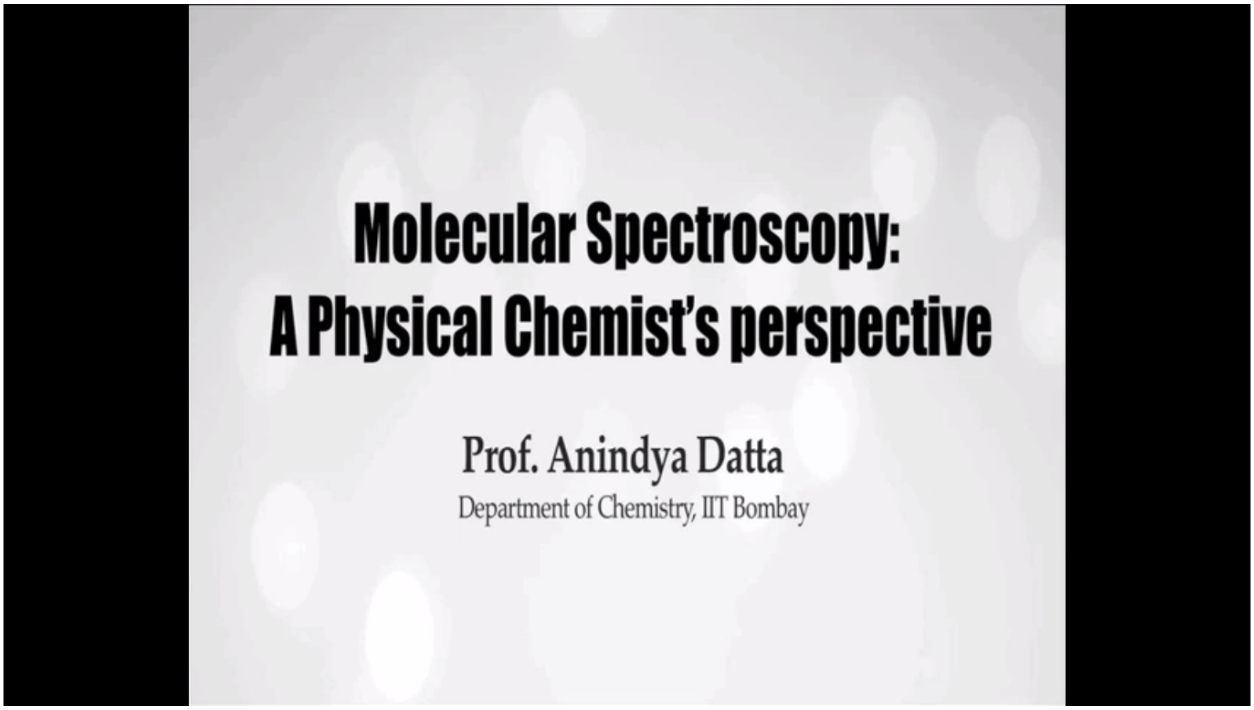

Molecular Spectroscopy:
A Physical Chemist's perspective

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Lecture No. - 21

Level System: Concluding Remark – I

Anindya Datta: So this is the topic for today. So the first module of today's discussion is concluding remarks one on two level systems. And there I hope that we'll be able to answer or at least visit a question that many of you have asked several times; the question that you've asked always is what about T. You're integrating over μ that is fine what about T. Actually that answer has been given but it makes sense to talk about it once again.

So of course I don't have to write what two-level system is again and again. We are talking about absorption and then from there we have arrived at emission as well but so far what we have done is we have designated the lower level as l upper level as m and we have said that the wave function of this system is a linear combination Cl into PsiL [Indiscernible] [00:01:39] plus Cm into capital PsiM and what we have been trying to do is we have been trying to define the probability of transition, our probability of mixing of states by this quantity modular square of Cm where Cm is the coefficient of the wave function of the destination level in absorption higher level. What is the expression that we obtained for it? Let me see if I can remember. If I remember correctly the thing that we got was first of all there was this Ex0 square multiplied by transitional moment integral but transition moment integral using only μ x so let me write it like this μ lm square divided by 3. Are we okay with this? [Indiscernible] [00:02:36] radiation and all that. What is the next term that we got? We have taken care of radiation. We have taken care of transitional moment integral. Next if you remember was sin square π t by h into let me use a different kind of bracket here. π t by h into Em - El- h μ divided by square of Em- El minus h μ. Now those of you who have actually gone through a couple of textbooks would know that there are different ways in which you can write this. We have so far written it in terms of energy but in several textbooks this expression is written in terms of the frequency. In several textbooks it is written in terms of angular frequency Omega. And these conversions should not be a problem for you at all. Are you okay with that?

So just – is there a question? Yeah.

Student: [Indiscernible] [00:03:59]

Anindya Datta: Sorry because XYZ are all the same that's what we are assuming. So this expression is actually in terms of the X component. So –

Student: [Indiscernible] [00:04:12]

Anindya Datta: Yes one-third of square because it is not just transition moment it is the square of transition moment that contributes to probability. So contribution of each component is one-third. I'll just write a constant here. Some constant.

Student: [Indiscernible] [00:04:38]

Anindya Datta: I said square of this but then I didn't write since I said the square at the beginning. Now it's okay I don't really care about the constant for the moment. We are trying to discuss something else here. So whatever this is this is just a constant. Let's not even worry about this three. This you can easily convert to μ, to rho that's not a problem. Now so what you have been asking me several of you is that what we did is we said that you plot it and you get something like this. If I plot mod Cm square against let us say I plot it against frequency. If I plot it against frequency what is this? Is it 0? If I plot it against the denominator then of course this is 0 but if I plot it against frequency what is it? Let me write this expression a little different way then. I'll write Em- El as h μ 0 what is the μ 0 in this case? Em – El divided by h. So basically it is the resonance frequency. The frequency that resonates with the energy gap. I'll write this as h cube – h0 here also. Sorry, h μ 0 – h μ. Then I can easily take this out and write h square. I will write it very nicely. μ 0 – μ square and this comes out and the h that comes out gets canceled with this.

Now can you tell me what is this? What is the origin? Yes the origin is μ 0. so you have a spread on either side of the resonance frequency. That is all. So I hope that answers one part of the question. What is the meaning of negative. All it means is that in this case, on this side the frequencies are lesser than resonance frequency. On this side they are greater than resonance frequency that is all. Now the other question is what about T. Actually if you remember we are working at some constant T. We are working at initial time and what we did is we integrated between 0 and T. The moment you integrate between 0 and T that T is not really a constant. So you can take T equal to 1 unit or you can take T equal to 3 units or you can take T equal to 30 units. That is in your hand depending on how much you integrate but when we integrate over this band what we are essentially saying is we are working at some predetermined value of T and when you integrate of course what you mean is you are working with polychromatic radiation. Is that right? So all these radiations are available then only you can integrate over the entire band. Is that point clear. That's what we have done so far.

Now today let us do something like this. Let us see what happens to this mod Cm square if I work at different chosen values of T. suppose I work at T equal to 1 unit I see what I get. Let us and I work with T equal to 3 units then with 30 units. How does mod Cm square change and since you don't want to change two variables at the same time what we will do is we will work with some monochromatic radiation. Frequency of the monochromatic radiation of course is μ. So if you remember in our earlier discussion we said that this actually arises from uncertainty in energy on the excited state. We had talked about lifetime. We'll revisit the issue of lifetime today. that's fine.

Are you okay?

Now what do you think this function will look like say some constant into sin square π t into 0 – μ. If I try to plot mod of Cm square, so you should write M against time T. Let us say we are evaluating Cm square for different values. First we do it for 1, 2, 3 so on and so forth. What kind of graph do you expect? What is the only function in T here? The sin square. So of course the graph that you get will be an oscillatory if not what will be the lower limit? What will be the upper limit? Lower limit has to be 0. It's Sin square not Sin. What is the upper limit? The upper limit is this. It's not 1 actually. Upper limit is this. In fact it is much less than 1 because I do not remember did we work out some value of transition moment integral in one of the classes earlier? We actually worked out. If not I'll give you a problem where you do it. All these are actually very small and another thing is if μ is very far away from μ 0 then what happens. The denominator is large. So this constant the entire constant is actually not very large. So it will never go up to 1. So what you get is you get something like this.

Of course, in this entire discussion we are neglecting something we'll come to that in a moment but tell me this, this is time T equal to 0. When does the signal become 0 once again. π t into μ 0 minus μ has to be equal to π. So π and π cancel. So T will be equal to 1 by μ naught minus μ. Very good. Where will it become 0 once again? 2 π the Sin square theta, theta has to be equal to 0, π, 2 π, 3 π, so on and so forth. Next is 2 π. So when it's 2 π what will this be? 2 by μ 0 minus μ and this maximum also is some constant multiplied by of course rho μ which is a property of light multiplied by square of, mod square of your transition moment integral divided by μ 0 minus μ whole square. So you're going to get an oscillation in Cm square. This kind of oscillation is called Rabi oscillation. Not Rabi, Rabi oscillation. What does this mean? That means if you can do this experiment for long enough then you don't really get a constant population of the excited state. It builds and then comes down. Builds again and comes down once again. That is it shows an oscillatory behavior. That is point number one. Point number two is when does this maximum become large? Look at this. When rho μ is large then the maximum amplitude will be large. When the transition is allowed, when mod square of transition moment integral is large then also the maximum probability is going to be large and when you are close to resonance μ 0 minus μ is small then also this maximum amplitude becomes large.

Have you understood point number one first? In this kind of oscillation the maximum amplitude is going to be larger when you are close to resonance when the transition is allowed and when you use intense light. That's point number one. Point number two is now look at the X-axis. What happens when μ is close to μ 0. This frequency of oscillation will become smaller. That means when μ is, let us say μ is very very close to μ 0, what will happen? This is 0. The next 0 will come much much later. So actually you need to see only say up to this part. So when you are close to resonance frequency this is another approach towards resonance. When you're close to resonance frequency what happens is this frequency of oscillation also becomes, frequency becomes small, time period becomes large. Frequency becomes really small so the probability of this also this turning back of the excited state population for probability of getting your system in the excited state also becomes less. So you get to sample the initial part.

Point number three what [Indiscernible] [00:15:16] was saying is that we are working under the ambit of perturbation theory. So actually cannot work with too long a time. Is that what you're trying to say? Yeah please don't forget that. If you work with too long a time then you can consider that your perturbation is too much especially you are saying that you want a strong light to make the transition happen. At the same time if your time is also too large then your perturbation theory doesn't hold. So essentially whatever discussion we have had is confined to this part and even this Rabi oscillation kind of behavior that we get that is only an approximate behavior because if you really work at such a long time that we get to see this oscillation it is very highly probable actually that's what happens is that this expression will get modified. You will not just get – see this oscillation it will be modified by a damping function or something like that. But we will not go there. We confine ourselves into this first region but the important thing that we have learned here is that if we can look at the system long enough so if you go off resonance what happens? If you go off resonance? This is large. μ 0 minus μ is large then what happens? Then all these minimum points will come close to each other. Then you can perhaps see oscillation even when you are not going to even within the ambit of your first order perturbation theory. The only thing is that in that case the maximum amplitude will also be very small. So it will not be easy to see it. It's not as if you cannot do it experimentally, you can it but it's still not an easy experiment. It's a difficult experiment.

Now this Rabi oscillation is significantly important in areas of contemporary interest like quantum computing. So when you use computers you know computer does not understand too much. It only understands two things on or off, yes or no, 0 volt or 5 volt. So basically that is a two-level system. It works on binary logic in that case what you want to do is if you want to make a quantum computer which are supposed to be much much more efficient, much smaller than computers that we use now there Rabi oscillation becomes important. So maybe some of you will work in that field. So I thought we'll just introduce this today. can I move ahead now?

Now let us discuss one more question. As we have seen you have two levels and light comes and interacts with this. It is possible that light comes and interacts with the ground level and causes absorption. It's also possible that it interacts with the excited state and causes stimulated emission. The question is for a two-level system if you do the experiment sufficient number of times you you get net absorption or do you get net stimulated emission. If I translate this question to perhaps a more tangible form this is what it would mean. This is your sample. A sample that has two energy levels in it. You shine it with light of appropriate frequency and you look at the light that comes out. If you have net absorption then your Iem should be less than I absorption. Is that right? Some amount of light is absorbed after whatever stimulated absorption, stimulated emission processes take place finally number of photons that come out is less than number of photons that went in per second. In that case your net absorption. What happens if you have net stimulated emission? In that case Iem should be greater than Iabs, isn't it? Don't forget when this photon comes and part of the system whatever the excited state the molecule emits one photon and the photon that you had put in is also there. That is conserved.

So in fact you get one more photon out of the system. So in other words you get amplification of light. You get what is called a gain. Another word for this is loss. Another word for this is gain.

So the question is you get net gain or do you get a net loss? What happens in a two-level system? Is the question clear? Now what happens if you have net stimulated emission? Gain is more. So let us see. If that is the case this is what you should get. You know already that Einstein's B coefficient for absorption is equal to Einstein's B coefficient for emission. So for absorption what is the rate billion rho µ Nl. What is Nl? Population of level l. What is the rate of stimulated emission? B rho µ into I cannot hear you. You are 70 people in class and I should be able to hear better. What do we multiply that for a emission? You understand what I'm talking about right? This rate you say is B rho µ Nl. What is this rate? It is B rho µ into Nm, isn't it because B contains probability, rho µ contains the intensity of light, energy density and Nm is the population of the excited state. Nm.

So now if you have to have net stimulated emission or net gain of course B rho µ Nm has to be greater than B rho µ Nm NL that boils simply to Nm by Nl must be greater than 1 or I can put it like this Nm divided by N must be greater than 1/2 where N is simply the sum of the populations of the lower level and the upper level. Makes sense? This phenomena is called population inversion. Are we okay so far? Have you understood the problem? In that case what we do is that is a signal for us to end this module.

In the next module we are going to see whether this is at all possible to achieve in case of your two-level system. This is the end of module 1.