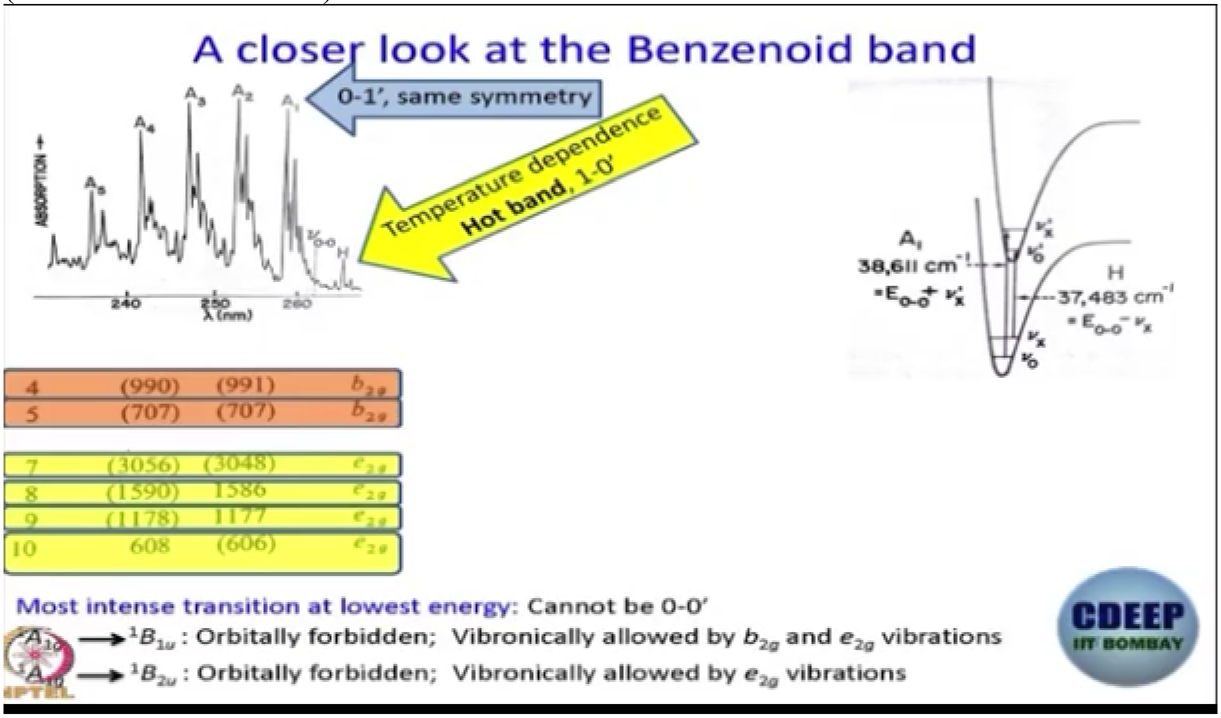

A closer look at the Benzenoid band

0-1′, same symmetry

Temperature dependence
Hot band, 1-0′

4	(990)	(991)	b_{2g}
5	(707)	(707)	b_{2g}
7	(3056)	(3048)	e_{2g}
8	(1590)	1586	e_{2g}
9	(1178)	1177	e_{2g}
10	608	(606)	e_{2g}

Most intense transition at lowest energy: Cannot be 0-0′

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$^1A_{1g} \rightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations

So experimentally we can find out, read off from the spectrum what those values are, so this here is the diagram that we have drawn, the only difference is here I have told you what the values are, the values actually are 37,483 centimeter inverse, 38,611 centimeter inverse, okay, so I know this left hand sides, so what are the unknowns here? Epsilon 0 0 dash and nu bar V, two unknowns, two equation, we can solve the two equations and find the two unknowns, right, I think that's child's play for us now to do that.

What is the approximation? The approximation is we are setting the 2 nu bar or nu values to be the same as the only approximation we've used, so doing that you just take, add them up you get a value of 262.8 nanometer for the band origin,
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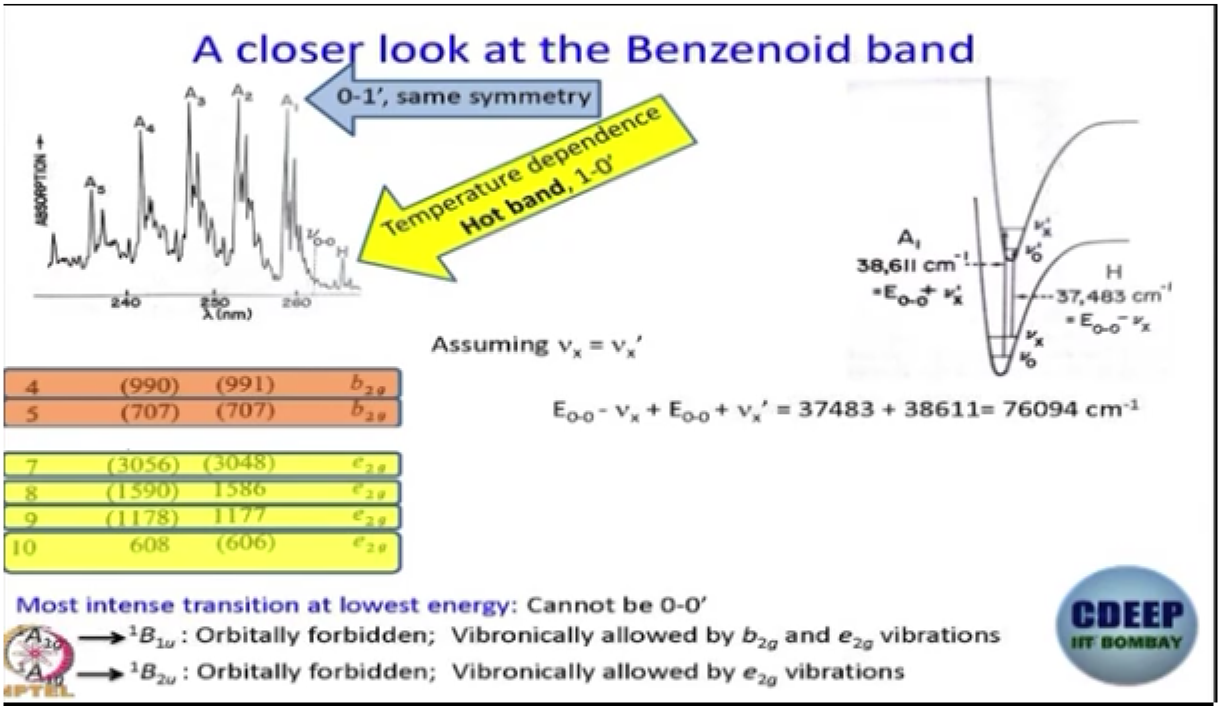


A closer look at the Benzenoid band

0-1′, same symmetry

Temperature dependence
Hot band, 1-0′

A1
38,611 cm⁻¹ = $E_{0\text{-}0} + \nu_x'$

H
37,483 cm⁻¹ = $E_{0\text{-}0} - \nu_x$

Assuming $\nu_x = \nu_x'$

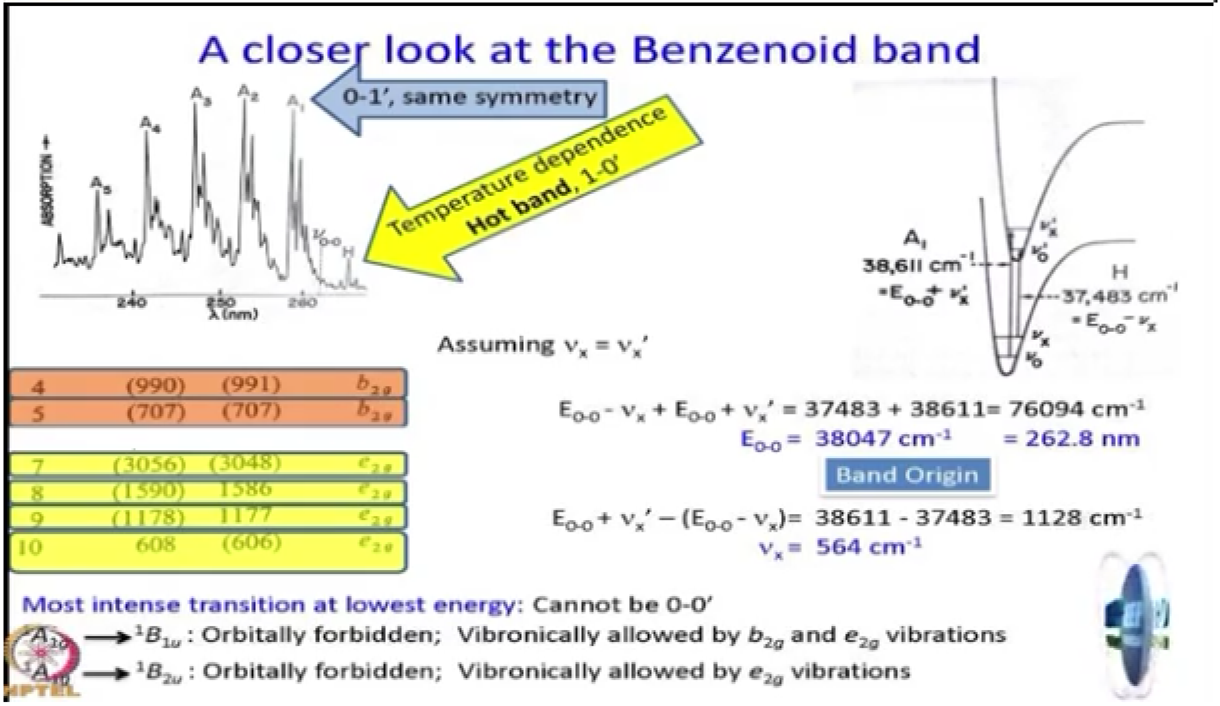
4	(990)	(991)	b_{2g}
5	(707)	(707)	b_{2g}
7	(3056)	(3048)	e_{2g}
8	(1590)	1586	e_{2g}
9	(1178)	1177	e_{2g}
10	608	(606)	e_{2g}

$E_{0\text{-}0} - \nu_x + E_{0\text{-}0} + \nu_x' = 37483 + 38611 = 76094\ \text{cm}^{-1}$

Most intense transition at lowest energy: Cannot be 0-0′

$^1A_{1g} \longrightarrow {}^1B_{1u}$: Orbitally forbidden; Vibronically allowed by b_{2g} and e_{2g} vibrations

$^1A_{1g} \longrightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations



A closer look at the Benzenoid band

0-1′, same symmetry

Temperature dependence
Hot band, 1-0′

A1
38,611 cm⁻¹ = $E_{0\text{-}0} + \nu_x'$

H
37,483 cm⁻¹ = $E_{0\text{-}0} - \nu_x$

Assuming $\nu_x = \nu_x'$

4	(990)	(991)	b_{2g}
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9	(1178)	1177	e_{2g}
10	608	(606)	e_{2g}

$E_{0\text{-}0} - \nu_x + E_{0\text{-}0} + \nu_x' = 37483 + 38611 = 76094\ \text{cm}^{-1}$

$E_{0\text{-}0} = 38047\ \text{cm}^{-1} \quad = 262.8\ \text{nm}$

Band Origin

$E_{0\text{-}0} + \nu_x' - (E_{0\text{-}0} - \nu_x) = 38611 - 37483 = 1128\ \text{cm}^{-1}$

$\nu_x = 564\ \text{cm}^{-1}$

Most intense transition at lowest energy: Cannot be 0-0′

$^1A_{1g} \longrightarrow {}^1B_{1u}$: Orbitally forbidden; Vibronically allowed by b_{2g} and e_{2g} vibrations

$^1A_{1g} \longrightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations

when you subtract that gives you the value of the frequency, so this is what we have been able to do, first of all even though we don’t see the band origin in the spectrum, we have been able to work it out by the statement, right, have we done something like this earlier? Band origin that was not visible in the spectrum we worked it out, have we done this earlier? Mithai? Manoj? Where, when? You are right, we have done it earlier in this course, when? In which situation? Sorry, ground state, Raman’s spectroscopy of what kind of compound? That is also right, sorry, Boltzmann extrapolation yes we did, but even before that you remember when we talked about this low vibration of spectrum we had this PQ band, sorry PR band, the Q band was missing but we said that we can find out where the vibrational frequency supposed to have been there, right, something similar so nothing new really, so first thing we can do is we can find the band origin, second thing that we can do is we can find the vibrational frequency, right, so now we know that a vibrational frequency or vibration with energy of about 564 centimeter inverse is the one that couples with electronic motion to make this transition vibronically allowed.

What is the next step? Look at this table and tell me is there anything that is close to 560, is there any vibration in that table that is somewhere close, and when I say somewhere close we can be very liberal about it, yes, only one we can say is very close and that is this last one 606, okay, and what is the symmetry of that? E2G, alright, and next part we are not going to do in detail but just believe me when I say that there is no signature of E2G vibration anywhere in the spectrum, right, so what does that mean? This band this benzenoid band that we are interested in becomes vibronically allowed due to participation of an E2G vibration.

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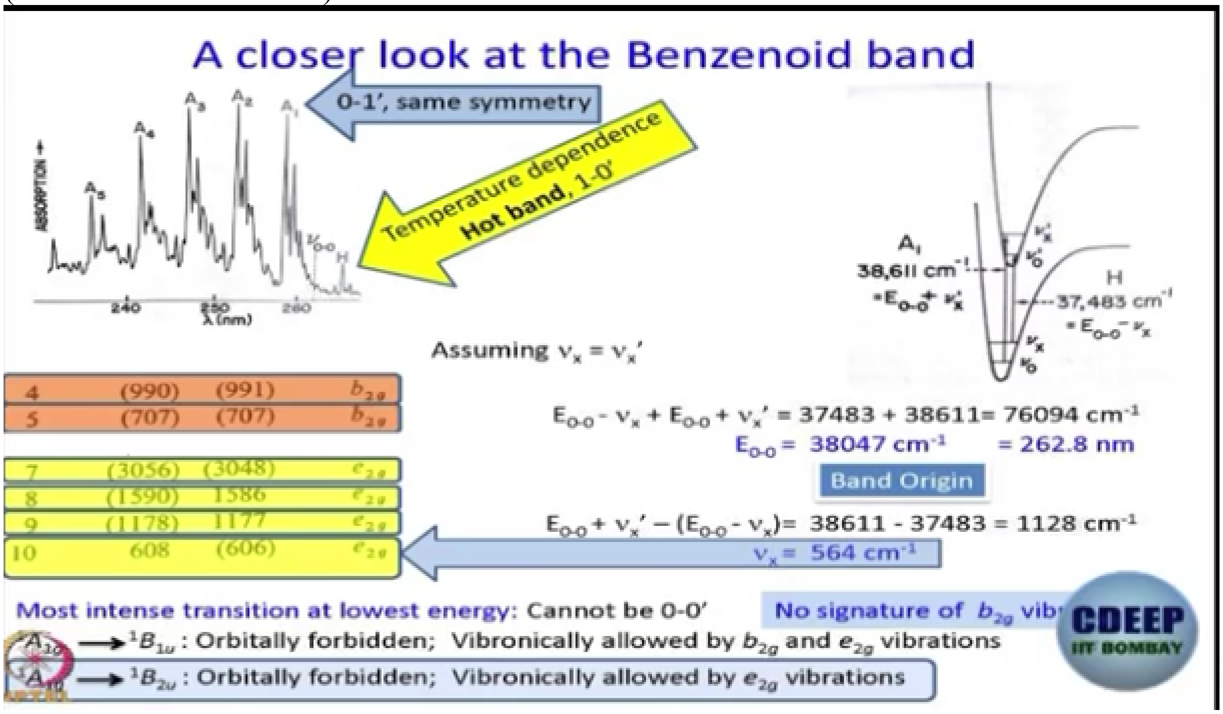

A closer look at the Benzenoid band

Assuming $v_x = v_x'$

4	(990)	(991)	b_{2g}
5	(707)	(707)	b_{2g}
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8	(1590)	1586	e_{2g}
9	(1178)	1177	e_{2g}
10	608	(606)	e_{2g}

$$E_{0\text{-}0} - v_x + E_{0\text{-}0} + v_x' = 37483 + 38611 = 76094 \text{ cm}^{-1}$$

$$E_{0\text{-}0} = 38047 \text{ cm}^{-1} \quad = 262.8 \text{ nm}$$

Band Origin

$$E_{0\text{-}0} + v_x' - (E_{0\text{-}0} - v_x) = 38611 - 37483 = 1128 \text{ cm}^{-1}$$

$$v_x = 564 \text{ cm}^{-1}$$

Most intense transition at lowest energy: Cannot be 0-0′

No signature of b_{2g} vib

$^1A_{1g} \longrightarrow {}^1B_{1u}$: Orbitally forbidden; Vibronically allowed by b_{2g} and e_{2g} vibrations

$^1A_{1g} \longrightarrow {}^1B_{2u}$: Orbitally forbidden; Vibronically allowed by e_{2g} vibrations

Now if you go back to what we had learnt a little while ago cingulate A1G to cingulate B1U is vibronically allowed, not only by E2G but also by B2G vibration. The other one is vibronically allowed only by E2G vibration, okay, well there are a few steps in between but for now we can just say that hence this benzenoid band is assigned to the second transition, alright, so this is our spectrum, we had already assigned the strongest band to the fully allowed cingulate A1G to cingulate E1U transition,

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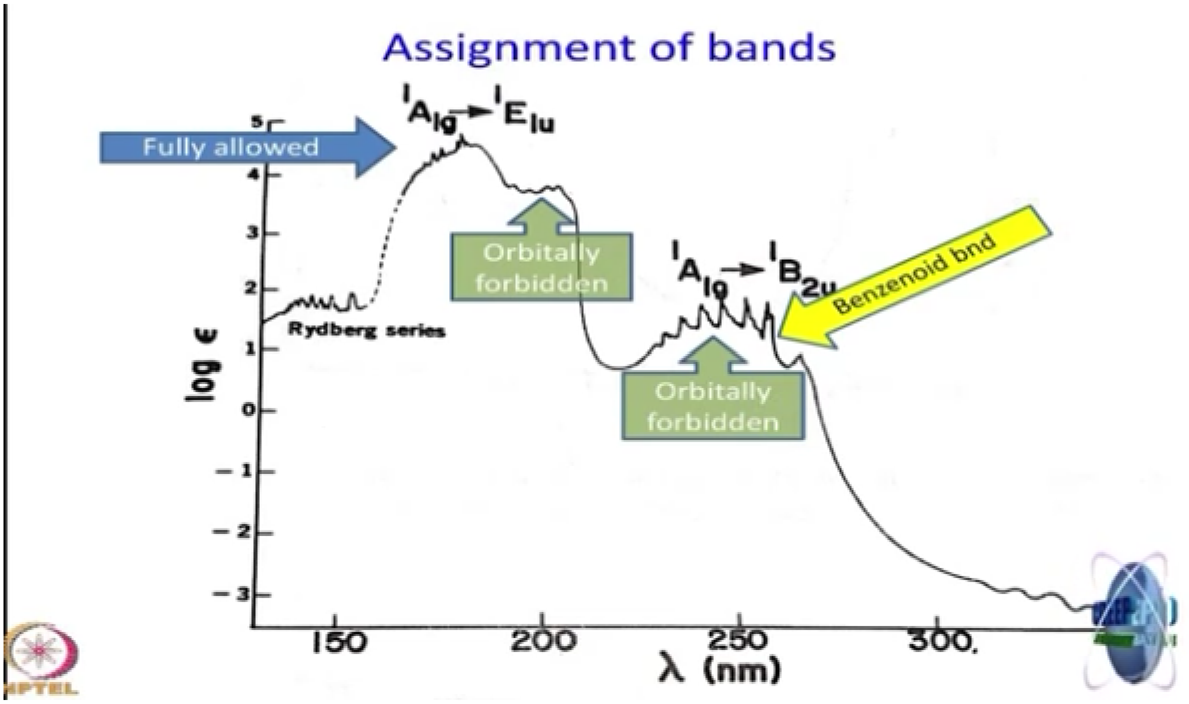

Assignment of bands

Fully allowed

Orbitally forbidden

Benzenoid bnd

Orbitally forbidden

we have worked out that the benzenoid band is due to cingulate A1G to cingulate B2U vibration, sorry cingulate A1G to cingulate B2U transition, now we are left with one orbitally forbidden band and we are left with one situation, right, another kind of transition, we assign it, cingulate A1G to cingulate B1U, okay, you could also tried to analyze this, you might think why is it that we are working with this and not that, alright, so if you work with this, if you are lucky perhaps you will be able to identify two vibration, but it is easier to work with the benzenoid band because we have a well-defined structure here, if you see this one the structure is not really all that well-defined because there is a significant overlapped between two bands, so it make sense to work with the benzenoid band and then fill in the other one by whatever is left, alright, so we've almost done with the assignment, the only part left is this.

Now if you look at phosphorescence spectrum, I think you are familiar with fluorescence and phosphorescence, aren't you?
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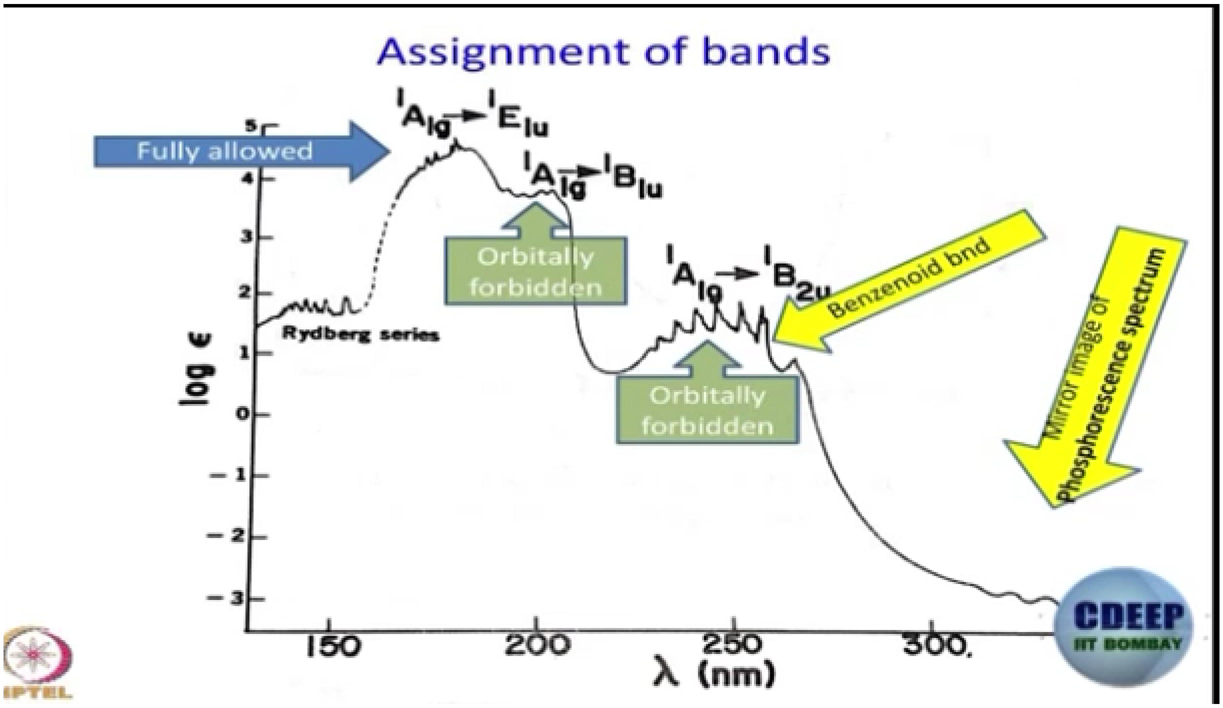

Are we familiar with fluorescence and phosphorescence? What is fluorescence? So first of all let us say it is an emissive deactivation path way of an excited state, both fluorescence and phosphorescence are emissive deactivation path ways of excited state, so now tell me what is it that differentiates between fluorescence and phosphorescence, Jaswinder? Okay, cingulate excited state to cingulate ground state radiative, not radioactive, radiative transition is fluorescence and triplet excited state to cingulate ground states is phosphorescence, right, that is correct but I'd like to expand the definition a little more and make it more general, a radiative transition between two states of same multiplicity, same spin multiplicity is called fluorescence.

Radiative transition between two states of different spin multiplicities is called phosphorescence, it does not have to be cingulate to cingulate, triplet to triplet radiative transition is also fluorescence, okay, suppose you are something with the triplet ground state then cingulate to triplet will still be phosphorescence, triplet to triplet will be fluorescence, so this is the more general definition that when you have a radiative transition between two states of same spin multiplicity that is fluorescence, when the two states of different spin multiplicities that is phosphorescence, it turns out that this weak band is a mirror image of phosphorescence spectrum, and thereby it is assigned, so we understand that it's a cingulate to triplet, well by both intensity and this mirror image relationship it is a cingulate to triplet kind of transition and we'll not discuss further but it's really cingulate A1G to triplet B1U transition, alright.

That brings us to an end of the discussion of absorption spectrum of benzene and that is sort of the climax of what we wanted to do in electronic spectroscopy. So we are done with electronic vibration rotation. In the last class we might come back to rotational spectroscopy and we might talk about the influence of nucleus spin on rotational spectra and also the influence of symmetry on rotation, on population of rotation that levels if you have time, but before that next what we want to do is we want to now go to a completely different kind apparently, apparently different kind of discussion that is of NMR spectroscopy.

NMR of course is the most commonly used spectroscopy technique used by chemist and I'm sure you have already been exposed to NMR spectroscopy almost all of you in other courses, but still what we'll do is we'll start from the beginning, right, we've had so many classes, it is okay if he spend one class in revising basics. So next day we are going to, and have revised our concepts in NMR then we will talk about pulsed NMR, and once you are done with that the end of, not end really, the remaining part of the discussion of NMR spectroscopy will be the quantum mechanics of NMR, for that we'll need to know the variations here, we'll need to know time independent perturbation theory.

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