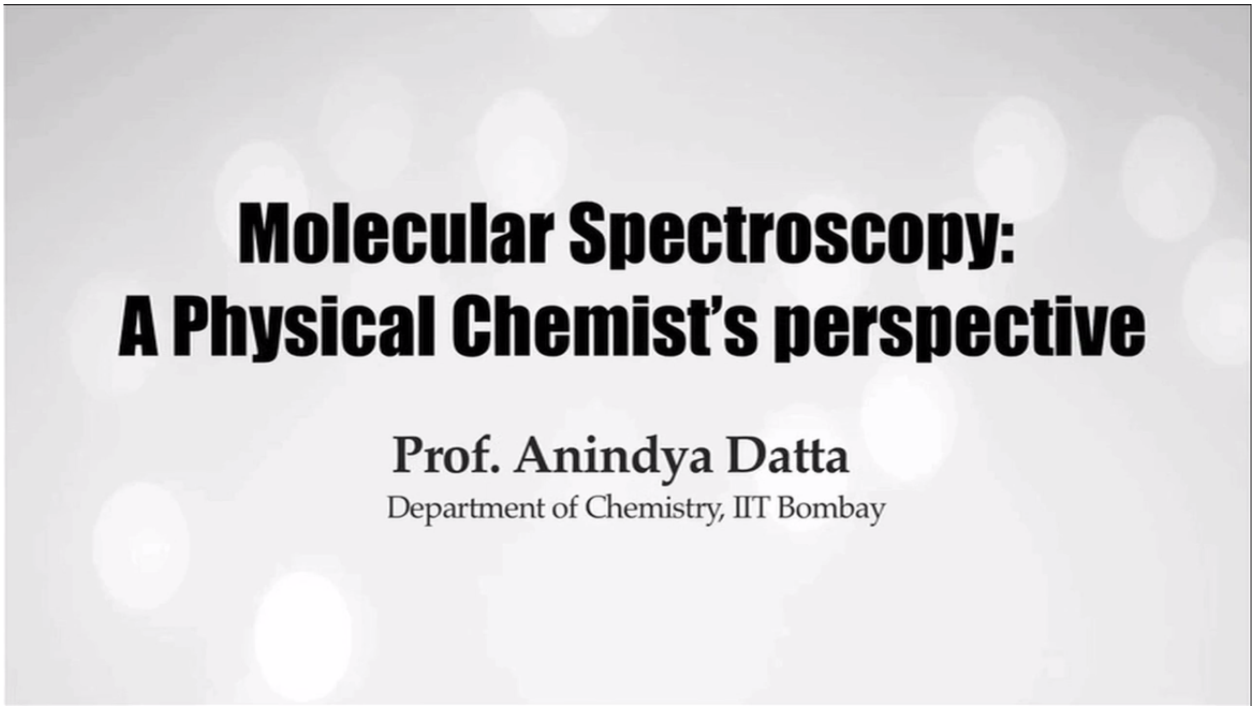

Molecular Spectroscopy: A Physical Chemist's perspective

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Knowledge is supreme.

Anindya Datta: We have been talking about these rules that allow us determine the symmetries of electronic states. When we say electronic state we have understood that we mean what is the symmetry of the and when I say symmetry I definitely mean which symmetry species or which irreducible representation. So symmetry of states means irreducible representation to which the electronic wave function belongs.

The way I get the electronic wave function is via a continued product of all the occupied [Indiscernible] [00:01:00]. So we have seen all the easy cases yesterday. We will see another easy case today.

So what have we said earlier we have said that the way you determine the symmetry of a state is that you take the product, direct product of everything and you basically multiply the representation see what you get. So if all the Mos are doubly occupied then what happens each of them give rise to a total symmetric representation because something multiplied by something else so something multiplied by itself is totally symmetric. That is something that we have learned while we discussed the normal modes of vibration same thing [Indiscernible] [00:01:45]

Then we said that suppose you have one electron in an orbital which is not paired. Example would be [Indiscernible] [00:01:56] 2 plus one electron in an orbital so there is only one singly occupied molecular orbital. In that case whatever is the symmetry of that orbital is the symmetry of the state because everything else is totally symmetric anyway.

Then we said what happens when we have two electrons in two non-genertive orbitals. We take a direct product and then when you take a direct product it is not necessary that you are going to have a single state because the direct product more often than not leads to a reduced [Indiscernible] [00:02:31] representation. If both the wave functions participating in the direct product are one dimensional if both the wave functions belong to one dimensional representations then their direct product is also one dimensional but if any one of them is more than one dimensional then you get a reducible representation not an irreducible representation. Are we clear about that?

I have two irreducible representations say gamma I and gamma j. if I take a direct product of these to get something gamma then if this is one dimensional and if this is also one dimensional then the product is one dimensional. If one of them is one dimensional and the other is two dimensional what is the representation that you get by doing the direct product? What is the dimensionality of the representation that you obtain from the direct product? Yes. Two. And if this is 3 dimensional and this is 4 dimensional then what is the dimensionality of the product? Yeah? 12. And more often than not usually these are all reducible representation. That's what I am saying.

So you should be able to reduce them and get a sum of irreducible representations. We are going to encounter a situation like that right now. What we did not discuss last day and we will discuss today is what happens when you have two electrons in two degenerate orbitals. Of course everybody is familiar with an example of such an situation. What is that example? I need to hear you. Oxygen. It's written on the board. Oxygen. Everybody knows the electron configuration of oxygen, oxygen is something like this. I am not drawing the arrows intentionally. It's like this. What are these orbitals? What are the homos for oxygen, dioxygen? Pi star. So pi star means what pi g or pi you? Pi g. so we have great respect for orbital that are symmetric with respect to inversion. So those pi orbitals are called pi g. if they are [Indiscernible] [00:05:19] then we don't call them g any more.

So how will I determine the symmetry of this state? The basic working is the same. You still take a product of the two. So first let us take the product and see what happens. This is pi g this is also pi g. so what we need to do is we need to take the direct product pi g cross pi g. what is the symmetry point group of dioxygen? D infinity h. so say that. What is the problem in saying that? D infinity h. so we need to see d infinity character table. As usual we will do the long cut first and then we will learn the short cut. Pi g cross pi g. what is Pi g. This is pi g. And once again this is pi g. so what is pi g cross pi g? What are the characters that you get? So two into four what is the second one, what is the second one? What is the character of c infinity phi? Yes. Four cos square phi. What is the third one? Third one is very easy. Even I can do it. 0 multiplied by 0 is 0. What is the fourth one? Vivah? Pi g cross pi g. [Hindi language] [00:07:08] what happens when you multiply two by two? Four, excellent. Then. Yes. 4 cos square phi again, plus or minus? Okay. You said so. Then 0, okay that is where the character table ends. I got confused because I was wondering where this [Indiscernible] [00:07:39] came from. There is actually the next column.

This is your – this is the representation that I have got and at least [Indiscernible] [00:07:50] this character table this is definitely a reducible representation. How do I reduce a reducible representation. What is the formula? 1 by h the problem is h is infinity here. H is infinity. So you will not be able to use the formula. How do I do it? I do it the hard way. Now you have to slug it out. You can still do it but you cannot use the formula. You have to do it by inspection. Let us see if you can do it by inspection and usually when I do things like this I always go wrong. And students get it right. So I am hoping that you are going to get it right now. So let us see.

What is it? First one is 4. How do I get 4? No, even before the first one let us look at the character of I because the good thing is since there is point of inversion you either have g or u. Looking at I we should be able to tell what kind of thing we get. In fact we don't even have to do that. We are doing pi g cross pi g. what did we discuss in one of the earlier classes? What is g cross g? G cross g is g. u cross g is g. g cross u or u cross g that is u. So we do not have to bother about these. We should only worry about these. So when we try to do it in the root [Indiscernible] [00:09:14] way we should only look at [Indiscernible] [00:09:18] and I have got four so how can I get four? Many combinations. I can add this and this or I can add this and this and this or I can have pi g plus 2 into sigma g plus or I can have pi g plus two into sigma g minus. There are many ways. Or I can have four sigma g plus or four sigma g minus so let us see what it will be.

To do that what is the base star? Let us see what is this one? Four cross square phi and there I have two cos phi. It might be a little easier if I try to tackle that first. Now how do I write cos square phi? I think we all know that. Cos square phi because my hope is here I have cos phi here I have cos 2 phi so if I get somehow and I have a square, everybody knows cos square phi is related to cos of 2 phi. So from there I get a hint that maybe delta g is involved. So let us see if I can write that. Cos square phi 2 cos square phi minus 1 is equal to cos of 2 phi. Isn't it? So I have – what do I have here? I don't have cos of 2 phi. I have cos 2 phi multiplied by 2. So how do I get that? Multiply it by two this becomes four and this become two. Four cos square phi minus two. So four cos square phi is something I already have. How do I get minus? Am I making sense? No? So what I am trying to do is I am trying to write this as gamma. This is your gamma. This is what you have got. I am trying to write it as something like a1 multiplied by sigma g plus I will write like this, maybe write like this, sigma g plus a2 multiplied by sigma g minus plus a3 multiplied by pie g plus a4 multiplied by delta g. So I need to find a1, a2, a3, a4. I didn't – don't need to worry about the us. So how do you find a1, a2, a3, a4? That's all I am saying.

Can you do it? So you saw what I am doing. I am trying to look at individual characters and from there I am trying to figure out what the coefficients are. Tell me what the coefficients are? Delta g is definitely there. There is no doubt. So one thing is if delta g is there delta g is a two dimensional basis. How many dimensions are you left with? The reducible representation you have is four dimensional. So it is either delta g plus delta g or it is delta g plus sigma g plus sigma g minus or it is delta g plus 2 sigma g plus or it is delta g plus 2 sigma g minus. Actually one thing we can do without getting into much trouble is that just [Indiscernible] [00:12:24] them out. Can it be two delta g? Two delta g doesn't match. Can it delta g plus 2 sigma g plus? No. Can it be delta g plus 2 sigma g minus? Then I am only left with delta g plus sigma g plus plus sigma g minus. Does that give you the same answer? Yes. Actually that is a better way. I think I was going in a very round about manner. It's not required. So what we get is we get that pi g cross pi g this gives me delta g plus or maybe I will write the one dimensional rep first. I will erase this because this is not required.

It is sigma g plus plus sigma g minus plus delta g. You agree with that. Sorry?

Student: [Indiscernible] [00:13:19]

Anindya Datta: Work it out, see if it will work. Delta g you have the characters. 2 2 cos pi etc. etc. if you add 2 sigma g plus what will you get? 2 plus 2 four that is okay. but then you get 2 cos 2 phi plus 2. That is also okay. zero. Zero is not coming. Somewhere it will go wrong. You will always get a unique combination. There is no doubt about that. That's one good thing about symmetry. If you go wrong it is very easy to figure out that you have gone wrong. Alright. So this is what it is. so this is the root four method. It's not that diffficult also. But then if we are – if we really want to be lazy then what we need to do is we need to know another kind of table over and above character table that is called the product table. So see actually this product tables are also available. And you might notice that this sigma g and all are not mentioned here. What is given is just sigma plus sigma minus pi. So this is what is given.

You take pi sigma minus what do you get? You take sigma minus sigma minus what do you get. So on and so forth. Just looking at the table you can figure out. And then g or u that comes from what is that, g cross g or g cross u or u cross g or u cross u. So actually product tables are there but at least so this course I am not going to provide you the product table. In case I ask you to work out well for anything you should be able to do it. For d infinity h you have to do it by inspection or c infinity b for all other non infinite point groups you will be able to use that celebrated formula of ours. So let us not bother about product table. Let us see what we have here. What we have determined so far? We are working with oxygen. Oxygen has two electrons in the degenerate pi g orbitals. We have worked out what are the symmetries of the states that are generated by taking a direct product of the symmetries of these two, pi g and pi g. Three kinds of states are generated.

How many states is this? This is one, this is two, and this how many delta g gives you how many states? One, two, three, four, infinity. Two because that is two dimensional representation. Now let us see. What had we done earlier? What had we done for say Helium star? Did we discuss Helium star the previous day? Helium star means one electron in pie in sigma u one electron in the upper two sigma g. You understand what I am talking about. For homonuclear diatomic what is the lowest molecular orbital? It is sigma g plus. I call it one sigma g plus this is one sigma u plus or minus? Plus or minus? If you have forgotten let's do it quickly. This is the mo. What is the character of e that is one, what is the character of c infinity, minus one. That what's make it u. What is the basically we are – it either this or that. So sigma v if I give sigma v is it plus or minus? Plus. Then what is it? Is it sigma u plus or sigma u minus. I think I went too fast and confused you, right. Are we clear? Are we all on the same page on this? What I am saying is this is your anti-bonding orbital. Let us see what are the characters of each symmetry operation.

For E it is plus one. For C infinity what is it? It is not minus one that was a confusion. Is it? Yes. It is plus one. And what is the next one? Sigma V. Sigma V is plus one. Then I minus one that's why it is u I is somehow in my mind I is confused. Small I with c infinity. Okay. what is the character of sigma V you said plus. And I is minus. So sigma V plus I minus is this combination. So it is sigma U plus. You can go ahead and work out there you still see it. It is one sigma U plus.

Next one is you can think the sigma orbital found by combining two 2s bonding combination of two 2s orbital that is again I will call it 2 sigma g plus. So what I am saying is for Helium Helium 2 this is the ground state configuration. So if I move one electron, promote one electron from here to here what is the symmetry of that state? One electron is in sigma U plus. The other one is sigma g plus. So symmetry of this state is sigma g plus cross sigma U plus what will that be? What is Sigma g plus cross sigma U plus? As long as we know the table of one we should be able to figure it out. If we don't know the table of one then we got a problem.

Do you all know the table of one? Who among us doesn't know the table of one? Who [Indiscernible] [00:19:18] don't know the table of one? Should I recite it one ones are one. One twos are two. One threes are three. So sigma g plus is all ones. So the direct product is sigma U plus. This we had done. Okay. Then what did we do? we said that the sigma U plus we can get singlet as well as triplet. Remember. Remember that? Sigma U plus can give you two states actually. One is singlet sigma U plus. And the other is triplet sigma U plus. I am not talking about oxygen right now. I am talking about the excited state of Helium. Helium 2. not atom Helium 2.

So that is one singlet sigma U plus and triplet sigma U plus. What would be the wave function so that what is singlet sigma U plus? For that the special part is symmetric. Special part is symmetric. For this it will be sigma U plus let us call the electrons one and two. One sigma g plus is electron number two. Is that a good enough special part. What do I have to do? I have to take the other combination. Sigma U plus two sigma g plus one and then I can take plus or minus. If I take plus then the spin part has to be alpha beta minus beta alpha. If I take minus then the spin part has to be alpha alpha or beta beta or alpha beta plus beta alpha. Remember. So both are possible. The first one is singlet. Second one is triplet. So if we proceed along the same lines here, then we can assign singlet and triplet to everyone. How many states do we get?

From here if we now incorporate the spin part I should get singlet sigma g plus triplet sigma g plus singlet sigma g minus triplet sigma g minus singlet delta g triplet delta g. how many states is that? Eight. I want the first answer. Eight. How many agree with eight? How many disagree, what's your answer? Ten. So I have got a bid at eight I have got another bid at ten. Do you have any other bid? We will sell to the highest bidder. 12 now this is getting arbitrate. You have to justify why 12? each singlet state is how many states. One. Each triplet state is how many states [Indiscernible] [00:22:22] then why would I call it triplet? Triplet state is three state isn't it, remember that's why we are repeating that so many times. Alpha alpha, beta beta alpha beta plus beta alpha. Three states. It's just obsessed by the book written by the [Indiscernible] [00:22:40] and that's why we stop at two states. Not necessary we can have three states. Triplet. Triplet is three states. So let us now count. Singlet sigma g plus how many states is that? One. So let's count. One. Triplet sigma g plus how many states? Three. So one plus three four. Singlet sigma g minus. How many states? Four plus one five. Triplet sigma g minus. Eight. What about these? Singlet delta g how many states? Nine? Two. So eight plus two ten. And triplet delta g how many? Six. So 16 states. 16 states is what we get from this electron configuration of oxygen. This downstate electron configuration of oxygen seemingly gives rise to 16 states. But there is a problem actually. Not all these 16 states are accepted. We just assigned singlet and triplet to everything, anything and everything. That's not necessarily the case because here the thing is here you have two electrons in degenerative orbitals. So their spins are actually correlated to each other. Let us see if I can draw boxes and try to see how many states I actually should get [Indiscernible] [00:24:14] removed. Those who have studied terms symbols and all will be familiar with this treatment. I will draw it like this. I am drawing four boxes. So this is my orbital A, this is orbital B. This is A. This is B. what are the two spins possible up and down. I will draw two arrows for those or I will write alpha beta something like that. In how many ways can I fill in two electrons here. I have two electrons. How many ways should it be? Four places and two objects. two identical objects. how many ways can I feel four places with two objects? Two identical objects. Yes?

4c2, how much is 4c2? Six. Why is it not 4p2? Yeah? Yes the objects are identical. Permutation counts only when distinguish between the objects. here the combination is only thing that is important. So we know that we should be able to draw six so let me draw six boxes first. So I will fill in the box. I will just draw circles or something this is one way in which I can fill. Number two, number three, number four, five, six. So what I am saying is there should only be six states, not 16. So there must be some way by which I should be able to eliminate ten out of the 16 states that I have generated here. How do I eliminate? Any guess?

Poly principle. What is poly principle? The overall wave function total wave function means space part multiplied by spin part has to be anti-symmetric with the [Indiscernible] [00:26:40]. Total wave function has to be anti-symmetric. So let us see how many of these are anti-symmetric, how many of these are symmetric. To do that first of all let us think singlet and triplet, which ones are symmetric which ones are anti-symmetric. The spin part. The spin part is singlet symmetric or anti-symmetric? And triplet is symmetric. So I should write singlet only with these symmetric space parts. I should write triplet only with anti-symmetric space part.

Now which of these space parts are symmetric? Which are anti-symmetric? Sigma g plus is it symmetric or anti-symmetric? Sigma g plus is totally symmetric representation. Right or wrong? So it is symmetric of course. So should I write singlet sigma g plus or should I write triplet sigma g plus or should I write both? You understand what we are trying to do here? If the space part is symmetric then the spin part must be anti-symmetric. If the space part is anti-symmetric then the spin part must be symmetric. Alright. Clear so far?

Now what I am saying is this sigma g plus I hope you all agree is totally symmetric. So the spin part must be anti-symmetric. So between singlet and triplet which one is anti-symmetric? Singlet. Alpha beta minus beta. Triplet is alpha alpha beta beta, alpha beta plus beta alpha. Triplet is symmetric. So only singlet sigma g plus will survive, triplet sigma g will not be there. So I will just write singlet sigma g plus will be there.

If I go to sigma g minus and delta g, now what happens? Triplet which one will be triplet? Actually it is easier to work with your one dimensional representation so let us just see what sigma g minus is. so sigma g minus if you look at the characters, so if you apply well you cannot use I you have to think of operations that cause an exchange. And if any of these operations have a character of minus one then it is anti-symmetric. So I okay is plus one no problem. What about c2? C2 causes an interchange. C2 causes interchange. So what is it then? Sigma g minus should it be symmetric or should it be anti-symmetric? Anti-symmetric. So if the space part is anti-symmetric what should the spin part be? Symmetric. Triplet. So I get singlet sigma g plus plus triplet sigma g minus and in fact to get the third one you can even cheat. You don't need to even understand. Just see how many we have got. We are going to get six states. You know that. How many have we got so far? One plus three four. How many more? Two more. If I write one delta g that is enough. So it has to be singlet delta g. so triplet delta g is how much? It can never be triplet delta g because triplet delta g would mean six states there already. Total you are allowed to have six states so it will naturally will not be triplet delta g. and to understand why delta g is so what is it symmetric or anti-symmetric? Symmetric. That maybe a little difficult because it's two dimensional will not go there but it's not very difficult. If you work out the singlet – if you work out the one dimensional representation space part.

So this is what we get. Singlet sigma g plus plus triplet sigma g minus plus singlet delta g. how many states? One plus three, plus two six. So what are we saying here? We are saying that out of this electron configuration we actually generate three states. See in our earlier discussion of oxygen all of us know that the ground state of oxygen is triplet. And the way we have got it is that we said there are two degenerative orbitals. So the electrons should be parallel to each other. Here we are doing a little more detailed treatment of it. We are saying that you can actually get three states. However, since the electron configuration is same you look at these, you have two singlet states one triplet state. Which one will have lower energy? [Indiscernible] [00:31:31] and this time [Indiscernible] [00:31:34] configuration is same. So triplet set will have lower energy. So of the same – this is the part that we need to understand very well that even for the same electron configuration we can actually get different states of different energy. So what you get is get three states the lowest of which is your triplet sigma g minus. What will be the second lowest state or second highest state in this case they are the same? And what will be the highest energy state? See first what have we used so far to identify the lowest energy state we have used [Indiscernible] [00:32:24] now if you look at the other two both are singlet. Sigma and delta both are singlet. Now [Indiscernible] [00:32:31] will not work. What will I use then?

This is singlet this is also singlet. Do they have same energy or do you expect them to have different energies? Different energies. That we can even tell intuitively. Which one should have lower energy and why? Okay half the people say sigma g plus, half the people say delta g plus. A delta g. half will be right always. So if you say sigma g plus you have to justify why. If you say delta g you have to justify why. Which one has more degeneracy? So which one should have lower energy. Delta g.

so spin states are same usually degeneracy have lower energy. So this is what you have singlet delta g and this is singlet sigma g plus. So ground state of oxygen is still triplet. The two excited states immediately higher in energy are still singlet and I will just write the energy values you don't need to remember them, 7882 and 13121 this energy gap is 7882 centimeter inverse and this is 13, I have such bad memory. 121. Same inverse. We will come to the implication of these. Swati don't get distracted please. So 7882 what kind of radiation would that be? Microwave, IR, visible, UV, X-ray. Gamma ray. What would it be 7882 centimeter inverse? 13121 is I think something like 572 nanometers or 670 nanometers. I forgot. Visible red. So this is red. 13121 centimeter inverse. This one is near infra red. 7882.

So you kind of get the idea of what kind of energy gaps are there. Now tell me something do you expect transition to take place between triplet sigma g minus and any of these levels? [Indiscernible] [00:35:04] so actually you don't expect too much of transition to take place but when we say forbidden forbidden is never 100% forbidden a little bit of cheating is always there. So that is why what happens has anybody seen liquid oxygen? No. Liquid oxygen is blue in color. Liquid oxygen is actually blue? Why? Because of this. Not because it is para-magnetic. Because this it's 13121 centimeter inverse is absorbed so you see complimentary color. Last year about a year ago there was an accident in [Indiscernible] [00:35:46] lab and apparently the accident happened because some oxygenation reaction was going on at low temperature. So liquid nitrogen was there and then oxygen was being passed so oxygen condensed and the student performing it wanted to see what is this blue little liquid that has formed. So he took all the glasses went very close and that is when the apparatus decided to burst. So fortunately no serious damage to him happened. But then there was so much blood it was scary. So please be careful when you do such experiments. You should never liquefy oxygen. Liquid oxygen is explosive. But the point is it is blue. That's one thing we will learn from here. But then you don't see the blue color in gaseous oxygen. Why don't you see blue color in gaseous oxygen? Because it is too dilute and the spin forbidden is not seen but when you condense it you can see even that. That's point number one.

Point number two is those of you who well everybody we have all seen ads of these creams and stuff. Nivea cream and so on and so forth very often they don't say it is [Indiscernible] [00:37:09] anti-oxidants or people tell you that you should eat a lot of fruits. That is how you get anti-oxidants. So where is this fat from anti-oxidants where does that come from? What is the issue with oxidant? The issue is this ground state is triplet. Excited states are singlet. So if you can somehow take oxygen to singlet states it becomes very very reactive. And that is what happens that is what causes things like aging. Singlet oxygen in your skin causes wrinkles to appear. So this anti-aging skins they claim that they have something in that cream that will react with that singlet oxygen quickly so that you still look young. [Indiscernible] [00:37:52] need right now. That is 15-20 years later. But that is what it is. And it is actually something that shows up in a disease and in a therapy. How many of you know of the disease called porphyria? The porphyria does it remind you of some chemical, some molecule? Porphyrin right. So cow cattle often develop these disease called porphyria. The thing is simple. Cattle eat grass. Grass contains chlorophyll. Chlorophyll contains porphyrin. So degradation product of chlorophyll is not suppose to come to the skin. In this disease what happens is it comes and accumulates in the skin of cattle and then when they graze in the sun this porphyrin kind of molecules will start [Indiscernible] [00:38:46] again. Porphyrin kind of molecules are very good what are called photosynthesizers. Those of you who are studying photo chemistry course will perhaps have encountered the term or will encounter the term photosynthesizers. As you said it's not easy to go directly from here to here. But you can have an organic molecule which you [Indiscernible] [00:39:10] from singlet to singlet state then it goes from singlet to triplet state and then that triplet state reacts with this triplet ground state of oxygen to produce singlet oxygen. That kind of molecule is called a photosynthesizers. Porphyrin is a good photosynthesizer. So in this disease what happens is when cattle go out and raise in the sun his accumulated porphyrin in the skin causes this photosynthesization production of singlet oxygen and that is what gives them blisters. It's actually very painful disease. And in very very rare cases even human beings can have porphyria. I knew at least one such person. So she could not go out in the sun. if she went out in the sun she would develop blisters.

So that is something that comes directly out of all these group theoretical discussion a disease porphyria. And it's also the basis of treatment. The treatment is called photodynamic therapy. It's anti-cancer because everybody knows that what are the ways in which one treats cancer? Yes. Radio therapy. Anything else? Chemo therapy right. In chemo therapy what do you do? You inject the patient with a lot of poison in the hope that the poison is going to kill the tumor. What happens more often than not is that it kills the tumor but it kills the patient along with it. That is why it's not – many times you will hear of patients not surviving chemo therapy. So that is why for many decades there has been a search which is not completely successful yet for something that will be very specific to tumors and again the answer lies in this porphyria. So somebody had done the experiment once which showed that porphyrins can actually accumulate in tumor tissues and their photosynthesizer that is [Indiscernible] [00:41:07], So can we inject the patient with porphyrin and keep the patient in dark? The porphyrin will go and localize in tumor and then when you shine light then this porphyrin is going to form reactive singlet oxygen and then oxygen will kill the tumor and nothing else. Because singlet oxygen is not produced anywhere other than irradiated portion of the body. So photodynamic therapy is an accepted modality of treatment in USA and I think I cannot pronounce the name of the hospital. That's the problem. Sree Chitra Tirunal or something like that hospital in Cochin is also doing clinical trials on it. Now we are in an age where we have a second generation and even third generation drugs for photodynamic therapy but of course I only showed – told you the bright side of PDT it's called PDT photodynamic therapy. There is dark side as well. But the point I am trying to make is that all these things that we are doing actually have manifestations and application in real life as well. It's not just [Indiscernible] [00:42:14].

Okay. So this is what it is. So we have learned how to determine these symmetries of states even of oxygen which has electrons in two degenerative orbitals. Well there is not much to talk about electronic transitions orbital. We have already said this orbital selection rule. You understand that the triplet product has to contain in the transition moment integral has to contain a totally symmetric representation. That is when it is orbitally allowed. Sometimes what happens is it's not orbitally allowed. It becomes allowed vibronically, by coupling of vibration with your electronic motion. So maybe what we will do is we will start with an example next day because this totally symmetric representation thing is something that we have vision black and blue while talking about normal mode. So we don't have to repeat it. So let us talk about a specific example. Let's talk about Benzene the next day. And in Benzene let us see why the spectrum looks like what it does which of the transitions are totally allowed, which are orbitally forbidden but vibronically allowed.