

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

**CDEEP
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**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

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**Lecture No. – 52
Electronic States and
Transitions of Benzene**

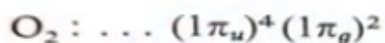
Alright, so we are nearing the end of our discussion of electronic spectroscopy, this really is the climax of our entire discussion of electronic spectroscopy. What we will try to do now is using the principals that we have learned of quantum chemistry, quantum mechanics and symmetry we are going to do a case study for once.

We'll try to see what the spectrum of benzene looks like, and why it looks like what it does, we'll try to assign the bands of benzene to the best of our abilities, and while we do that we'll learn something else that is called vibronic coupling, right. So we start with the electronic states and transitions of benzene, all the figures that you see except the once that I have drawn are from Harrison Bertologist book, this discussion has been done very nice in Harrison Bertologist book you can follow it for this part, right.

(Refer Slide Time: 01:28)

Recapitulation: Ground state configuration of O₂

D _{∞h}	E	2C _∞	...	∞σ _v	i	2S _∞	...	∞C ₂	
Σ ⁺ _g	1	1	...	1	1	1	...	1	
Σ ⁻ _g	1	1	...	-1	1	1	...	-1	R _z
Π _g	2	2cos(φ)	...	0	2	-2cos(φ)	...	0	(R _x , R _y)
Δ _g	2	2cos(2φ)	...	0	2	2cos(2φ)	...	0	
...	
Σ ⁺ _u	1	1	...	1	-1	-1	...	-1	z
Σ ⁻ _u	1	1	...	-1	-1	-1	...	1	
Π _u	2	2cos(φ)	...	0	-2	2cos(φ)	...	0	(x, y)
...	

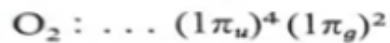


If you remember the last time we met which seems like a long time ago, we had discussed the case of oxygen, and in oxygen we had said that the electron configuration was 1 pi U4, 1 pi G2, alright, so what is the unique feature of this? The highest occupied molecular orbital that we have is doubly degenerate and these orbitals have two electrons, so in the simplest case scenario we just draw two orbitals and two arrows pointing in the same direction, right, but as we learnt if we do a little more treatment, little more detail treatment of this scenario what we do is in order to find the symmetry of the state, we need to take the direct product of the symmetries of the orbitals that are singly occupied and in this case those orbitals are pi G, so what we did was, we did pi G x pi G and in doing that we obtained 3 different states, (Refer Slide Time: 02:33)

Recapitulation: Ground state configuration of O₂

D _{∞h}	E	2C _∞	...	∞σ _v	i	2S _∞	...	∞C ₂	
Σ _g ⁺	1	1	...	1	1	1	...	1	
Σ _g ⁻	1	1	...	-1	1	1	...	-1	R _z
Π _g	2	2cos(φ)	...	0	2	-2cos(φ)	...	0	(R _x , R _y)
Δ _g	2	2cos(2φ)	...	0	2	2cos(2φ)	...	0	
...	
Σ _u ⁺	1	1	...	1	-1	-1	...	-1	z
Σ _u ⁻	1	1	...	-1	-1	-1	...	1	
Π _u	2	2cos(φ)	...	0	-2	2cos(φ)	...	0	(x, y)
...	

$$\pi_g \times \pi_g = \Sigma_g^+ + \Sigma_g^- + \Delta_g$$



3 different symmetries, sigma G+, sigma G- and delta G, alright.

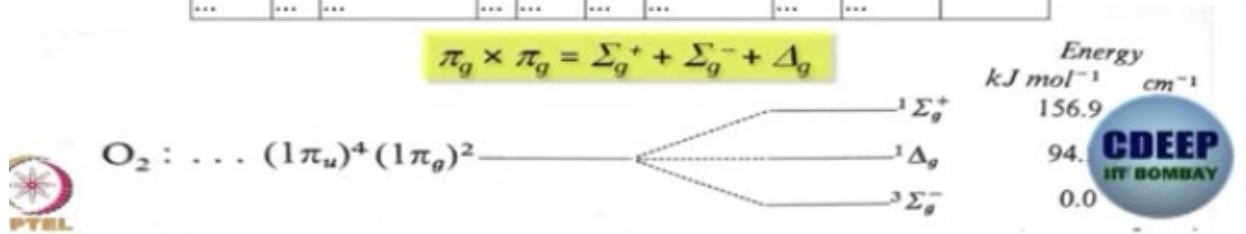
And the other thing that we discussed is that you cannot just assign singlet and triplet to anything and everything here, because if you take singlet and triplet of all these you get a total of 16 states, but then not all of the states are allowed by poly principal so in order to maintain a total wave function that is anti-symmetric, we found that, we end up only with 6 states, and the 6 state makes sense because if your remember we had drawn those boxes, 4 boxes which I had fill with 2 electrons there also we had obtained 6 states.

(Refer Slide Time: 03:25)

Recapitulation: Ground state configuration of O₂

D _{∞h}	E	2C _∞	...	∞σ _v	i	2S _∞	...	∞C ₂	
Σ _g ⁺	1	1	...	1	1	1	...	1	
Σ _g ⁻	1	1	...	-1	1	1	...	-1	R _z
Π _g	2	2cos(φ)	...	0	2	-2cos(φ)	...	0	(R _x , R _y)
Δ _g	2	2cos(2φ)	...	0	2	2cos(2φ)	...	0	
...	
Σ _u ⁺	1	1	...	1	-1	-1	...	-1	z
Σ _u ⁻	1	1	...	-1	-1	-1	...	1	
Π _u	2	2cos(φ)	...	0	-2	2cos(φ)	...	0	(x, y)
...	

$$\pi_g \times \pi_g = \Sigma_g^+ + \Sigma_g^- + \Delta_g$$



So the 6 states we obtained are singlet sigma G⁺, singlet delta G, and triplet delta G⁻, and we had discussed that the triplet state is the lowest energy state and the other two are higher energy states, we had discussed what the energies are and we had discussed how, first of all, all these 3 states arise out of the same electron configuration, right, it is just a combination of different special and temporal parts corresponding to the same electron configuration which is this, 1 π_u⁴, 1 π_g², that is the first thing to understand that the same electron configuration can actually give you different states, and secondly we had said that of course this transition between them would be not allowed, they are spin forbidden but still there can be a little bit of transition because you can have spin orbit coupling which makes, which ascribes a little bit of allowed ness to even spin forbidden transitions and that is why we said in liquid state oxygen has a faint blue color.

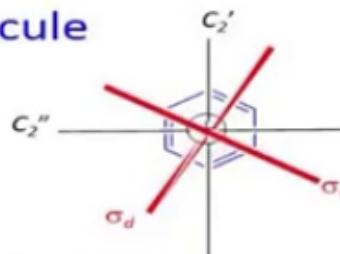
And finally we discussed how this kind of energy level diagram or rather this kind of arrangement of energy levels has a profound implication in the application of oxygen in biological systems, how you can have an organic molecule which you can excite to a triplet state and this triplet state can photosynthesis oxygen to produce singlet oxygen which is very highly reactive that can be the cause of disease like profilia, it can also be the basis of a treatment like photodynamic therapy, and this is what we had discussed last day.

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Benzene: a D_{6h} molecule

Character Table

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	-1	1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0



Product Table (partial)

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}
E_{1g}	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$
E_{2g}	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$



Today what we will do is we will extend our discussion to a bigger molecule which is benzene, benzene of course everybody knows the structure, what I have done here is I have shown you the character table and since there are many symmetry operations, let us not be confused about which one is which, okay, let's just quickly go through the character table of benzene, of course E, everybody understands, C_6 not difficult to see, where is C_6 ? C_6 is perpendicular to the benzene ring and it goes to the center.

What is C_3 ? And why do I have two C_6 ? Where is the other C_6 ? Yeah, one is clockwise and the other is anticlockwise, great. What is C_3 ? C_3 is just C_6 square, clockwise or anticlockwise, are we clear? Then what is C_2 ? C_2 is C_6 cube, right, start from here, another C_6 , another C_6 , that's essentially is C_2 , why do I not write $2C_2$? I've written $2C_3$, I've written $2C_6$, why have I not written $2C_2$? Because it's the same right, no matter whether you turn clockwise or anticlockwise you get back the same configuration, so C_2 there is only one, but then there are two more kinds of C_2 s, C_2 dash and C_2 double dash, where are they? They are perpendicular to the C_2 axis, alright.

What is C_2 dash? C_2 dash is C_2 axis that goes through opposite atoms, and C_2 double dash is a C_2 axis that goes through the center of part, this is the convention that is followed when we write the character, of course you could take the different convention, opposite convention and write your own character table, but then the problem is your results, your Mulliken nomenclature and everything will be little different from what it is in the text book, in fact there are text books in which the opposite convention is used, so whenever we have a big molecule we have to be absolutely sure which convention is in use there, alright.

So we are done with all the axis, center of inversion is very easy to understand, then S_3 is also very easy to understand I hope, C_6 axis doubles as S_3 axis as well, S_6 same thing, σ_h is the plane of the molecule, horizontal plane of symmetry, σ_d and σ_v once again matter of

convention, sigma D is the plane that goes through the center of the bonds, and sigma V goes through the atoms, okay, in some cases just exactly opposite convention is followed, but the convention we had followed is this, and this is how you get this character table.

And one thing that I know like to use because otherwise the problem becomes very long is a product table you know what a product table is? You had to working with that products right, so suppose I have to do B1G x E1G, what is it? B1G x E1G will give you E2G, and here I have only shown a partial character table otherwise the font size will be too small, we think to remember is that whenever we have G x G we get G, whenever we have U x U we get G, whenever we have G x U and U x G we get U, so I hope it will not be difficult to use this partial character table even if we have some U symmetries as well, alright, great.

Now it is time to look at the molecular orbitals of benzene that we are all familiar with, these are the molecular orbitals of benzene and I hope everybody understands what I mean when I write like this,

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State Diagram and Electronic Transitions

	E	2C ₆	2C ₃	C ₂	3C ₂ '	3C ₂ ''	1	2S ₃	2S ₆	σ _h	3σ _d	3σ _v
A _{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A _{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B _{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B _{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E _{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E _{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A _{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A _{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B _{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B _{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E _{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E _{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0

what I have done is I have shown the P orbitals, molecular orbitals as you know are generated by taking linear combinations of atomic orbitals, the atomic orbitals in question here are the PZ orbitals if you take the benzene ring to be in XY plane, right, so you can say that whenever I have an empty circle I'm looking down from the top right, empty circle means say plus loop and solid circle means minus loop or the other way around doesn't matter, so when I have something like this what would be the symmetry of that? The lowest energy atomic orbitals, sorry molecular orbital, what would be the energy? Yes, A1G, A1G is totally symmetric, do you agree? That the lowest energy molecular orbital here will be A1G, do you all agree? I don't agree, because this molecular orbital has to be anti-symmetry with respect to sigma H, right, has to be anti-symmetry with respect to inversion as well, so cannot be totally symmetric, the state will be A1G

I agree with you, because in the state we'll have completely filled orbitals, but the molecular orbital is not A1G.

What is the symmetry? What is the character for E? 1, what is the character for C6? C6 is 1, what is the character for C3? 1, so this kind of rotation where there is no conversion from top to bottom of the plane, character should be 1, so C6, C3, C2 all this three should be one, alright, so what is it? A or B? Has to be A, right 1 or 2 that we will see. Accha G or U that we can say very easily, G or U? U, so we don't even look at these, we look at these, okay. C2 with respect to C2, what will it be, plus or minus? C2, C2 what happens when I apply C2? This is my plane, C2 and C2 dash both are like this, if I apply C2 you see the other phase right, right, so suppose this phase is plus, this phase is minus, when I apply C2 or it can be C2 dash, sorry, when it is C2 dash, what I am saying? I said C2 that's why you got confused I'm sorry, C2 of course it is +1, but what about C2 dash? What about C2 double dash? Character has to be -1, so 1, 1, 1, 1, -1, -1, -1, -1, S3 turn and reflect, -1, -1, S6 -1, sigma H -1, sigma D +1 because there is no top to bottom conversion, sigma H+1, so which one is it? You are right it's A2U, okay.

So do not jump to conclusions because it can be tricky, A2U these are the next higher energy pair is E1G, of course 2 are there degenerate so they must belong to 2 dimensional representation you can work it out, the way to work it out is to actually write the expression of the wave functions, maybe I'll give it to you as a homework, so suppose you call this ψ_1 and suppose you call this ψ_2 and let us say I number like this, carbon 1, 2, 3, 4, 5, 6 okay, what will ψ_1 be? $-\psi_1$, no sorry what did I say? This hallow circle is plus we said right, ψ_1 will be ψ_1 where ψ_1, ψ_2 these are all P orbitals, PZ orbitals of the atoms.

$\psi_1 + \psi_2 - \psi_3 - \psi_4 - \psi_5 + \psi_6$ are we clear? Of course there will be normalization factor we can neglect it, what about this? Which one was 1, this is 1 right, in this case coefficient of ψ_1 is 0, so it is $\psi_2 + \psi_3 - \psi_5 - \psi_6$, alright, what happens when you apply C6? It will move and accordingly you can write the expression of ψ_1 dash, accordingly you can write the expression of ψ_2 dash, then what you have to do is you have to generate the transformation matrix, once you do that you can convince yourself that this actually belong to E1G, I'll not get into that but you can do it yourself, okay, is there any other way of doing it? First of all it is A2 dimensional representation right, if I want to take a short cut, assuming that I've not gone wrong anywhere, I can actually work out E1G without working out the entire transformation matrix by taking some short cut, what is the short cut? First of all, suppose I don't know this, I know it is G, right, can you see that it is G? This one is G, is this also G? Of course, what about this, is this G or U? Will this be G or U? Start from here this is plus, go through the center, go through the other side, remember what going through the other side means? This is plus, you have to go here, right, so this one is it G or is it U? These are U, these are G, so already one third of the problem is done, in fact two thirds of the problem is done because you know that the only two dimensional representations are E, so I know it has to be E, I know it has to be, I know this is U and this is G, I only have to figure out 1 or 2, so in this case question is E1G or E2G, right.

Let us see E1G and E2G, where do they defer? They defer in the character S3 and all are very difficult to do, in the character of sigma S's right, minus with respect to sigma H that is E1G, plus with respect to sigma H that is your E2G, right, so this one is it minus with respect to sigma H or plus with respect to sigma H? Plus no, sigma H, so E1G, right, so this is my shortcut, I

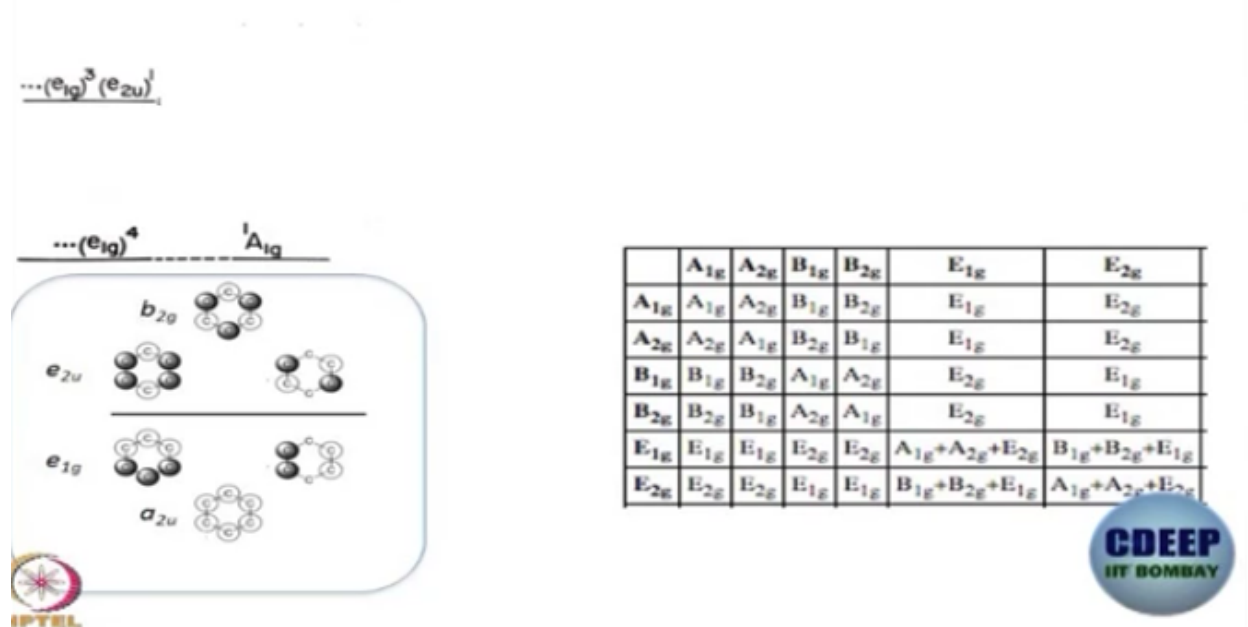
don't really have to work out the matrix all the time, if I use the character table is given, character table makes our life a lot easier as we have actually learnt in the inorganic chemistry class where without even understanding what character table is you could use it and get your results, right, so here hopefully you understand a little more.

Similarly you can work out that this is E2U and I leave it to you to work out that this is B2G, alright, I hope everybody can do this now, and I am within my rights if I ask question on this, and not necessarily in benzene, alright, great.

Now let us get to the business that we really want to do, this is my electron configuration, right in ground state and excited state, agreed, ground state we have of course we have A2U too well, but the homo is E1G 4, these are fully field. Excited state means first excited state one electron will go from E1G to E2U, so instead of E1G 4 I have E1G 3, E2U 1, understood everybody, see if you don't understand everybody? See if you don't understand please ask, you are okay with the symmetries of the all molecular orbitals I hope, now do you agree with this? For the ground state how many electrons are there? How many 5 electrons are there? 6, how will they be filled? 2 2 2, so A2U 2, E1G 4, okay, and all the MO's that are there are actually doubly occupied, so what will be the state? What will be the symmetry of the state in that case? Ground state, all occupied MO's are doubly occupied, in that case Vishwaroop's original answer now is correct.

When all field MO's are doubly filled then it is a totally symmetric state right, so this is a singlet A1G state, okay, alright, singlet because all the terms are paired you can just go by that. (Refer Slide Time: 18:12)

State Diagram and Electronic Transitions

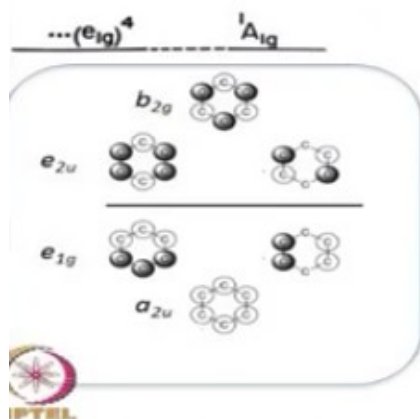
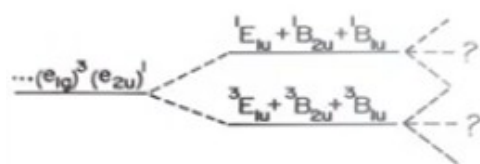


What about, what happens when there is an excitation? Homo lomo excitation, homo is E1G, lomo is E2U, if I have homo-lomo excitation instead of 4 electrons here I'll have 3, so I get E1G 3, and now I have one electron in E2U that gives me E2U 1, agreed now? Okay.

Now how do I find the symmetry of this state? What are the MO's that are singly occupied? 1 E1G and 1 E2U, okay, so to determine the symmetry of the state I have to do E1G x E2U, do you agree? Because 1 E1G orbital is singly occupied, 1 E2U orbital is singly occupied as we have discussed earlier we get the symmetry of the overall wave function or the state by taking direct product of the symmetries of the singly occupied molecular orbitals, so we need to do E1G x E2U, understood? Sambit? Now of course you can do it, it's not such a big deal but since we have this product table we can just see, what do we have to do? E1 x E2, right, forget GU for now, E1 x E2, E1 x E2 what do I get? B1 + B2 + E1, and in this case I'm doing G x U, so what will be the direct product G or U? It will be U, so this one will be B1U + B2U + E1U. Please tell me if you are all okay with this, have you all understood that since E1G and E2U orbitals are singly occupied, I have to take a direct product of those, direct product of E1, neglecting this G and U for now, direct product of E1 and E2 is B1 + B2 + E1 and since I am doing G x U, E1G x E2U, instead of G I'll have U here, right 1 x -1 is -1, so that direct product gives me B1U + B2U + E1U, alright, so the states that you can generate are these.

And see I can have singlet as well as triplet, now the two electrons that are there in singly occupied orbitals they are in orbitals of different energies, if the two electrons were in orbitals with same energy then you would be restricted by Pauli principle, right, not all wave functions would be allowed, but now one electron is in E1G, one electron is in E2U, (Refer Slide Time: 21:24)

State Diagram and Electronic Transitions



	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _{1g}	E _{2g}
A _{1g}	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _{1g}	E _{2g}
A _{2g}	A _{2g}	A _{1g}	B _{2g}	B _{1g}	E _{1g}	E _{2g}
B _{1g}	B _{1g}	B _{2g}	A _{1g}	A _{2g}	E _{2g}	E _{1g}
B _{2g}	B _{2g}	B _{1g}	A _{2g}	A _{1g}	E _{2g}	E _{1g}
E _{1g}	E _{1g}	E _{1g}	E _{2g}	E _{2g}	A _{1g} +A _{2g} +E _{2g}	B _{1g} +B _{2g} +E _{1g}
E _{2g}	E _{2g}	E _{2g}	E _{1g}	E _{1g}	B _{1g} +B _{2g} +E _{1g}	A _{1g} +A _{2g} +E _{2g}

so I can take combinations that are singlet, I can take combinations that are triplet, so you'll end up getting all the states, singlet and triplet E1U, B2U, B1U, and the reason why we have these dash lines and question mark is that we are working under that approximation that whatever state we generate that is the state we work with, that is not necessary. I don't know if you have studied configuration interaction in 4 to 5, have you studied configuration interaction in CH4 to 5, maybe not, that is not in CH5, 6, 0. So when you study configuration interaction you learn that actually states or rather electron configurations or I can say states, states which have the same



symmetry and same energy actually mix to produce one state with lower energy, one state with higher energy, in fact you encounter the situation I'm sure.

Have you heard of no crossing rule? No crossing rule, some have heard, some have not, but no crossing rule is a really manifestation of configuration exactly, but for now let us neglect all this dash arrows and question marks, let us stick to singlet and triplet E1U, B2U, B1U. If there is a question this is a time to ask, any question? Shubham, no question, very good. Then we will proceed, so yes sir, yeah, yeah, oh no, no, what all it means is that there are 6 states, total 6 states are there, they have shown the singlet states together and triplet states together, but actually they don't have the same energy, so don't think they have the same energy, you see these three lines actually indicates that they have different energies, but which one is higher, which one is lower we don't want to worry about that right now, that will require a rigorous quantum chemical calculation, that's all it means. What it means is that by symmetry arguments you get 3 states, singlet and triplet, triplet is written lower because you know that everything else being same triplet will have lower energy, but which one of this singlet states is higher in energy, which one of this triplet state is higher in energy, for that you will need to do a little more involved quantum chemical calculation they are not getting into that, are we okay? Any other question? Can I go ahead? Great.

So now the next question to ask is which of this transitions are allowed, (Refer Slide Time: 24:16)

State Diagram and Electronic Transitions

...(e_{1g})³(e_{2u})¹

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

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

?

?

?

$A_{1g} \rightarrow E_{1g}$:

$A_{1g} \rightarrow B_{1g}$:

$A_{1g} \rightarrow B_{2g}$:

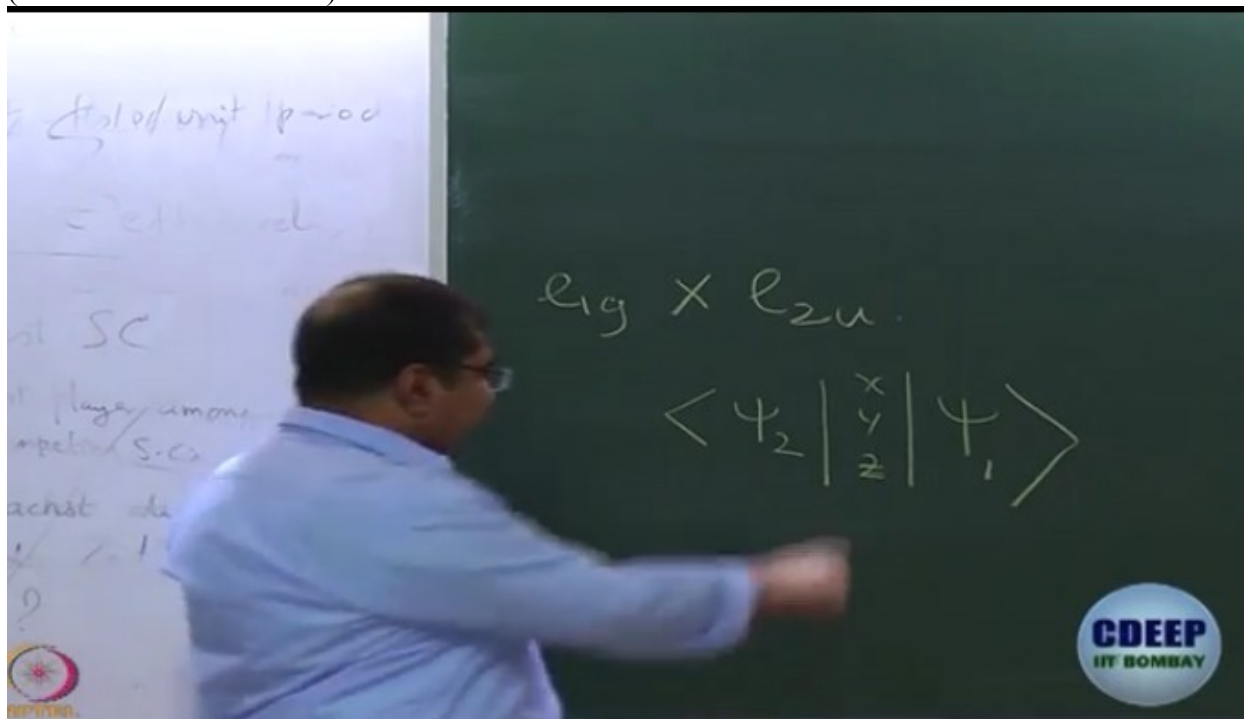
...(e_{1g})⁴ $^1A_{1g}$

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}
E_{1g}	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g} + A_{2g} + E_{2g}$	$B_{1g} + B_{2g} + E_{1g}$
E_{2g}	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g} + B_{2g} + E_{1g}$	$A_{1g} + A_{2g} + E_{2g}$

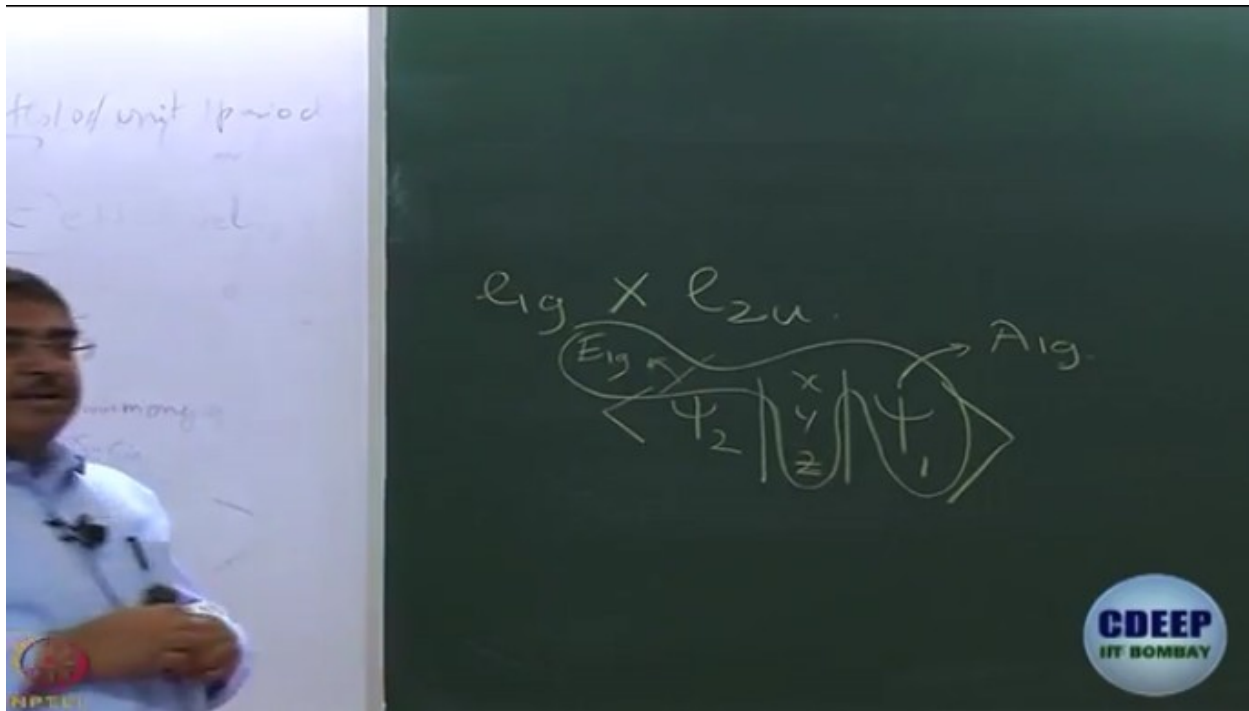
D_{6h} : z has a_{2u} symmetry, (x, y) have e_{1u} symmetry

see your ground state is A1G and singlet A1G of course ground state is singlet right, so only singlet to singlet transitions will be spin allowed, okay, we are only talking about the orbital allowedness or orbital forbiddenness at the moment, so the implicit assumption is that we are talking about singlet to singlet transitions, because ground state is not triplet definitely, so singlet to triplet transitions will only occur if there is a strong spin orbit coupling, we are not talking about that at the moment, so but from the view of the symmetry only which of these will be

allowed, A1G to E1U, A1G to B1U, A1G to B2U, how do we decide? Which of these are orbitally allowed? How do I decide, which of these are orbitally allowed? Yes, yeah, I heard an answer. No laporte is different don't, think of a general treatment, what is the transition moment integral? It is something like this, right, sai 2, sai 1 integrated over all space, and in the middle what do you have? Mu and mu as you know has X and Y and Z components, alright.
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What is the sai 1? What is the symmetry? What is the symmetry of sai 1? Not just G, A1G, sai 2 is E1U or B1U or B2U, whatever it is, okay, so the question is let us say we are talking about, what is the first one we have written? E1G, E1G, so the question is does one of this triple products contain the totally symmetric representation,
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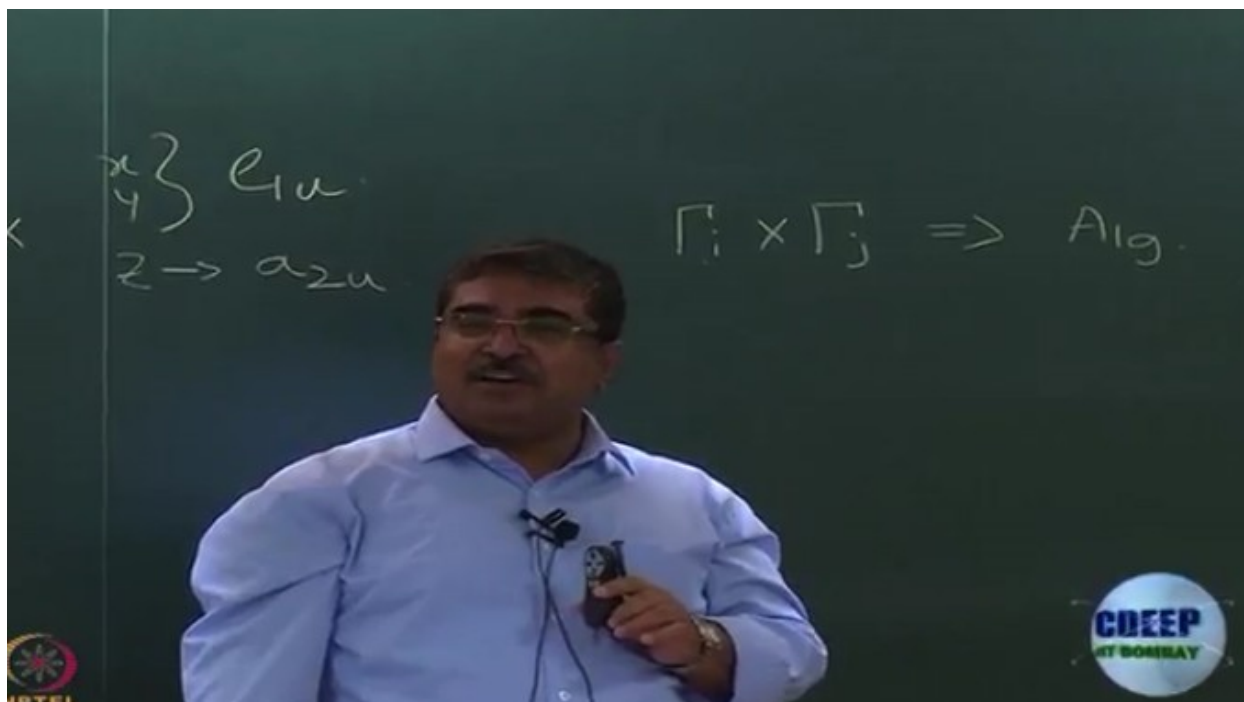


remember the integral is going to be non-vanishing, when the integrand is totally symmetric, so what we really have to do is to find the symmetry of the triple product and see whether it has A1G or not, alright, agreed, great.

So now one good thing has happened already, ground state is A1G, right, ground state A1G means that multiplied by anything will give back the same thing, we don't even have to worry, we only have to worry about the direct product E1G cross, whatever is the symmetry of X or Y or Z? Similarly we have to worry about the direct product of B1U and whatever is the symmetry of X or Y or Z, B2U whatever is the symmetry of X or Y or Z, right.

Now one thing that you will, yeah I am sorry, okay, right, right you are right. Have I written E1G here? E1U, you are right, okay. So of course to do that I need to tell you what is the symmetry of X and Y and Z, and this is what is written here I don't know if you have noticed Z is A2U, and X and Y together for a basis of E1U, okay, Z is A2U and X and Y together is E1U, alright that comes from the character table.

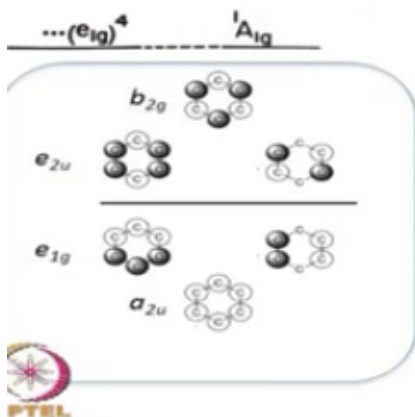
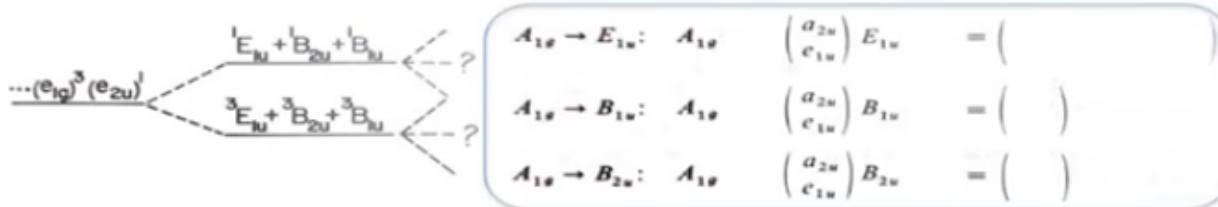
Now with this information without doing anything else, without looking at the character table or without looking at the product table, can you tell me whether this A1G to E1U transition is allowed or not, allowed? Why Raksha? So Raksha is trying to do it by gerade and ungerade only, but don't forget gerade and ungerade only tell you about inversion, so it can tell you whether something is not allowed, but there might be transitions that seem to be allowed because it's a gerade and ungerade, but it might not be allowed by something else, you have to look at all symmetry operations, and if you remember once small working formula that we have worked out is you have this $\Gamma_i \times \Gamma_j$, when will it contain say A1G, we had worked this out, when will the direct product $\Gamma_i \times \Gamma_j$ contain a totally symmetric representation? (Refer Slide Time: 29:29)



Yes, when both are same of course they will contain, remember that then everyone will be multiplied by a 1, every -1 will be multiplied by -1, so both are same definitely they will contain totally symmetric representation, so you see E1U and X and Y together for a basis of E1U, so E1U x E1U must contain A1G, so it is allowed, okay, orbitally allowed.

And then if you want to do a little more detail treatment we can see, this is what we are trying to evaluate, right, first one is A1G you don't worry about, here the problem is in _30:18_ other way compared to what we are working, but doesn't matter, E1U x A2U or E1U, B1U x A2U or E1U, B2U x A2U or E1U,
 (Refer Slide Time: 30:34)

State Diagram and Electronic Transitions



	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}
E_{1g}	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$
E_{2g}	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$

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

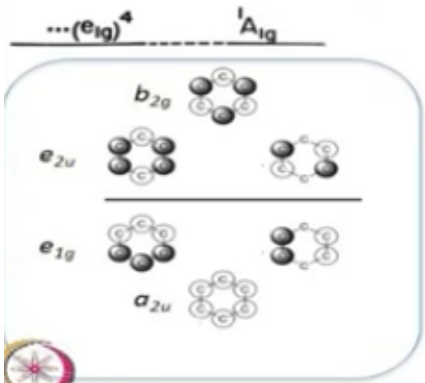
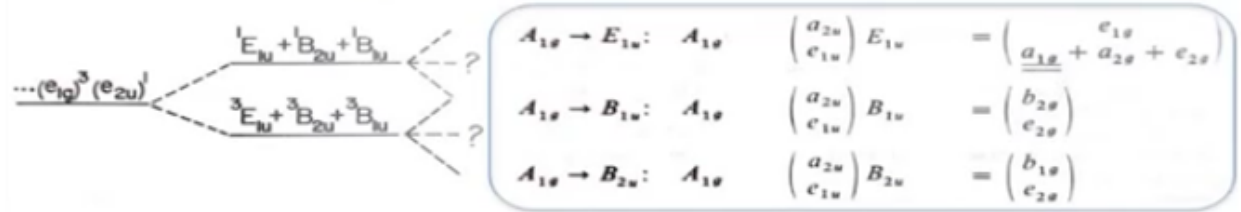


so even without working out anything more you can I think see that A_{1g} to E_{1u} is allowed, and it's allowed through X and Y directions, the other two are not allowed orbital, alright, and then to convince us a little further let us take help of this product table, and let us see what the direct products are, $A_{2u} \times E_{1u}$, $A_2 \times E_1$ what is it? E_1 , E_{1g} because you are doing $U \times U$. $E_{1u} \times E_{1u}$ what is it? E_1 will give me $A_1 + A_2 + E_2$, should it be G or U? I'm doing $E_{1u} \times E_{1u}$, G right, so it will be A_{1g} and this is our A_{1g} , this is what we are looking for, $A_{1g} + A_{2g} + E_{2g}$ this is what you will get, alright.

And this A_{1g} is what makes it allowed, what about $A_{2u} \times B_{1u}$? $A_2 \times B_1$, what do you get? B_2 , and should it be G or should it be U? Yeah, $A_{2u} \times B_{1u}$, G, B_{2g} and $E_{1u} \times B_{1u}$ is also E_{2g} , similarly you can work out this as well and you can convince yourselves that in only one case I get A_{1g} and that is A_{1g} to E_{1u} transition, so that is what tells us that singlet A_{1g} to singlet E_{1u} is a fully allowed transition, what is the meaning of fully allowed transition? Spin allowed as well as orbitally.

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State Diagram and Electronic Transitions



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

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



The other two are orbitally forbidden, alright, so this is what we arrive at, that for benzene now we know what the symmetries of the orbitals are, we know what are the ground state and excited states involve, at least for the lowest energy transitions and we have been able to determine which of this transitions are fully allowed, which of this transitions is fully allowed and which are not orbitally allowed, of course singlet A1G to singlet B1U is it spin allowed? This transition here of course it's orbitally forbidden, is it spin allowed? Forget the orbital part, singlet to singlet that is spin allowed right, singlet A1G to singlet B2U, orbitally forbidden I agree, is it spin allowed? Right, yes, it is spin allowed, Jaswinder has a doubt, doubts, fine.

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(Refer Slide Time: 34:23)

State Diagram and Electronic Transitions

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

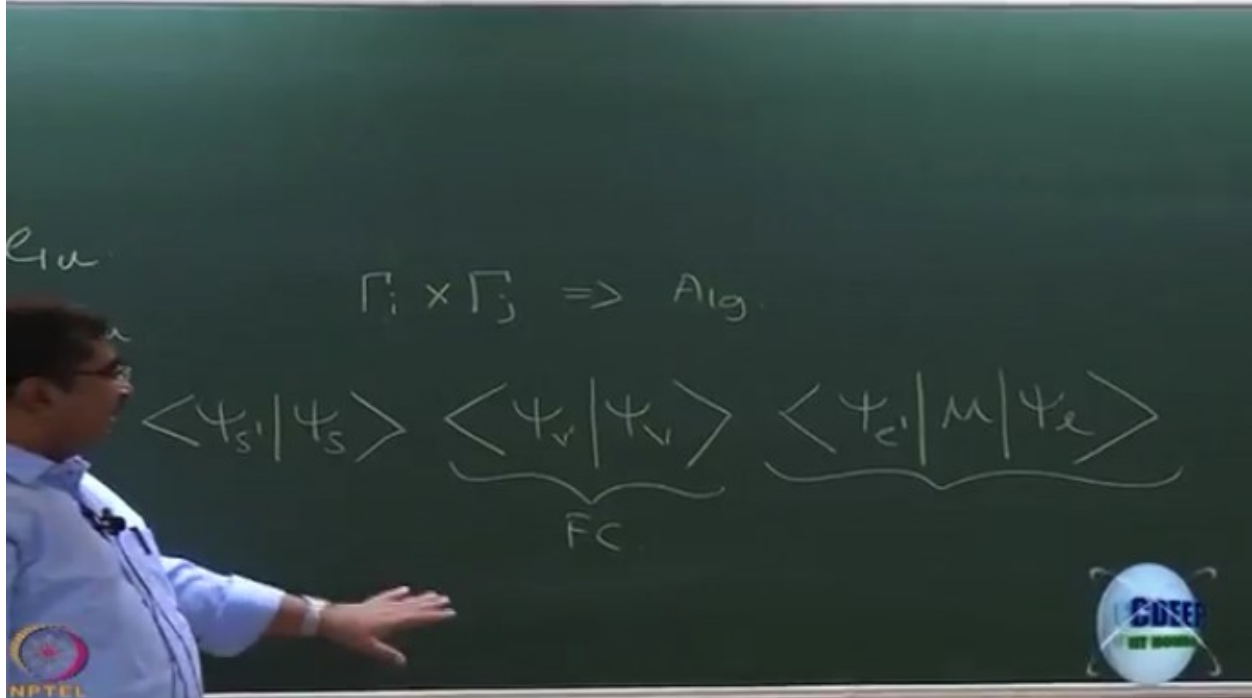
$^1A_{1g} \rightarrow ^1E_{1u}$: Fully allowed

$^1A_{1g} \rightarrow ^1B_{1u}$: Orbitally forbidden;

$^1A_{1g} \rightarrow ^1B_{2u}$: Orbitally forbidden;

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

You agree with me that for these two transitions they are orbitally forbidden, now I'm asking you to forget about the orbital part for the moment, I'm saying both of these are singlet to singlet transitions, so from the point of view of spin are they allowed or are they not allowed? Remember what the transition moment integral is, or how we wrote it, we wrote transition moment integral as $\int \psi_f^* \hat{\mu} \psi_i$ integrated over all space, so far what we have discussed is this, right, this part we have said that for until now our discussion, in our discussion we said that this is the Franck Condon factor,



it decides the intensity. This part decides whether a transition is spin allowed or not, alright, so if I forget about the rest of the factors think only about this then I know that singlet to singlet is a spin allowed transition, that's what I am saying, that even though it's orbitally forbidden it is spin allowed. Doesn't mean that we are going to see a band corresponding to it, we'll see what happens, alright, but it is a spin allowed orbitally forbidden transition, agreed, and the first one is a fully allowed transition, okay. So in the next part we'll see whether there is any way in which this orbitally forbidden transitions can become allowed or not.

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