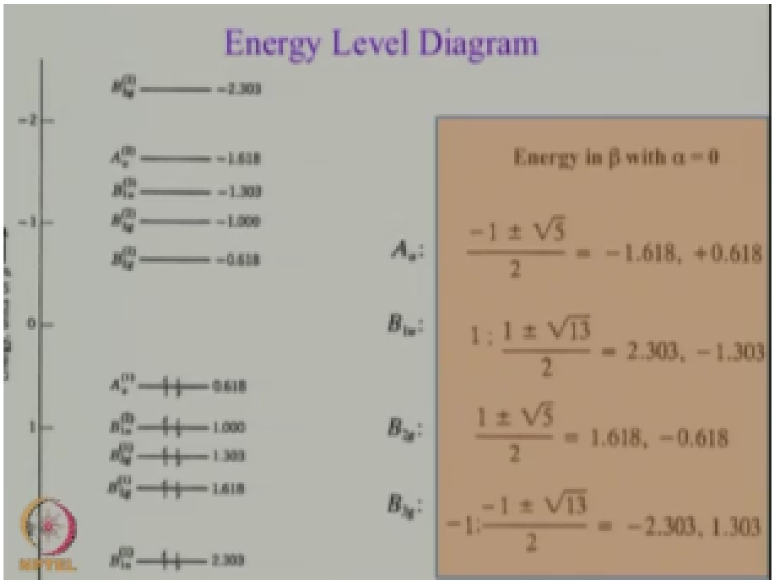
Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 61
Naphthalene - III

Right, now we begin our concluding session on naphthalene. This is where we have got so far. We have got the energy level diagram and we know what kind of energy is associated with what kind of symmetry.

(Refer Slide Time: 00:26)



Energy Level Diagram

Energy in β with α = 0

A_u: $\frac{-1 \pm \sqrt{5}}{2} = -1.618,\ +0.618$

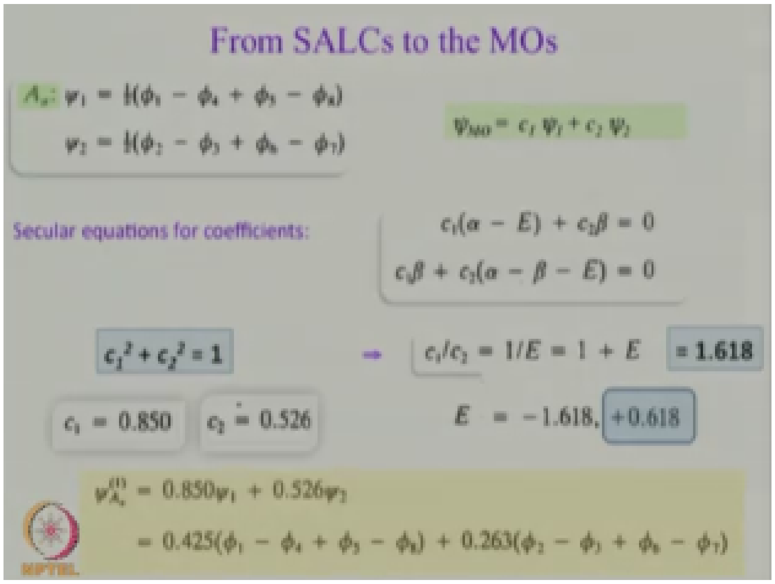
B_{1u}: $1 : \frac{1 \pm \sqrt{13}}{2} = 2.303,\ -1.303$

B_{2g}: $\frac{1 \pm \sqrt{5}}{2} = 1.618,\ -0.618$

B_{3g}: $-1 : \frac{-1 \pm \sqrt{13}}{2} = -2.303,\ 1.303$

What we do not know so far is what are the actual molecular orbitals. We have only been able to generate parts of them but we have not been able to generate molecular orbitals. So now, before going any further before going to spectroscopy let us try and generate the molecular orbitals of naphthalene knowing the SALCs. So let us start with A u.

(Refer Slide Time: 00:54)



From SALCs to the MOs

A_u: $\psi_1 = \frac{1}{2}(\phi_1 - \phi_4 + \phi_5 - \phi_8)$

$\psi_2 = \frac{1}{2}(\phi_2 - \phi_3 + \phi_6 - \phi_7)$

$\psi_{MO} = c_1\psi_1 + c_2\psi_2$

Secular equations for coefficients:

$$c_1(\alpha - E) + c_2\beta = 0$$
$$c_1\beta + c_2(\alpha - \beta - E) = 0$$

$c_1^2 + c_2^2 = 1$ → $c_1/c_2 = 1/E = 1 + E$ $= 1.618$

$c_1 = 0.850$ $c_2 \doteq 0.526$ $E = -1.618, \boxed{+0.618}$

$$\psi_{A_u}^{(1)} = 0.850\psi_1 + 0.526\psi_2$$
$$= 0.425(\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.263(\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

For A u we have 2 sets, right? it is something like half into phi i – phi j + phi k – phi l kind of combination, both of them. Now our task in hand is to generate a linear combination of psi 1 and psi 2 so that we get the MO. Please note that this MO is going to consist of 4 p orbitals. Phi 9 and phi 10 do not participate here because there is no A u in phi 9 and phi 10. Later on we will encounter a situation where phi 9 and phi 10 will also be contributing to the linear combination.

So if you have studied in organic chemistry, if you have seen these diagrams of pi molecular systems, you might have seen that sometimes on some of the atoms there is a dot, right? There is a dot, even in benzene it is there. What is the meaning of the dot? The meaning of the dot is that, that particular atom does not contribute to a molecular orbital of that symmetry. Okay, this is our task at hand.

We want to know what is this psi MO that we can generate by taking an appropriate linear combination of psi 1 and psi 2. What will be the symmetry of this psi MO if I work with this psi 1 and this psi 2? A? A is not enough. A u, okay you said u but I did not hear it. So A u, C 1 and C 2. Of course you can understand that you can have different combinations of C 1 and C 2. One is going to be plus, one is going to be minus and magnitudes can change.

So what you can do is once again you can set up secular equations for these. Exactly the same as what we discussed in the beginning of this discussion of naphthalene. The set of the equations this is what you get. C 1 multiplied by alpha – E + C 2 into beta. Of course, I have jumped a lot of sets here. I have only shown you only the final answer. I encourage you to work out these steps by yourselves.

If you do not understand, please come to me, we will try to work out together. So C 1 multiplied by alpha - E + C 2 multiplied by beta = 0 and the other one is C 1 multiplied by beta + C 2 multiplied by alpha minus beta minus E that is = 0. Two equations, what are the unknowns here? C 1 and C 2. Because we know what alpha is. We know what beta is. Do we know what E is? We will know what E is, is it not? Remember, we are talking about A u.

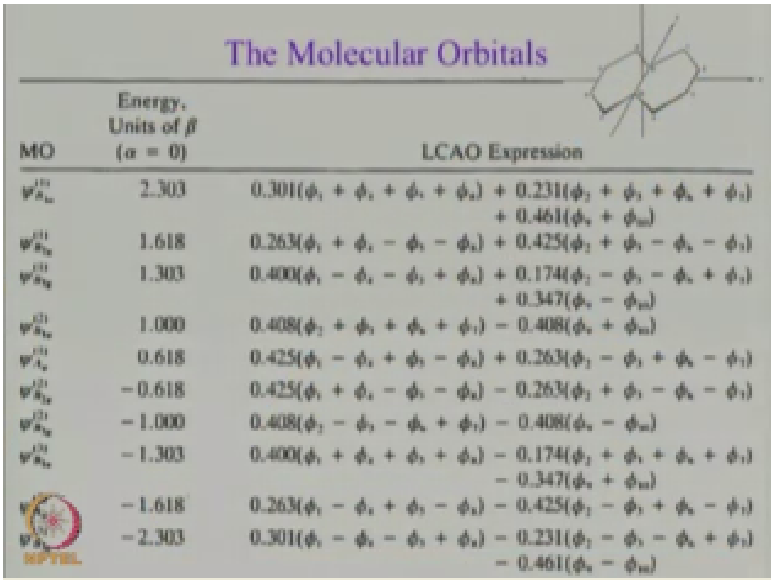
So E has to be – 1.618 or 0.618. Only two possibilities are there. So what you do is first of all you take 0.618 and substitute you are going to get, okay one more condition is C 1 square + C 2 square = 1. That I think is well known. So you have 2 equations. One is C 1 + C 2 = 1/E. It is also equal to 1 + E = 1.618. The other one is C 1 square + C 2 square = 1. Substitute you get C 1 = 0.85 and C 2 = 0.526, okay? So this is a plus combination.

If you want the other one, what you do is you take this – 1.618 and see this is all consistent, right? Because if you remember E = 0.618 that is for a bonding MO because multiplied by beta, beta is negative. E = - 1.618 that is the energy of an antibonding MO because it is multiplied by beta, beta is negative. So what we have got is, we have got C 1 and C 2 combinations, both are positive and now we are able to write the MO.

The bonding MO with A u symmetry turns out to be what you see in front of you, alright? We have been able to generate the MO. Good. So is that good or is that good? We have been able to write the MO now. So Joseph finally you are answered, right? We started with, so the whole idea of using symmetry is to simplify problems in quantum mechanics. We try and break up big problems into smaller parts but then we cannot afford to forget to combine them also, right?

That is what you are doing now. So you can do this for each and every symmetry of all the orbitals. If you have time and energy you can do it. This is the answer.

(Refer Slide Time: 05:56)



The Molecular Orbitals

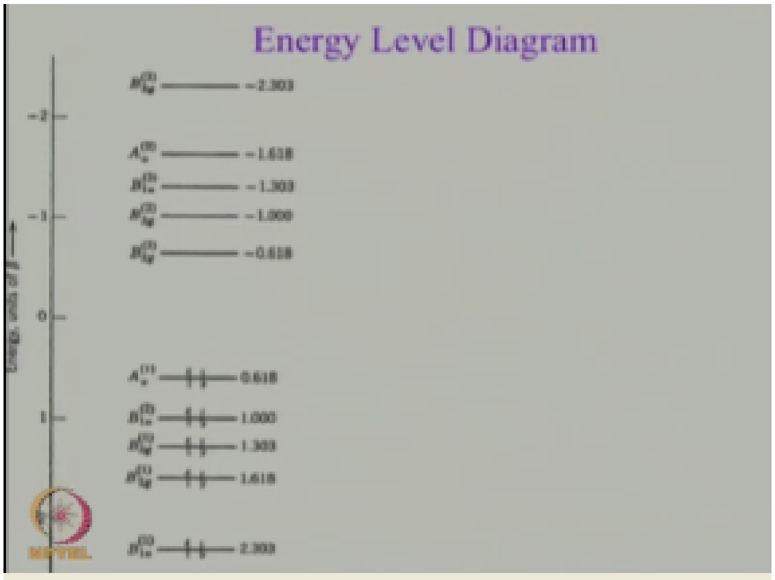
MO	Energy, Units of β $(\alpha = 0)$	LCAO Expression
$\psi_{B_{1u}}^{(1)}$	2.303	$0.301(\phi_1 + \phi_4 + \phi_5 + \phi_8) + 0.231(\phi_2 + \phi_3 + \phi_6 + \phi_7) + 0.461(\phi_9 + \phi_{10})$
$\psi_{B_{2g}}^{(1)}$	1.618	$0.263(\phi_1 + \phi_4 - \phi_5 - \phi_8) + 0.425(\phi_2 + \phi_3 - \phi_6 - \phi_7)$
$\psi_{B_{3g}}^{(1)}$	1.303	$0.400(\phi_1 - \phi_4 - \phi_5 + \phi_8) + 0.174(\phi_2 - \phi_3 - \phi_6 + \phi_7) + 0.347(\phi_9 - \phi_{10})$
$\psi_{B_{1u}}^{(2)}$	1.000	$0.408(\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.408(\phi_9 + \phi_{10})$
$\psi_{A_u}^{(1)}$	0.618	$0.425(\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.263(\phi_2 - \phi_3 + \phi_6 - \phi_7)$
$\psi_{B_{2g}}^{(2)}$	−0.618	$0.425(\phi_1 + \phi_4 - \phi_5 - \phi_8) - 0.263(\phi_2 + \phi_3 - \phi_6 - \phi_7)$
$\psi_{B_{3g}}^{(2)}$	−1.000	$0.408(\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.408(\phi_9 - \phi_{10})$
$\psi_{B_{1u}}^{(3)}$	−1.303	$0.400(\phi_1 + \phi_4 + \phi_5 + \phi_8) - 0.174(\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.347(\phi_9 + \phi_{10})$
[illegible]	−1.618	$0.263(\phi_1 - \phi_4 + \phi_5 - \phi_8) - 0.425(\phi_2 - \phi_3 + \phi_6 - \phi_7)$
[illegible]	−2.303	$0.301(\phi_1 - \phi_4 - \phi_5 + \phi_8) - 0.231(\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.461(\phi_9 - \phi_{10})$

Which orbital have you worked out already, this one, okay and where is its partner? Where is the other A u orbital, here right? Remember E is – 1.618. That turns out to be 0.263 multiplied by the first SALC - 0.425 multiplied by the other SALC. So you see there is a minus here, okay? And can you identify the bonding MOs. Can you identify the energies of the bonding MOs here? The top 5, right?

In fact the highlighted one is the highest occupied molecular orbital, okay? So what have we obtained so far? We obtained the expressions as well as energies of the MOs, okay? So far so good? This is your energy level diagram. You know what these are like.

(Refer Slide Time: 06:56)

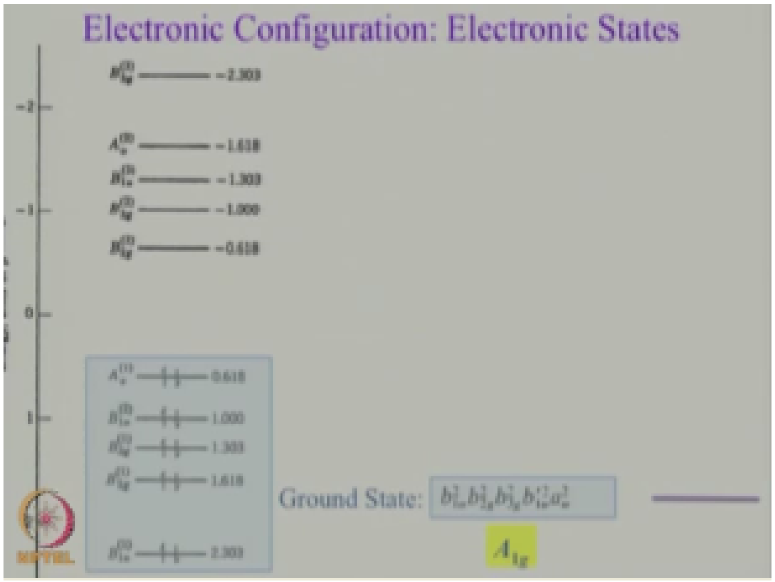
Energy Level Diagram



Now, of course this energy level diagram is not enough. We want to get into spectroscopy. Because well again this is a cliché I say everywhere. Experimental results are the only truth, right? Just theory is not enough. So where is my experimental result? What is the experiment that I do to see whether my quantum chemical calculation makes any sense or not? The experiment is spectroscopy, right?

As one of our illustrious colleagues had once said, spectroscopy is quantum mechanics in action. But then we have to arrive at spectroscopy from here as well. To do that first of all, what we do is we talk about symmetries of states which has been discussed earlier. Let us see if we can determine the symmetries of the ground state and the first few exited states.

(Refer Slide Time: 07:50)



Electronic Configuration: Electronic States

Ground State:

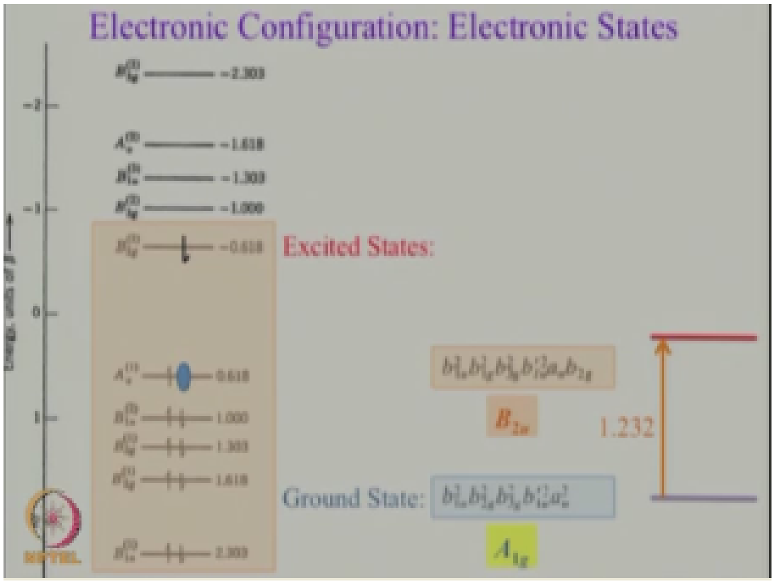
A_{1g}

What is the ground state? Look at this configuration. You have these 5 bonding molecular orbitals all of which are completely filled. So what is the, how do you name the state if all occupied orbitals are doubly occupied? First of all, singlet, triplet, doublet what is it? Singlet and what is the name of the state, it is the totally symmetry state, right? You basically take a product of everything, it will come out to be totally symmetric.

So ground state in this case is predictably singlet A 1g. I have not written the singlet here, but it is singlet A 1g, okay? Give me a sec. I think I have gotten a little carried away here and I have written an incorrect name. It is not A 1g. There is no 1 is it not? It is just A g. A 1g is there in benzene. So I have written A 1g that is a mistake. That is a hangover of benzene, alright? So A g. you can please correct it. It is A g, singlet A g. Fine. Now let us go to the next one.

This is one exited state that I can think of. How have I found it? By a HOMO-LUMO transition. HOMO to LUMO transition is the lowest energy transition. This is what it is. So what is the electron configuration now?

(Refer Slide Time: 09:37)

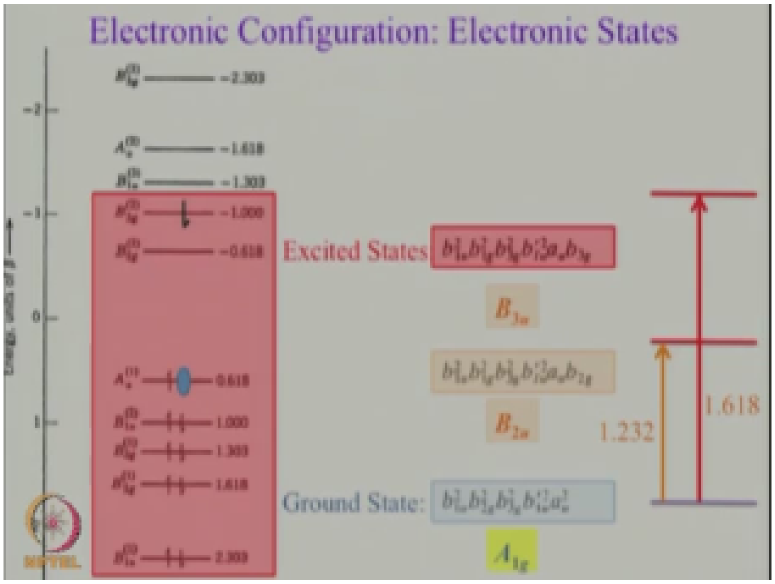


Electronic Configuration: Electronic States

It is b 1u 2 b 1g 2 b 3g 2 b 1u 2 a 1u and b 2g. So all the doubly occupied orbitals do not matter any way, right? What matters is A u and B 2g. So A u cross B 2g what will I get, direct product of A u and B 2g? Well, you can work it out looking at the character table or product table or you can remember direct product of A and B is always B. Direct product of g and u is always u. So what you get is B 2u. And remember we write states, symmetries of states in capital letters.

We write symmetries of orbitals of wave functions in small letters okay. So this is your exited state obtained by HOMO to LUMO transition. Next, okay well let us finish this. What is the energy? This one is 0.618. HOMO and LUMO is – 0.618. What is the energy gap? 1.232. So that transition should have energy of 1.232. What kind of transition is it? A g singlet A g to singlet B 2g transition, okay? Now, next let us think of another one.

(Refer Slide Time: 11:06)

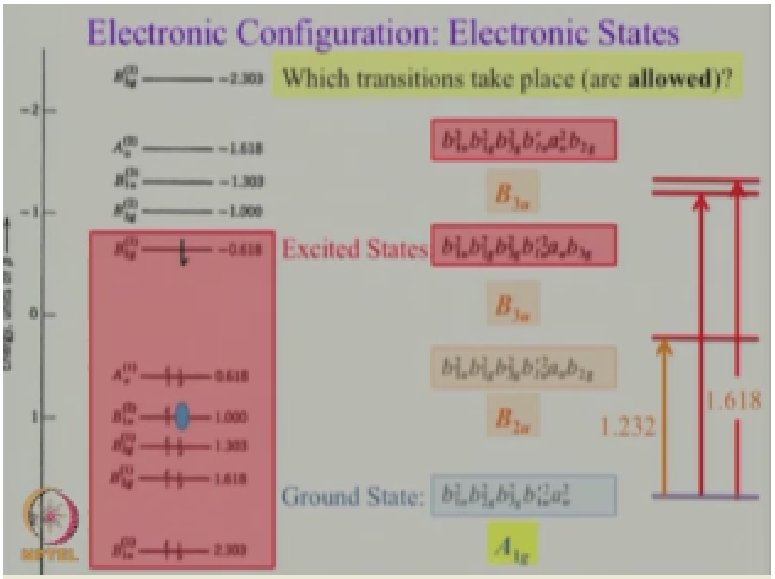


Electronic Configuration: Electronic States

Let us say I have performed a HOMO to LUMO +1 transition. That will have higher energy. What is the energy difference now? 1.618, is that right? 1.618. This is – 1 and this is 0.618. -1 – 0.618 is – 1.618 multiplied by beta, beta is actually – 1 in our convention. That becomes 1.618. Now see, what is the electron configuration now? A u B 3g. See only the orbitals that are singly occupied matter. A u B 3g what will be the direct product of A u and B 3g, B 3u?

So this is a B 3u configuration and the energy is 1.618. Let me try another kind of excitation now. What have I done so far? I have done HOMO to LUMO. I have done HOMO to LUMO +1. Now, let me try HOMO -1 to LUMO. Higher energy lower energy, it is best that we work out. This is – 0.618, this is 1. So what is it 1.618. So degenerate transition. So what we see is that we have, we expect a degenerate transition, a pair of degenerate transitions for HOMO to LUMO +1 and HOMO -1 to LUMO, right?

(Refer Slide Time: 12:45)



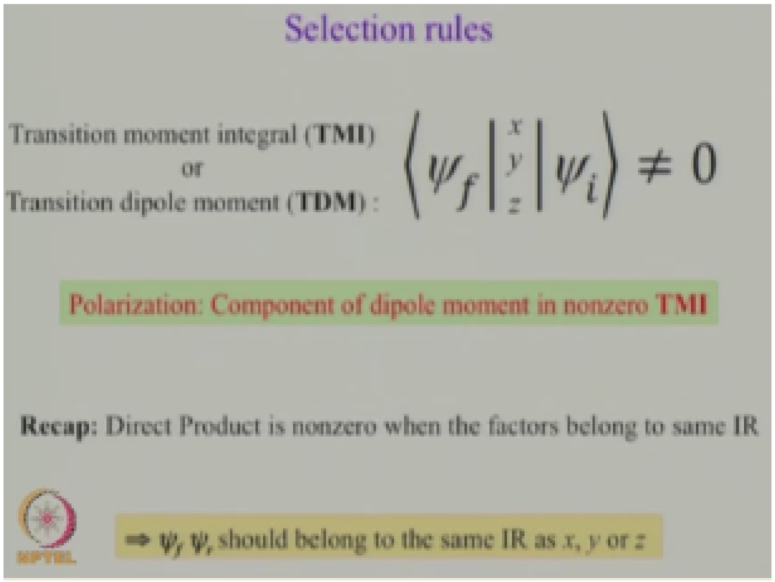
Electronic Configuration: Electronic States

Which transitions take place (are **allowed**)?

What is the symmetry of this configuration? A 2, A u and B 2g. Sorry, B 1u and B 2g. B 1u and B 2g what will it be? It will be B 3u once again. So this is what you expect. You expect one transition, just work it out from the character table it will follow. One transition of 1.232 beta and a doubly degenerate transition of 1.618 beta, okay? And the symmetries of transition are A g to B 2u and A g to B 3u. That is what you expect.

Which of these transitions are allowed, which of these transitions are not allowed? I think we know the generic answer to this question.

(Refer Slide Time: 13:46)



Selection rules

Transition moment integral (**TMI**)
or
Transition dipole moment (**TDM**) :

$$\left\langle \psi_f \middle| \begin{matrix} x \\ y \\ z \end{matrix} \middle| \psi_i \right\rangle \neq 0$$

Polarization: Component of dipole moment in nonzero **TMI**

Recap: Direct Product is nonzero when the factors belong to same IR

⇒ $\psi_f \psi_i$ should belong to the same IR as x, y or z

The generic answer to this question is that transitions are allowed when transition moment integral is nonzero and from the point of view of symmetry an integral is nonzero when the integral is or when the integral at least contains a totally symmetry part and if you now think first of all that psi i, psi i is, what is the wave function from which the upward transitions begin? It is A g, right totally symmetric anyway. So you do not even bother about it.

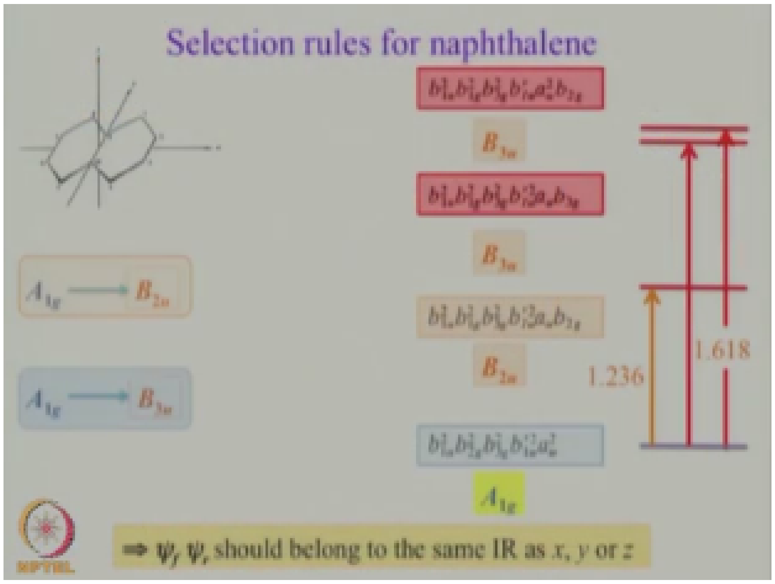
We bother about the direct product of psi f and mu. What is the symmetry of psi f, what is the symmetry of mu? Dipole moment. Of course dipole moment is a vector and it can have x or y or z component. So what you worry about is what is the symmetry of the direct product of the final wave function and either x or y or z. In our case, what are the final wave functions, what are the symmetries. One is B 2u, one is B 3u.

And what are the symmetries of x or y or z for D 2h? x belongs to which symmetry species? To which symmetry species does x belong? B 3u. What about y? B 2u. What about z? B 1u, okay. So that is what we worry about and of course we know that the component of dipole moment that gives you a nonzero transition moment integral that determines the polarization of the light absorbed or transmitted.

And then you might remember that when you are talking about a direct product, a direct product has or a direct product contains the totally symmetric representation only when these 2 functions of the direct product belong to the same symmetry species. That is the theorem that we had worked out earlier. So essentially the problem boils down to does the destination wave function belong to the same symmetry species as x or y or z.

If I go one step further, I can say that the transition is going to be allowed if the destination configuration has B 1u or B 2u or B 3u symmetry. If it is B 1u then the transition will be z polarized, if it is B 2u then it will be y polarized, if it is B 3u then it will be x polarized, okay? And we know very well that the destination states are B 2u and B 3u.

(Refer Slide Time: 16:49)



Selection rules for naphthalene

$A_{1g} \longrightarrow B_{2u}$

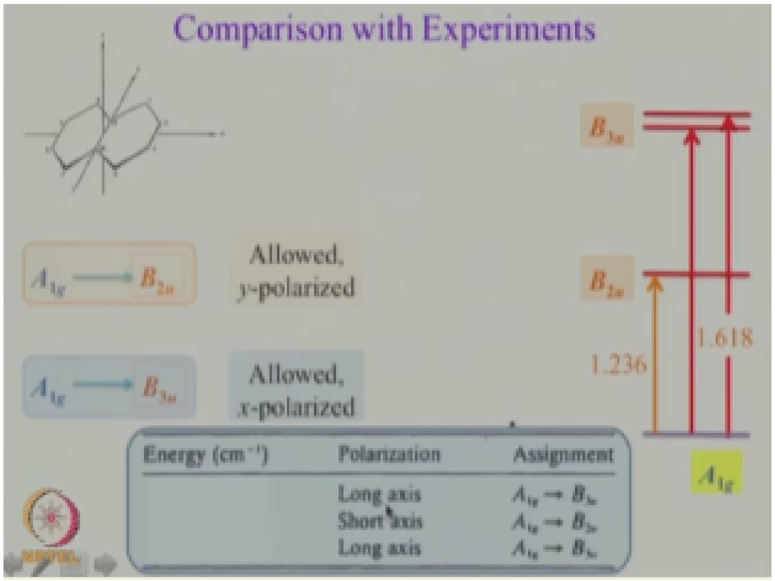
$A_{1g} \longrightarrow B_{3u}$

$\Rightarrow \psi_f\, \psi_i$ should belong to the same IR as x, y or z

These are the two kinds of symmetries. So now you can answer the question. Is A, again I have written A 1g unfortunately and it took me 4 years to notice it, A g, A g to B 2u is it allowed? It is allowed and y polarized. A g to B 3u, is it allowed? It is allowed and x polarized. Or if you can, if you want to write it in terms of this long axis and short axis terminology then we will say that A g to B 3u, this transition, first of all do not forget our expectation so far is that this A g to B 3u is a doubly degenerate, higher energy transition.

That should be polarized along long axis, x is long axis right? And A g to B 2u that is the lower energy singly degenerate, well non-degenerate transition that should be polarized along the short axis, okay?

(Refer Slide Time: 18:03)



Comparison with Experiments

$A_{1g} \longrightarrow B_{2u}$ Allowed, y-polarized

$A_{1g} \longrightarrow B_{3u}$ Allowed, x-polarized

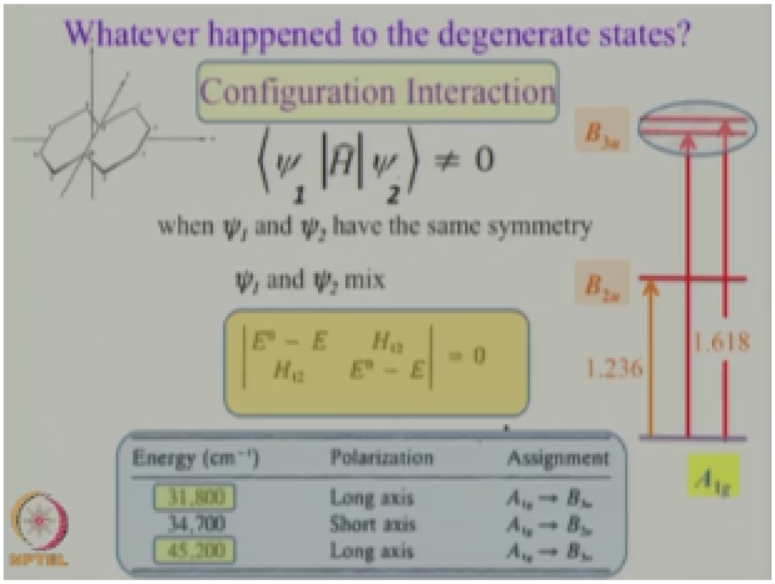
Energy (cm^{-1})	Polarization	Assignment
	Long axis	$A_{1g} \rightarrow B_{3u}$
	Short axis	$A_{1g} \rightarrow B_{2u}$
	Long axis	$A_{1g} \rightarrow B_{3u}$

This is what you expect and now moment of truth. We have to look at actual spectroscopic data and compare. This is your spectroscopic data. You do have 3 transitions. One along short axis and we assign it to A 1g to B 2u. We have two other transitions polarized along long axis. We assign them to A g to B 3u, right?

Now the expectation is that this energy for this short axis polarized transition should be lower than the other two and the other two should have the same energy. That is the expectation, this is the reality. It is true that the transition that is polarized along short axis has the lowest energy. It is not true, not true actually, not true. So what we see is that first of all you do not have these 2 degenerate transitions.

You actually have 3 transitions and the short axis polarized transition which you expected to be the lowest energy transition is actually a transition of intermediate energy. So now we are a little confused. Until now we were doing fine. But now we are faced with the question what happened? Where are the where are my degenerate states. Whatever happened to the degenerate states?

(Refer Slide Time: 19:36)


Whatever happened to the degenerate states?

Configuration Interaction

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle \neq 0$$

when ψ_1 and ψ_2 have the same symmetry

ψ_1 and ψ_2 mix

$$\begin{vmatrix} E^0 - E & H_{12} \\ H_{12} & E^0 - E \end{vmatrix} = 0$$

Energy (cm⁻¹)	Polarization	Assignment
31,800	Long axis	$A_{1g} \rightarrow B_{3u}$
34,700	Short axis	$A_{1g} \rightarrow B_{2u}$
45,200	Long axis	$A_{1g} \rightarrow B_{3u}$

And the answer is configuration interaction happened. Configuration interaction means you have two configurations which have same energy or nearly same energy and then they have the same symmetry. In this case, these are they become talkative configurations. They do not remain by themselves, they talk, they mix and when they mix, when wave functions mix, you end up getting linear combinations one of which is lower energy, one of which has higher energy.

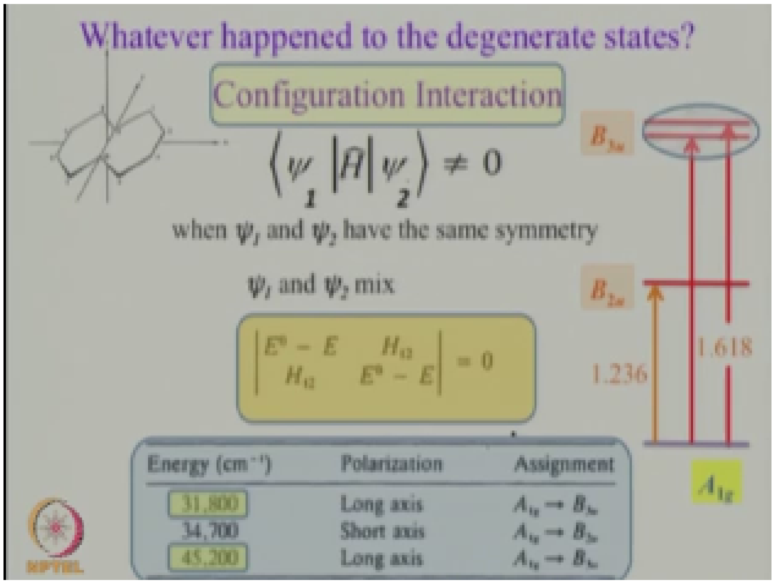
That is exactly what happens. And extent of this is determined by this interaction integral, integral of psi 1 H ps1 2 over all space. That is not equal to 0 if energies are comparable and symmetries are same. So that is what has happened essentially. So what has happened is this degenerate pair that you had have formed linear combination, mixed and then due to mixing, again you will be able to write a pair of separate way. Now you are getting used to this, right?

And you will have this secular determinants. Now you see this secular determinant again when you expand you are going to get this quadratic equation in E right? It is going to have 2 roots, okay? So one root will be less than 0, one will be more than 0. So due to configuration interaction this kind of spreading takes place. So you often say no crossing rule. States of same symmetry do not cross each other.

Actually that is something that helps us understand things. But it is actually not right. It is the other way round. There is no question of no crossing. Actually they mix. And when they mix they form 2 states. So what you see here is not repulsion between states. It is mixing of states which gives you one state of low energy, one state of high energy, right? This is the answer. So now if I now combine this theory with experiment what can I do?

This short axis polarized transition of 34,700 that has not, that has got nothing to do with configuration interaction, right? We know what the expected value of energy of it is in terms of beta, right? What is it? What is that energy? 1.2 or something, 1.236.

(Refer Slide Time: 22:01)



Whatever happened to the degenerate states?

Configuration Interaction

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle \neq 0$$

when ψ_1 and ψ_2 have the same symmetry

ψ_1 and ψ_2 mix

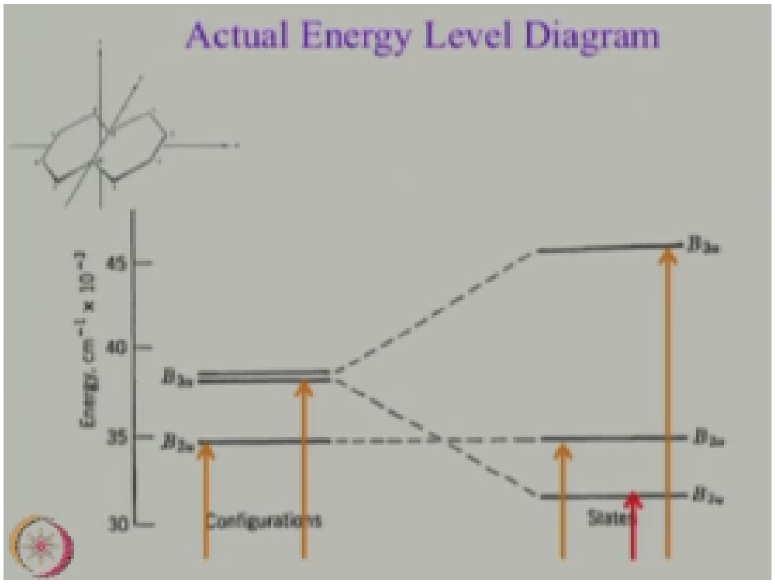
$$\begin{vmatrix} E^0 - E & H_{12} \\ H_{12} & E^0 - E \end{vmatrix} = 0$$

Energy (cm^{-1})	Polarization	Assignment
31,800	Long axis	$A_{1g} \rightarrow B_{3u}$
34,700	Short axis	$A_{1g} \rightarrow B_{2u}$
45,200	Long axis	$A_{1g} \rightarrow B_{3u}$

So we can might as well say that this 34,700 cm inverse that is 1.236 beta - 1.236 beta and that gives me an experimentally determined value of beta. That was the question, how do you determine beta. I do not know how to determine it theoretically. There is a way, I do not know so much. But what we have arrived at is, how we can determine a value of beta experimentally, okay? And now what more can I get from here?

I know these values right? 31,800, 45,200 and I have already determined what is the value of beta, 34,700. I can actually work out this interaction energy and everything. So by mixing theory and experiment I can kind of get a good idea, a good quantitative idea of the entire scenario. Okay, so this is what it is.

(Refer Slide Time: 23:13)


Actual Energy Level Diagram

Remember, what we got initially, we thought we have got the electronic states. But they were not the final electronic states. They were configurations. And these configurations if they have the right energy and right symmetry they can actually interact to give you the final states. That is what has happened here, okay. That is the end of the story for naphthalene. So in discussing this, we have learnt several things.

First of all, we have learnt how to solve this complicated, well organic chemists may not agree that this is complicated. They sometimes handle much bigger molecules, but quantum chemists will agree that this is a complicated problem. So you have learnt how to simplify complicated quantum mechanical problems using symmetry and in the process we learnt also this business of configuration interaction which tells us that it is not always 0th order.

Very often configurations that you produce can also interact with each other and give you a picture that you do not expect at first class, right? That is why naphthalene is a good case study. That is it, thank you.