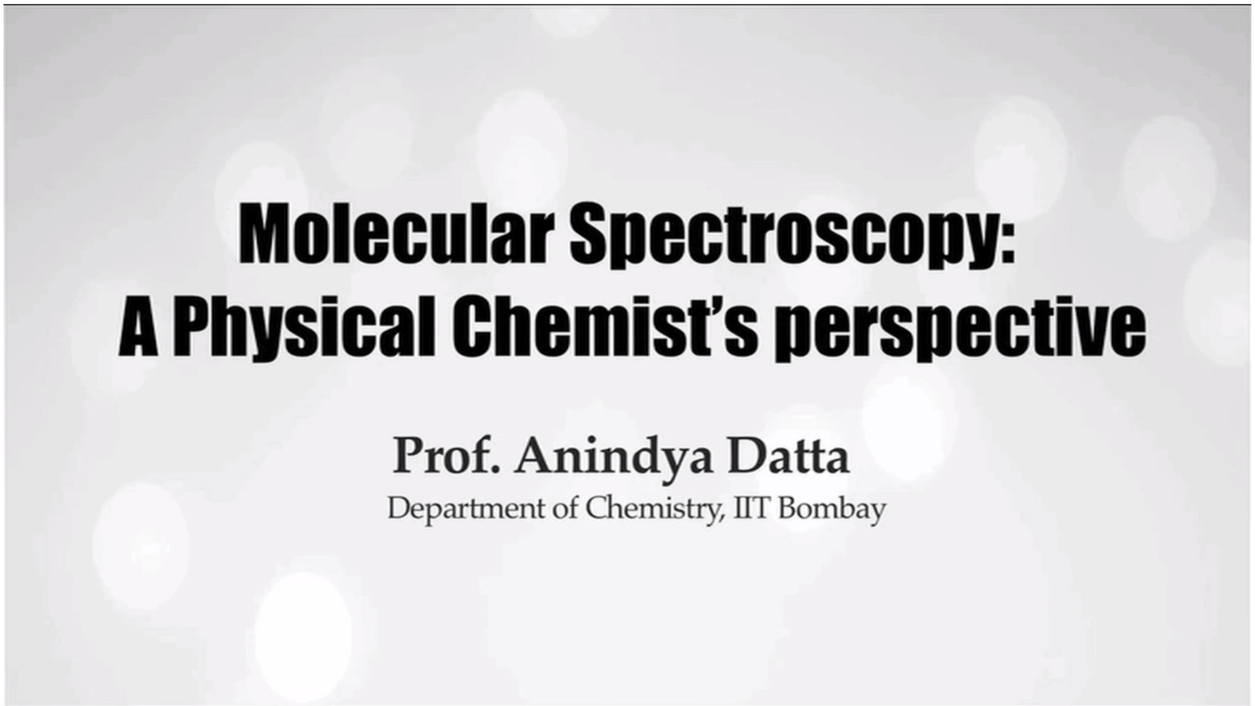
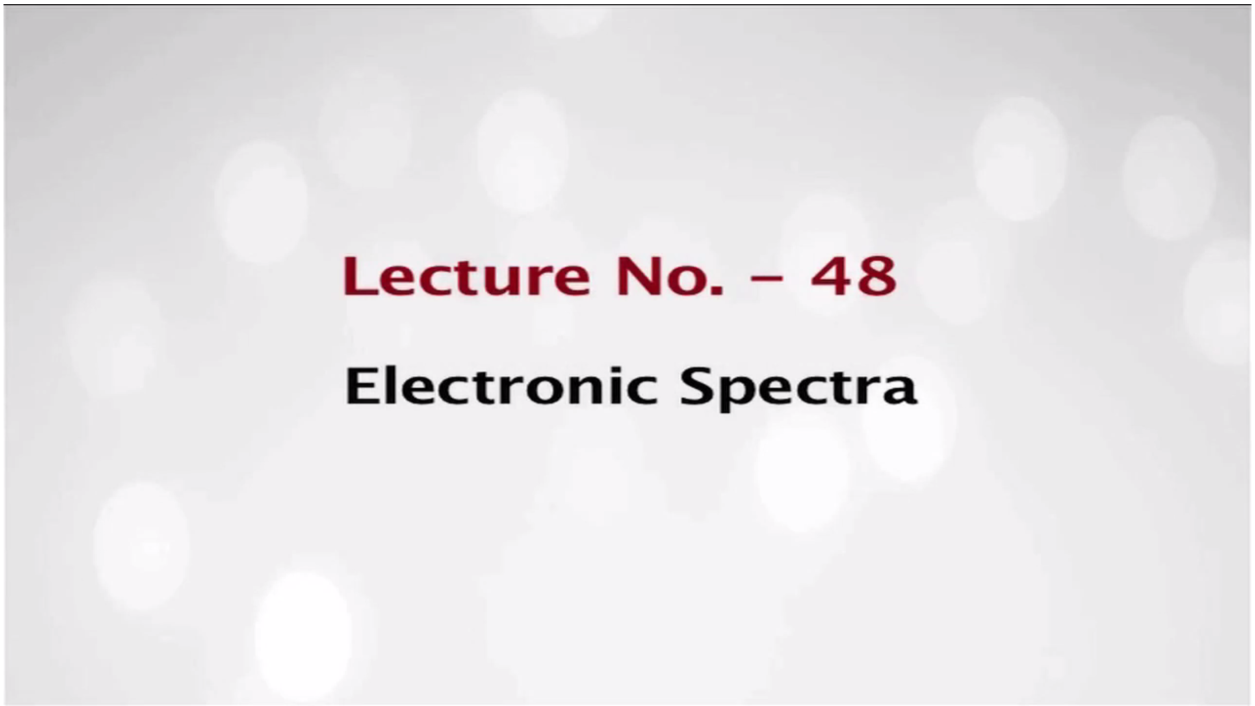


Molecular Spectroscopy:
A Physical Chemist's perspective

Prof. Anindya Datta
Department of Chemistry, IIT Bombay



Lecture No. – 48

Electronic Spectra

All right, so we are discussing electronic spectroscopy. Today, let us talk a little bit about what electronic spectra actually look like and what is it that we can learn from them. This part that we will discuss in the next half hour and so is best learned from Banwell's book. It is not anything different.

What have we leaned so far? We have said that we are working under this Born-Oppenheimer approximation, which says the total wave function is given by ψ_{es} ψ_v where v is vibration, r is rotation, e is electronic, s is spin. So we are writing the spin orbital wave function together, but of course, we can split it into ψ_e ψ_s. In fact, we did that when we talked about transition moment integral, and we wrote the transition moment integral finally as $<\psi_v|\psi_v>$ while doing it, so far we have neglected ψ_r. Today, in fact, we are going to talk about effect of rotation, but then we will not derive the selection rule for it, you can try and derive it yourself, but not today, maybe a little later, multiplied by $\psi_{es}|\mu|\psi_e><\psi_{s'}|\psi_s>$. Transition moment integral has to be non-zero for a transition that takes place. So we said that this factor is not necessarily 0 because ψ_v and $\psi_{v'}$ are wave functions from electronic maniforce, different vibrational maniforce, different electronic states.

What is this called? Franck-Condon factor, very often it is written as chi. Of course it might be a little confusing for us, because we are already using chi for character and we are using characters very frequently, but as you know, the same symbol is often used for different quantities. So please remember that chi is also written as a symbol for Franck-Condon factor. So what Franck-Condon factor does essentially is -- what Franck-Condon factor essentially does is that it modulates the intensity of transition. But what determines whether the transition will take place or not are these two, these integral and this one. If this is non-0, that gives rise to the orbital selection rule, and if this is non-0, this gives rise to the spin selection rule.

In fact, we have already derived one of them. What is the spin selection rule that we came up with? From here, we had got $\Delta_s=0$, but we also got something else, something that is not actually written in any of these books that we study. What is it that we got? Yes, I mean got mean I just told you and then I asked you to satisfy yourselves that $\Delta M_s=0$, this is the condition. Total spin angular momentum does not change. Z component -- what does M_s stand for? It stands for the Z component of total spin angular momentum. So Z component also does not change. This is the spin selection rule, and spin selection rule is the most stringent of all. So spin forbidden transitions are really, really weak if they are at all seen.

Orbital selection rule, as we will see in the next couple of classes, there are way of bypassing the orbital selection rule. And one of the orbital selection rules that you know already, somebody asked me in the last class is Laporte selection rule. If both are D orbitals, both are centrosymmetric and this μ is not centrosymmetric, and it is antisymmetric with the spectra version. So the triple product is antisymmetric. That is why the DD transitions are orbitally forbidden, but then they do can take place, because what you do is you can have a coupling between vibration and electronic motion. So that is called vibronic coupling as we are going to study. Due to vibronic coupling, it is not always impossible to bypass this orbital selection rule. So as we are going to study in the next couple of days, vibronic coupling can actually give you bands that are otherwise forbidden orbitally.

Spin selection rule is more difficult to break. How spin selection rule -- how can you work around spin -- well, you cannot work around. How do molecules sometimes work around spin selection rule? Yes, by what is called spin orbit coupling. So if you cannot write like this, if you have to continue writing ψ_{es}, then you do not have this integral coming out, okay. So that is called spin orbit coupling, and in fact I was -- I should modify what I just said, you can work around this as well, because the spin orbit coupling integral, the interaction integral that has a term in mass. So if you bring in a heavy item, then you have greater spin orbit coupling, and so transitions that otherwise don’t place, can take place, right.

So this is where we are. This is what we’ll deal with once we talk about symmetry of states. Before that let us finish the discussion that we were having about diatomic molecules, okay. Let us focus on this, the Franck-Condon factor. As we have discussed briefly, Franck-Condon principle requires transitions to be vertical. Vertical means X axis is internuclear distance, so internuclear distance does not change during an electronic transition. The basic idea is the same, nuclear are heavy, electrons are light. So when you have electronic motion, in that time scale, you cannot nuclear motion also. So this is your Franck-Condon principle.

The other thing that we have discussed briefly or some of you may even know is that we can have different situations. The way I have drawn it here, the equilibrium bond length -- how do I know what is equilibrium bond length is, internuclear separation and we get the minimum. So it is possible that the equilibrium bond length is exactly same for ground and excited state, then this is the situation. Then Franck-Condon sector is actually maximum for the 0-0’ combination. See most of the transition will take place from the center, right, because that is where $\psi \psi^*$ is maximum. So in this case, the spectrum is expected to look something like this. This here is the 0-0’ transition this maybe 0-1’, this maybe 0-2’, this maybe 0-3’ so on and so forth. Remember dashed indicates a vibrational level in the higher, upper electronic state.

Which way does energy increase, this way or this way? 0-0’, 0-1’, which one has higher energy? 0-1’ right, so energy increases this way, so I can write like this, $\tilde{\nu}$ increases this way. Let’s not forget that. What happens when the situation is something like this? Actually I’ve drawn in the other way, it was something like this. So now, you see this transition will be the most probably one. So what is this, 0’, 1’, 2’, 3’ 4’. So if this is your 0-4’, this is going to be the most intense transition, other will go down, 00-3’, 0-2’ so on and so forth. This way also it will go down. So that gives you a maximum in the absorption spectrum, and of course, we have internuclear separation -- and we have separation between two successive lines due to the separation between the vibration levels and the excited states. We will have an occasion to come back to this shortly.

What happens if the internuclear distance in the excited state is smaller than the internuclear distance of the ground state, same thing happens, you still go to the maximum, and then the situation is this. Now a vertical transition from the center takes you to a state, which corresponds to a dissociated state, okay. That is something that will cause dissociation. So what will happen is you have -- so now $\tilde{v}$ increases this way I'll draw it the other way. I am drawing $\tilde{v}$ to be increasing from right to left, so I'll draw it that way. So this is exactly a flip image of what you see in Banwell's book, and then you have a continuum, because once you have excited beyond the dissociation limit, then of course you get a continuum, because your atoms can move with whatever kinetic energy that is there.

So this is called this $\tilde{v}$ where this continuum beings is called the dissociation limit, okay. Let us see, what this dissociation limit is, this is your dissociation limit, a state up to this. This I will say is E_{DL} -- maybe I'll write ε_{DL}, so that we remember everything is in centimeter inverse. Now what is this energy? This is something that we have studied when we talked about anharmonic oscillator. What is this energy? What does that mean? How do we write it? We write D0, isn't it, right. That is the energy that you have to provide to take your molecule from v=0 state to such a v state that dissociation occurs, okay, in ground state. So what is this then? That is also some kind of D0, right. That is also D0, but not for the ground electronic state, for the excited electronic state. So we will write it D0', okay.

One more thing that I want to draw is this. What kind of a transition is this one, v=0 to v'=0, we'll call it $\varepsilon_{0\text{-}0}$. This is called the band origin. Are we clear with the definitions? Now let us see, what do I get when I add one of those quantities to another quantity. What happens, what do I get if I add, say, $\varepsilon_{0\text{-}0}$ to D0', $\varepsilon_{0\text{-}0}$ to D0', what do I get? Yes, ε_{DL}, right, dissociation limit. So in your spectrum, if the dissociation limit is very well defined and if 0-0' transition is also very well defined in your spectrum, then in principle, you can decide what is D0', right, but the problem with this approach is that neither of these is usually very well defined.

So when you have something like this you can see that intensity is going down, right. So 0-0' is going to have a very small intensity here. Sometimes what happens is the intensity is so small that you don't even see it very well, all right, and dissociation limit is also something that is fuzzy. It's not so easy to see where exactly dissociation limit has begun. So if we use this and try to find out D0', then we'll perhaps get only an approximately value of D0', okay, but there might be little better ways. Which way? One thing I could perhaps write is this, let me write this.

What is this energy? Let us say I am a molecule AB, right, and then upon dissociation I get A and B. What is this, this energy? What do I have here in this situation, what do I have here for this internuclear separation? I have AB the molecule. What do I have here? A+B. What do I have here? A+B -- who is giving me the answer, I cannot -- you gave the answer, okay, right. Yeah, so this excited state of the product, right. So this is something that you can actually measure using, say, calorimetric measurements. So what you do is you take the atoms, right, and see what is their excited state. You can get it even thermochemically. So this ε_{ex} is something that you can measure directly and accurate.

So now if I rewrite, if I reformulate, what do I get? What is D0 + ε_{ex}, what is that? I can write this like this, ε_{ex} + D0. Now for a situation where I do have a continuum in the spectrum, now I am a little more comfortable, because that gives me more parameters to play around with. Suppose I can know this experimentally, is there any way in which I can determine D0, some other experiment? How do I find D0? See usually, you are right, there is no point in thinking you will not be right. So remember what we had discussed for anharmonic oscillator, if we look at three lines, right, what are the three unknowns that we have, one is anharmonicity constant, one is D0, and one is this equilibrium vibration frequency.

So if you just have the position of three lines, then you have three equations, three nodes. So if you look at the IR spectrum, then you should be able to determine D0. So one thing you can do is this you measure thermochemically. You can measure this -- you can find a value of this using IR spectroscopy, and then from there, you can find out the dissociation limit. Once you have dissociation limit, then if band origin is not very prominent, you can find out band origin, if D0’ is known; otherwise, we got a problem.

So once you know this, then it becomes -- you have a little bigger field to play in, but the thing becomes really interesting when you don’t have a dissociation limit at all. Suppose you have this kind of a spectrum, then what happens. Is there a dissociation limit here? There is no continuum. Can we find out the values of D0 or D0’ or something from there? Actually, we can. For that, what we’ll do is we’ll write the second part of this discussion. Of course, we’ll neglect rotational levels for now.

In Born-Oppenheimer approximation, we write the wave function as product of electronic and vibrational wave functions. How do we write the energy? Sum, right, separation of variables, sum. So what we can do is, we can write $\psi_{el} = \psi$ -- maybe $\psi = \psi_{es}$ -- $\varepsilon = \varepsilon_{es} + \varepsilon_{v}$, okay. So if this is the case, then what is my $\Delta\varepsilon$? When I go from this level to this level, $\Delta\varepsilon$ would be $\varepsilon_{0\text{-}0} + \Delta\varepsilon_{v}$. Do we agree with that? I go from -- it’s easier to draw like this. This is v=0, 1, 2, 3, this is v’, so 0’, 1’, 2’, 3’. Let us say, I have this transition, okay. What is the energy of this transition? I am saying this is $\Delta\varepsilon$. What is $\Delta\varepsilon$? This here is

ε_{0-0}. It’s needless to state once again that all upward transition has to begin at v=0, right Only v=0 is populated at ground state. So Δε, this is ε_{0-0}, plus what? This, I can call this $\Delta\varepsilon_v$. Is that right? What, it’s not right? Vertical transition, yes. No intensity may be different. Intensity is going to change, right. This is the intensity, but position will be there. Vibrational energies will be a little different from here to here, because the bond is weaker, right. So usually the vibrational energy is also different, but I have written it here, $\Delta\varepsilon_v$. What is the problem with that? Yes. No, so what we are doing is we are breaking it down into two parts. One we are doing 0-0, right, and then from there we are saying it’s $\Delta\varepsilon_v$.

Now we’ll write the expression. ε00’ plus what will it be, what is $\Delta\varepsilon_v$? What is εv? (v + ½) ṽv . x^3. Of course, we are considering it to be an anharmonic oscillator, right. The potential we have drawn is kind of a Morse potential, it has to be anharmonic. So ṽv . xe -, now to help you with that -- xe won’t be there. Fine then? $(v + \tfrac{1}{2})^2$ xe ṽv, okay, right. Minus what? Minus v=0. So are you now satisfied? We are taking same xe, same νv, everything the same. So you put 0, you put ½ ṽv - $(v + \tfrac{1}{2})^2$ xe ṽv, okay. So let us put v=1, what do we get? If I put v=1, what do I get? So this becomes, what - sorry, v=0, fine. What happens when I put v=1? 3/2, what is this, 9/4 -- maybe I’ll open the bracket, ¼. What do I get then? ṽv - 2xe ṽv. Are you okay with this?

What happens if I put -- so this is I can say $\varepsilon_{0-1'}$. What happens if I put $\varepsilon_{0-2'}$, what will I get? ε_{0-0} + 1, yeah, okay. Let us do it a little differently. Can you tell me -- I take 2, 0-v’ and 0-v’+1. We can work out the expressions for that. Let’s do it. Let’s work out the expression 0-v’ transition and 0-v’+1 transition. What will it be? So essentially, this is what I want to work out. Can you tell me what is the expression for Δε? I want to work out the expression for ε0-v’+1 - $\varepsilon_{0-v'}$. What do I get there? So (v’ + 3/2) ṽv - $(v' + 3/2)^2$ xe ṽv. From that you have to subtract (v’ + ½) ṽv - $(v' + \tfrac{1}{2})^2$ xe ṽv, right. What is the expression? Something like this, ṽv [1 - 2xc (v’ + 1)], something like this, right, this is what we get.

What is this Δε, what is Δε? Δε is the separation between two lines in the spectrum or this spectrum, right. This is Δε, isn’t it? We’ll draw it a little better. One of these separations is Δε, all right. So what happens if I plot Δε against v’, what kind of a line do I expect? Yeah, it is kind of stupid of me, because I said what kind of a line do I expect. We expect a line, well positive slope or negative slope, negative slope. So this is how, and of course don’t forget that v is discrete, right. So we expect this kind of a decrease, all right. So one thing we can do is this, we can just extrapolate, draw a line, and draw it until it cuts X axis.

If I work out the area under this craft, what does that area give? You understand what I am saying. You told me we are going to get a line with a negative slope, right. So if you extrapolate the line from Y axis to X axis, you’re going to get a triangle, right angle triangle. It’s very easy to work out the area under the triangle, okay. What does that area give me? Okay, let us say, I just take the first two points here. What does this area give me? Fine, let’s look at this now. This is one Δε, this is the next, this is the next, this is another Δε. If I add them all up, all the Δε, does that give me the area under the curve, right? So there is a Δε versus v, right. So if I just add up all the Δε that should give me the area under the curve.

So if I add up all the Δε what does that give me? This is one Δε, this is another, this is another, so on and so forth. So if I add them all up, what do I get? I don’t get dissociation limit, I get D0. But which D0, ground state or excite state? Excited sate, right. So this area, entire area is going to give me D0’. In excited state also -- we are taking the anharmonicity constant with the same -- where have we done that? Anharmonicity constant is so small that variations are negligible, okay. So this is one way of finding D0’ even if you don’t have dissociation limit, any spectrum should be able to give you that, and this kind of extrapolation is called a Birge-Sponer extrapolation. You can study it from Banwell’s book, you can also study it from 31:20 book, both have it.

So once you have D0’, then what can you find out? Suppose I don’t have a dissociation limit in my spectra, but in this way, I have found the 0’. $E_{0\text{-}0'}$ is there, D0’ is also there, so $\varepsilon_{0\text{-}0'}$ + D0’ = D0 + ε_{ex}, right. So from there -- so this is what I am using now. What are the thing that I know already? As I told you, ε_{ex} can be found by non-spectroscopic experiment. D0 is something that you can know using your IR spectrum. D0’ have you have just determined, so if your band origin is not very prominent, then you can find out band origin. That is one thing, but the bigger applicant is if you know band origin, you can find D0 also.

Now tell me suppose I know the band origin, I determine D0 this way. Is it better to find D0 this way or is it better to find D0 using IR spectrum? Actually there are pros and cons. There are factors that tell you that finding D0 using electronic spectrum is better, but there are factors that make determination of D0 from the vibrational spectrum better this way. What are the factor that favor determination of D0 from electronic spectrum, what are the factors that favor its determination from vibrational spectrum. What is the problem of determining D0 from electronic spectrum? What would be the problem? The problem would be resolution. IR spectra of course are recorded at higher resolution than electronic spectra usually. So if you want to make an electronic spectrometer that has sufficient resolution to give you information about vibrational levels that is a more difficult proposition. So resolution is a problem in determining D0 here.

So what is the advantage? The advantage is if you do it from your vibrational spectrum, then essentially how many lines do you have. You have fundamental, you have first over term, if you are lucky, you have second over term, nothing else, at most three points, right, at most three. And in the third one, the intensity is so less that era skip in there. Here in electronic spectrum usually, you can look at more levels, okay. So if you have more points, then of course it's a little better. So these are the pros and cons of determination of D0 using electronic and IR spectra, okay.

One last point, Birge-Sponer extrapolation is linear, right, but if you have a -- by the way when I am talking about electronic spectroscopy here, then usually what I really mean is electronic spectroscopy is gas space, where lines are really very sharp, and you get to see a lot of lines, you do this in liquid phase, lines are not going to be so sharp anymore. Lines are broad, and since they are broad, several lines join up, you lose out on the number of lines also, but suppose you have access to sufficiently high resolution spectrum, then what you see usually is, the expectation is this, linear variation. What you see in reality is that you see this kind of deviation, downward deviation.

Why do you think there is a downward deviation? Look at this spectrum, we are plotting Δε versus v', right. State line is what you expect. If there is a downward deviation, what can cause a downward deviation? Sorry, anharmonicity, yes, but anharmonicity is already accounted for, right, but, anharmonicity is the right answer. See the thing is if you remember what had we said, we had said that this -- how do you get the second term in the expression for energy for anharmonic oscillator. It is a first order correction term, right. And remember what we had also discussed that when you bring in correction, first order correction can come in as a first order term in v. the second order term would be square. Third order term would be cube and so on and so forth. So as v becomes higher and higher, then the second order, third order, these terms also become important, okay, and it's always negative.

So when you go to sufficiently high fees, then this is not a complete expression anymore. You have to account for the quadratic term, the term into the power 3, term into the power 4 and so on and so forth. So what you have is, towards the end you have a deviation. So that is another advantage. So that gives you the realistic picture, if you go to higher v levels, neither is this Birge-Sponer linear extrapolation, absolutely accurate, nor is the expression of the D0 that you'd get from anharmonic oscillator. Don't' forget for anharmonic oscillator, you get to interrogate only v=0, v-1, v=2, nothing beyond that. So this higher terms that are there, that actually contribute to D0.

Will you agree with me if I say that the higher terms actually contribute to D0? Because when you look at D0, you are looking at this, right. So you do have several higher vibrational levels coming in. So who is going to account for that? So actually, if you have access to sufficiently large number of spectral lines in electronic spectrum, the D0 value determined from that is a little better, all right. So this is your effect of vibrations on electronic spectra. What you get is you get a vibrational fine structure, vibrational structure, let us say. The involvement of vibrational levels render a vibrational structure to electronic spectrum.

We have encountered something like this earlier when we talked about ro-vibrational spectrum. We had seen that there is rotational structure in vibrational spectrum when you look at sufficiently high resolution vibrational spectrum, you can see rotational structure. Here also, when you have a sufficient high resolution, then you see vibrational structure in electronic spectrum, okay. What is the effect of rotational levels. Can rotational levels also have some effect, if you have really high resolution electronic spectrum, then the rotational levels should also give you some what is called fine structure. Fine structure due to rotation is seen in electronic transitions as well, all right.

So I am not going to derive the expression there, because we have done the derivation already once. So what is a real picture? This is on electronic level, these are the vibrational levels. Each vibrational level is associated with rotational level as well. So when we say that the transition originates here at v=0, what I really mean is that the transition originates in different J values, J levels, all right. So some selection rule is associated with this as well. Once again, we will not derive the selection rule now. Once we are done talking about symmetry of state and derivation of whether transition moment integral is 0 or not for electronic levels, maybe we'll come back to it.

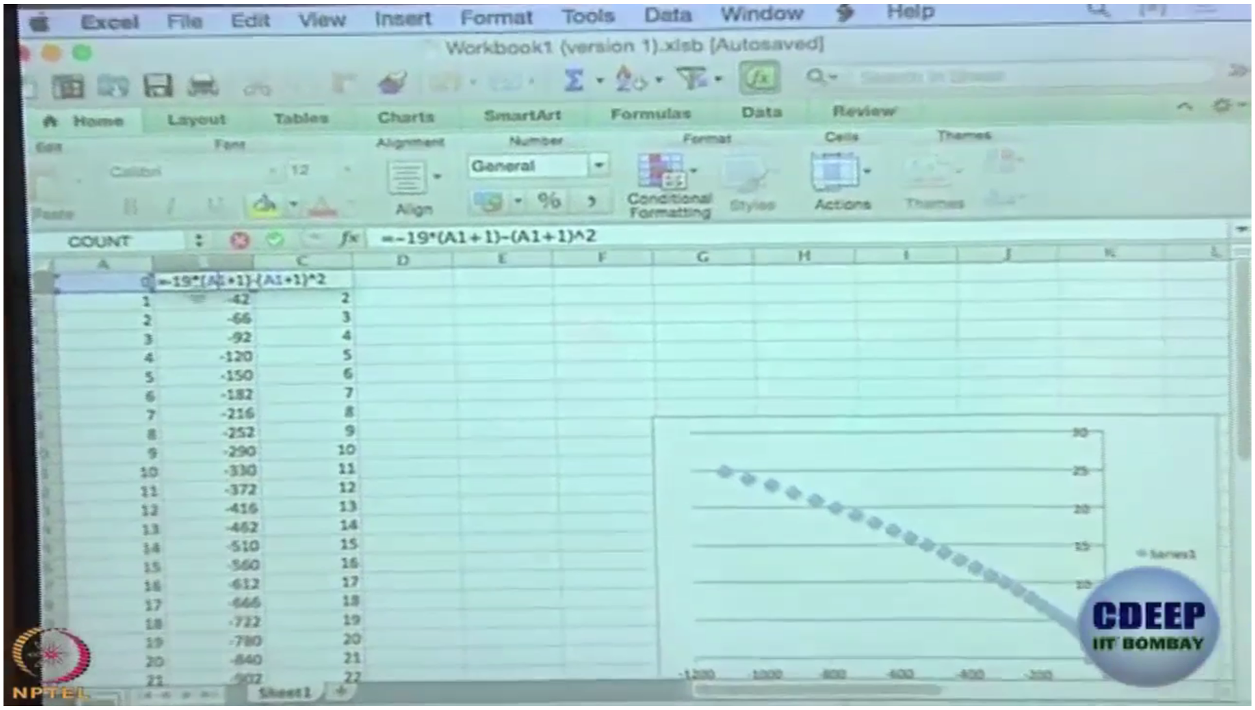
So selection rules you have rea, well, we are talking about once again diatomic molecules, ΔJ=0 for $^1\Sigma$-$^1\Sigma$ kind of transition. We can let in, if not 40:41, right. What is this small one large Σ, we are going to learn in detail tomorrow onwards. What this one means is this is not read as one Σ, it is read as singlet Σ. The small one subscript, that gives you the multiplicity of state. Σ gives you the symmetry of state. For now, just believe me that the ground state is always singlet Σ for all molecules, for all molecules in you have spin balance, okay. We'll elaborate upon this a little bit later one. Those of you who have studies LS coupling and all would perhaps already know that the ground state is $^1\Sigma$.

So this is the selection rule, ΔJ=0 -- now what am I writing, sorry. ΔJ = ±1 for $^1\Sigma$-$^1\Sigma$ for all other transitions I think, it is ΔJ = 0, ±1 provided this ΔJ = 0 transition does not take place for this (J"=0) - (J'=0), this is forbidden, for all other J values, ΔJ = 0, ±1 for all electronic transitions other than $^1\Sigma$-$^1\Sigma$, okay.

Now when you do this, you have to account for the rotational levels as well. So what will the expression be? Again, Δε = ṽ = ṽ -- what should I write it, I'll write e,v is that okay. Whatever expression we have got earlier, that is involving electronic and vibrational levels, whatever that expression is + you will get Δ [BJ (J=1)]. Makes sense. We know already that vibration energy of Jth level is BJ (J+1) ΔB J (J+1). So the question is, is B the same for ground and excited states or is B different. Usually, it's different. Is it larger, is it smaller? Smaller, why do you think so? You think it's smaller, didn't you. So why do you think it's smaller? Okay, you are right, but just tell me why.

Who also defend that B is smaller in the higher electronic state? Why is B -- okay, let me change the question. When is B smaller in the excited state? Why? B in inversely proportionate to r^2, so the equilibrium bond length is greater. You're right. So now the thing is if the transition is such -- so this is where the qualifier comes in. B in the excited state is smaller than B in ground state when obviously the R is greater, well, rather r^2 is greater. So if you have a transition that weakens the bond, then R will be greater, equilibrium bonding will be greater, right. So if I think it is something like, let us say, 44:39, there is a ψ ψ* transition. What has double bond in the ground state is a single bond in the excited state, right. So bond length, equilibrium bond length. That is when B should be lesser, but it is not necessary that all transitions in all kinds of electronic spectroscopy will weaken the bond. There can be something that strengthens the bond also, right, say, charge transfer transition, right. In that case, it will be the other way around. So the crux of the matter is that B is going to be different.

So when B is different, have you encountered a situation like that, where? Ro-vibrational spectrum once again. What was the expression we got in that case? We got something like (B'+B) (J+1), then plus or minus, -v' - v I think into $(J+1)^2$. We get the equation of a parabola. So what you get is you get equations of parabola in all the cases. In this case, what kind of a band is it when ΔJ = 0, ±0 of course, when ΔJ = 0, what band is it, what do we call it. We had a quiz or mid-sem question on that. A, B or C, which band is it? Neither A, nor B, nor C, right. Neha says, it is Q. Is she right? Q band. And what is ΔJ - 1, what is it? P. And ΔJ + 1? The only choice left is R, right. So remember, P, Q, R. So you understand that in this case you are going to have PR structure, in this case you are going to have PQR structure, but PR and PQR structure are actually interesting in this case, because you have a parabola. So what you have is, you have this lines going to lower energy and then turning back many times, okay.



=-19*(A1+1)-(A1+1)^2

A	B	C
0	=-19*(A1+1)-(A1+1)^2	
1	-42	2
2	-66	3
3	-92	4
4	-120	5
5	-150	6
6	-182	7
7	-216	8
8	-252	9
9	-290	10
10	-330	11
11	-372	12
12	-416	13
13	-462	14
14	-510	15
15	-560	16
16	-612	17
17	-666	18
18	-722	19
19	-780	20
20	-840	21
21	-902	22

So please read this part from Banwell's book. Tomorrow, we are going to just -- so that is what I had drawn here, the parabola. So if you see, this is J, these are the J values. These are obviously J+1, column C is J+1. So this one is 19 (a1+1), well, (a1+1) is just c - $(a1+1)^2$. So the way I have drawn it is this. I have taken B' and B to be 9 and 10 respectively, right. So 19 is "B1+B this is your -- it will be '-B. If this is the scenario, you get this kind of a parabola. So you see what does each point indicate? Each point indicates the position where the line occurs, all right, in terms of v and v'. So what you see is it keeps decreasing.

Now for one of the lines P or Q, this becomes minus. So please read this part from Banwell, and you'll see that you get the same kind of explanation as we got for the vibrational spectrum. We get this sum constant multiplied by P plus sum constant -- well sum constant multiplied by P^2 where P can be plus or minus. So when this is minus -- I am making a mistake, I'll show it tomorrow. So there you see that the place where it turns, that is called the band head. So tomorrow, maybe we'll quickly demonstrate this to you and then go on to discuss symmetry of states which will allow us to talk about the transition moment integral.