Chemical Applications of Symmetry and Group Theory

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Lecture – 38

Hello and welcome. Today we are going to look at the transitions between different electronic levels or different orbitals in particularly Natalie molecule.

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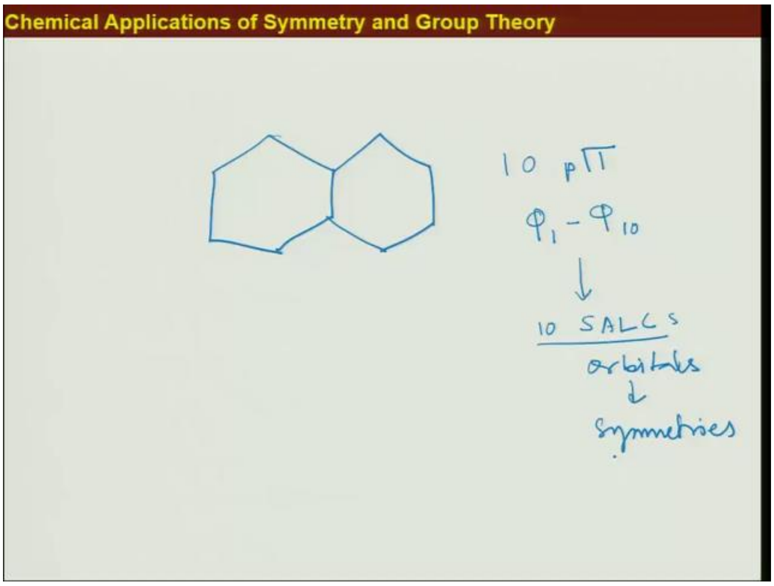

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10 pπ

$\varphi_1 - \varphi_{10}$

↓

10 SALCs

orbitals

↓

symmetries

So for Natalie molecule we earlier what we did, we took the all the 10 p by orbitals situated in each of the carbon atoms. So, total 10 p phi orbitals we took. So, we had like phi 1 to phi 10 and we formed the 10 SALC. So, this 10 SALC will give me 10 orbitals SALC, and these are all phi type orbitals.

So, now what why does orbitals and we also got the symmetries of those orbitals. So, in the next step we got those symmetries of these orbitals in meaning that particular we would do see presentation according to which this SALC transform as that in found out and we also use the book off approximation to particularly in assign the energies to different orbitals that we found here.

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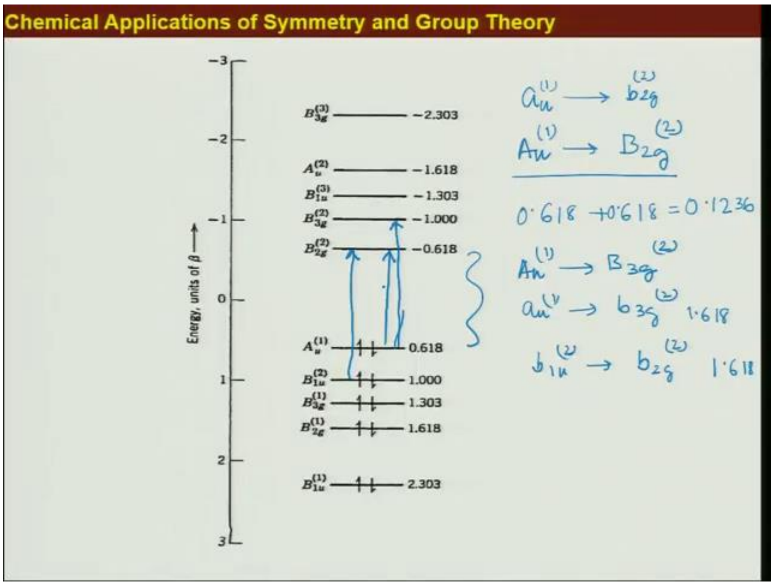
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$a_u^{(1)} \longrightarrow b_{2g}^{(2)}$

$A_u^{(1)} \longrightarrow B_{2g}^{(2)}$

$0{\cdot}618 + 0{\cdot}618 = 0{\cdot}1236$

$A_u^{(1)} \longrightarrow B_{3g}^{(2)}$

$a_u^{(1)} \longrightarrow b_{3g}^{(2)}$ 1·618

$b_{1u}^{(2)} \longrightarrow b_{2g}^{(2)}$ 1·618

So, ultimately we got this particularenergy diagram. So, we can see that there are different orbitals, having different amount of energy and we also use the poleis exclusion principle and hones soon to addance this electrons into the particular orbitals right.

So, now what we can think of, we can think of transition from one particular energy state to another one. Now he had all together I have 10 energy states. Now in principle I can take one electron from any of the given orbitals and put it into higher orbitals. So, thereby I can get an excited state, but whether that is actually allowed or not that we need to find out and we also know try to think about a particular transition which is viable within that energy that we can get from normally visible or u v radiation for our normal spectroscopic techniques.

So what is the lowest energy gap that I can think of can have a transition of an electron from a given state to an upper state. So that is; obviously, if you look at this phicture is a transition from here to this particular state that means, I am talking about a transition from au which is also marked as 1 because there are several there are orbitals with the same selective. So, to differentiate them here things are marked by this superscript 1, 2, 3 so on. In the order of increasing energy alright, so if I have a transition from this A1, au orbital to b 2g orbital, then that will give me the lowest amount of energy. So, what will be the energy for this transition? That will be 618 that is the gap between notices to state way. So, that will be this. So this will be 0.1236 that will be the energy that in it in terms of beta. So, this is the lowest in a transition that we can think of.

Now, what are the other 2 transition that I can think of, one is from this particular state to B3z. So, I can think of a transition which is Au1 to B 3g 2 orbital and just not one thing that I am calling this as orbital because they are all orbitals, they are the SALC that we formed out of the atomic p phi orbitals alright. So, this au or B 3g that we are writing right now this does not give me the state of electronic state. So, make it clear. So, mostly what we actually do instead of writing them as this capital au is preferred that u1 lights this in terms of the small letters. So, actually if I want to write this one in a proper way, I should write au if I want to mark this one then to b 2g and we will use this capital letter for the overall state.

So now, if I follow that terminology then I should write here also it is Au1 to B 3g 2. So, this transition we will have energy of 1.618 and I can think of another transition from b1u to b 2g. So, if I write b1u to b 2g that will also have energy of 1.618. So, both of them are having almost similar energy. Now if I want to know whether this 3u know in the lowest order transitions are allowed or not. If they are allowed then they are allowed in which polarization.

So, that we need to find out, how to tackle this problem, like I had this orbitals symmetries and I know that I think while trying to find out where their transition is allowed or not I need to find out the you know I need to worry about the wave functions of the particular state. I need to know how to get the state the electronic state of this whole system alright. So, let us try to do that.

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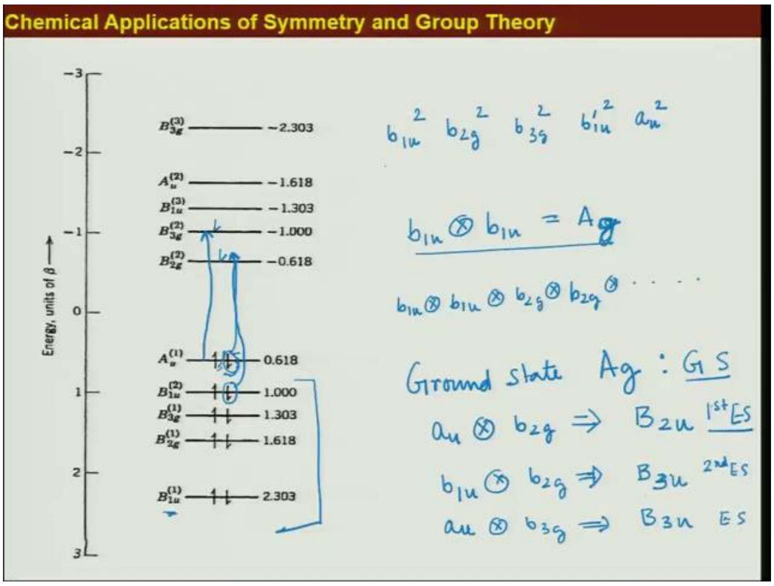

Chemical Applications of Symmetry and Group Theory

$b_{1u}^{2}\ b_{2g}^{2}\ b_{3g}^{2}\ b_{1u}'^{2}\ a_u^{2}$

$b_{1u} \otimes b_{1u} = A_g$

$b_{1u} \otimes b_{1u} \otimes b_{2g} \otimes b_{2g} \otimes \cdots$

Ground state A_g : GS

$a_u \otimes b_{2g} \Rightarrow B_{2u}$ 1st ES

$b_{1u} \otimes b_{2g} \Rightarrow B_{3u}$ 2nd ES

$a_u \otimes b_{3g} \Rightarrow B_{3u}$ ES

So, overall at first what do you have to do? We have to take one electron from one of the states and then we have to transfer it here. So, on whatever state I am trying to go to. So, we have transferred the electrons to that particular state. Now how do we write down the total overall electronic configuration, the electron configuration of this existing system which is the ground state? So, I have lower energy to the higher energy if I write down then my situation will be b 1u.

Now I will use a different symbol, symbol means here instead of writing those numbers within the parent basis which dictates that this is a separate Bu having a higher energy than the previous b 1u instead of that I will use the prying notation to differentiate 2 different u know states having the same isolation representation and we will use a superscript to indicate the number of electrons in that particular orbitals. So, this b1u orbital, it has a pair of electrons. So, I write b1u 2 and then next come b 2g to B 3g 2, b1u 2 know you see b1u already exists here. So, I will separate them by using a prime and then at last on one hand I have Au2. Now all this electrons at paired up right. So, in each orbital I have 2 electrons, each electron has symmetry of that particular orbital correct.

So, the overall state of that particular orbital, if I forget that I have any other orbital, I am considering say suppose b1u this particular orbital. So, b1u has 2 electrons. So, each electron has this makes to b1u. So, if I have to describe the state of the system of that say one better system having a pair of electrons, then it will be the direct product of these symmetries of each electron. Therefore, I will have b1u and the direct over between 2B1u. So, I will have a situation like b1u and what we will be the result? I know to irresuvla representation this is the square of the irerisible representation will contain that totally symmetric ir and here in this case since they are one dimensional I can directly say that this will be the total symetric irerisible representation that is A1g for the particular point that is d2 h. So, this I said about all the orbitals.

Now if you think that you have 5 different orbitals each one of them have 2 electrons each. So, for all of these orbitals, if you do this direct product overall you will get the symmetry of the state. So, essentially what you have to do? You have to do like b1u cross b1u then you have to get b 2g, b 2g and so on.

Now, in each one of them are giving is giving a total symmetric ir. So, all 2 be the since all of the orbitals occupied by 2 electrons then overall the state of the system that electronic state of the system is totally symmetric right. So, here for B2h if I look at, this is totally symmetric ir is Ag. So, if this is my right configuration of the grounds in which it is. So, the ground state has the symmetry of Ag right and we also now know that if that configuration has all of it was paired up, then I can easily ignore or I can only concentrate on the portion which the other orbitals which contain unpaired electrons. So, I should be worried about only those, but others will always give you totally symmetric illusion representation.

So, this is my ground state. Now we have to worry about the excited state. So, excited state which one? So, first we have to worry about this lowest energy transition right. So, that is from A1u to b 2g right, A1u to b 2g, if I make a transition, what I can do? I can take one of these electrons from here and I can transfer it here right. So, I will have instead of here, I can have it here. Now I have to find out; what is the electronic state of or what is symmetry of this state. I am taking the electron from this orbital to this orbital and getting a state.

So, first when I had all the system paired up in this particular case of naphthalene considered to be my ground state and my excited state will be where one of the electrons from au has moved to b 2g correct. So, this particular system has the symmetry if I remember my previous condition that which orbital is in W occupied, I do not worry about that because that will give me total symmetric or.

So, I will only consider these orbitals which have the unpaired electron. So, therefore, this part is redundant to me when I try to find out the excited state. So, then I have this au and I have to take a direct product of au to b 2g. Now this a2u to b 2g that gives me which particular ir, in that case I can easily take a look at my character table and I can see that au and b 2g gives me B 2u. So, this gives me a direct product which is B 2u right. So, we already know how to get this direct product side. So, B 2u is my first excited state right. So, this is my ground state and this is my first excited state.

Now, similarly what I can do? I have to find out what happens to the symmetry of the state when I have a transition from here. So, instead of this if I have a situation that, this electron is taken to this orbital. Well this one if it remains as such. So, this orbital is now occupied by a pair of electrons, while b1u is (Refer Time: 16:43), but and b two g is (Refer Time: 16:46). So, here what I have to do I have to worry about direct product b1u and b 2g. So, if you have a look at the character table carry out the direct product, you will see that this gives you B 3u. So, this is my next excited state. So, if I call it second excited states then I have to worry about the other one. So, that is Au2, B 3g.

So, if I have one electron transport to B 3g from au. So, this also supposedly having the same energy as that of this particular transition which gives you B 3u, so for this particular transition from au to B 3g, thus symmetry of state will be obtained by taking a direct product of au and B 3g and here after doing this you will see that this corresponds to again B 3u symmetric. So, you can say that they know this is also almost like these degenerate the previous excited state that in call. So, now, if I want to find out the whether or not the transition from au to b 2g or au to B 3g or b1u to b 2g they are allowed or not, I have to actually find out whether a transition from Ag to B 2u or Ag to B 3u are allowed or not.

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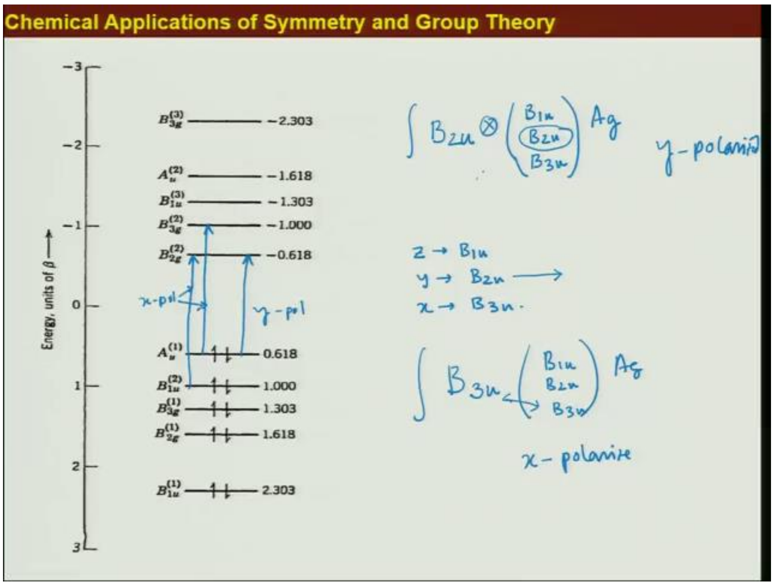

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$\int B_{2u} \otimes \begin{pmatrix} B_{1u} \\ \boxed{B_{2u}} \\ B_{3u} \end{pmatrix} A_g$ y-polarized

z → B_{1u}
y → B_{2u} ⟶
x → B_{3u}.

$\int B_{3u} \begin{pmatrix} B_{1u} \\ B_{2u} \\ B_{3u} \end{pmatrix} A_g$

x-polarize

So, in the next step, what you have to do? You have to solve this problem that is you have the excited state having symmetry B 2u and you have to take a direct product with the contusion policy system. So, therefore, if you look at the character table for deep B2h, then you will see that z transform as b1u, y transform as B 2u, while x transform as B 3u. These are the illusion representation. So, you have to have b1u, B 2u, and B 3u. So and then you have this Ag, which is totally symmetric ir and it presents the grounds electronic state.

So, what do you can do? You since this is totally symmetry illusion representation higher you do not care about this one. So, you find the direct contact between B 2u and b1u, B 2u and B 2u, b1u and B 3u. So, immediately you can see that the second integral that is B 2u and B 2u direct product, it will definitely give you Ag right. So, therefore, this transition with respect to y is allowed correct. So, here you can cross check what will happen if you multiply B 2u and b1u. So, if you look at the character table then you will see that B 2u and b1u will not yield Ag upon direct product and what about B 2u and B 3u that is also not going to give you the totally symmetric ir. So, only the transition is allowed overall and it is allowed in y direction.

Why y? Because this B 2u this has y as is basis. So, this particular transition will be y (Refer Time: 21:15). Now for the other two transitions, you have the same type of situation where you have B 3u as there is no illusion presentation for both the excited states and you have the same situation here b1u and B 2u or B 3u and then you have Ag. So obviously, you can see that B 3u and B 3u direct product, that is going to survive because that is going to give you the ire risible representation and if you check the character table what you will see? You will see that the direct product between B 3u and b1u B 3u and B 2u and you will not give you Ag. So, any illusion representation that is not errestcul ir is not going to give you nonzero value for the overall transition moment integral.

Now, B 3u I can see that forms the where x from the bases as called the B 3u or x transform of B 3u. So, therefore, again for this transition, that is first transition this one it refers to transition from here to here, the second transition refers to the electron making a transition from here to here and the third transition it refers to transition from here to here. So, first one we see that this is y polarized, while this one I can see B3 transformed as x transformers as B 3u.

So, therefore, this transition overall allowed and specifically this condition is x polarized right. So, if I have to mark here. So, this transition is y polarized, while this 2 are x polarized both of them. So, this as well as these both of them are x polarized. So, in this way we have learned about how to find out about the allowedness of any particular transition from one given orbital to another orbital and we also learned how to form find the symmetry of the state as well because at the end when you want to find the selection rule, you need to work with the state not with the orbital selection right.

So, you first find the symmetry of the state, first find out the symmetry of the orbital, and assign the electron symmetry to the electrons in those orbitals and then ultimately find the symmetry of the overall state and then use that to form your transition moment integral find the direct products and you find out where that contains totally symmetric ir or not if the answer is yes transition is allowed, if it is not transition is forbidden if it is allowed for in one of the particular direction or in a particular plane then we know that this is either polarized in that particular direction on that particular plane. So, we found here, that the trans less transition is allowed and it is allowed in the y direction, while the other 2 the next lowest transition they are allowed in extension.

So, in the following class we will try to get some more examples and explain these things. So, that the overall this particular case of electronic spectroscopy and how we use a group theory. Here whatever we did, we actually we did not do any hardcore mathematics here, to find out whether the integral will survive or not or we use we use the symmetry concept right we added the symmetry concept here to this electronic states and ultimately figured out without going into the detail of mathematics whether it will survive or not right.

So suppose particular transition is allowed. So you will get those pictures you are talking about, suppose you are talking about electronic transition. So, you will get electronic spectra; say probably in the visible range in the UV region of the spectra. Now what will be your know intensities. So, the intensity will depend on how much allowedness overall electronic transition is. What is the meaning? So, if you remember we had this three integrals Frankland factor and do you have this transition between 2 electronics orbitals and then spin overlap. So, if a particular a electronic transition is spin allowed, but it is orbital a forbidden then it is intensities very low and intensities are expressed I mean it is being easily you can talk in terms of the extinction coefficient. So, the extinction coefficient will be very low for orbital republican transition.

Now of spin forbidden transition, for which this site, start is prime, sighs start this integral is 0, while the orbital in the integral is nonzero, meaning that it is orbitaly allowed, but it is been forbidden in that case its intensity will be moderately higher and that will be reflected in its in its extinction coefficient right. Now when the transition is both spin allowed as well as orbital allowed, then we call it is totally allowed system or if both of them are forbidden then we call this totally forbidden system. So, for totally allowed system the bad will be extremely bright and then what does the Frankland factor do here. So, Frankland factor it dictates like how much is the overlap between 2 vibrational states involved in the overall electronic transition. So, the greater the overlap greater is the probability of transition. So, if there is no overlap then it is tend to 0.

So, this Frankland factor it modulates the intensities of an electronic transition. Suppose I have a totally allowed transition meaning that which is orbitaly allowed and also spin allowed, then Frankland factor will modulate the intensity. So, for a particular vibrational transition within the electronic levels for which the Frankland factor is higher it will have higher intensity for the particular band I am talking about while Frankland factor will modulate the overall electronic absorption intensity.

With this we will stop here today, and I thank you very much for your attention.