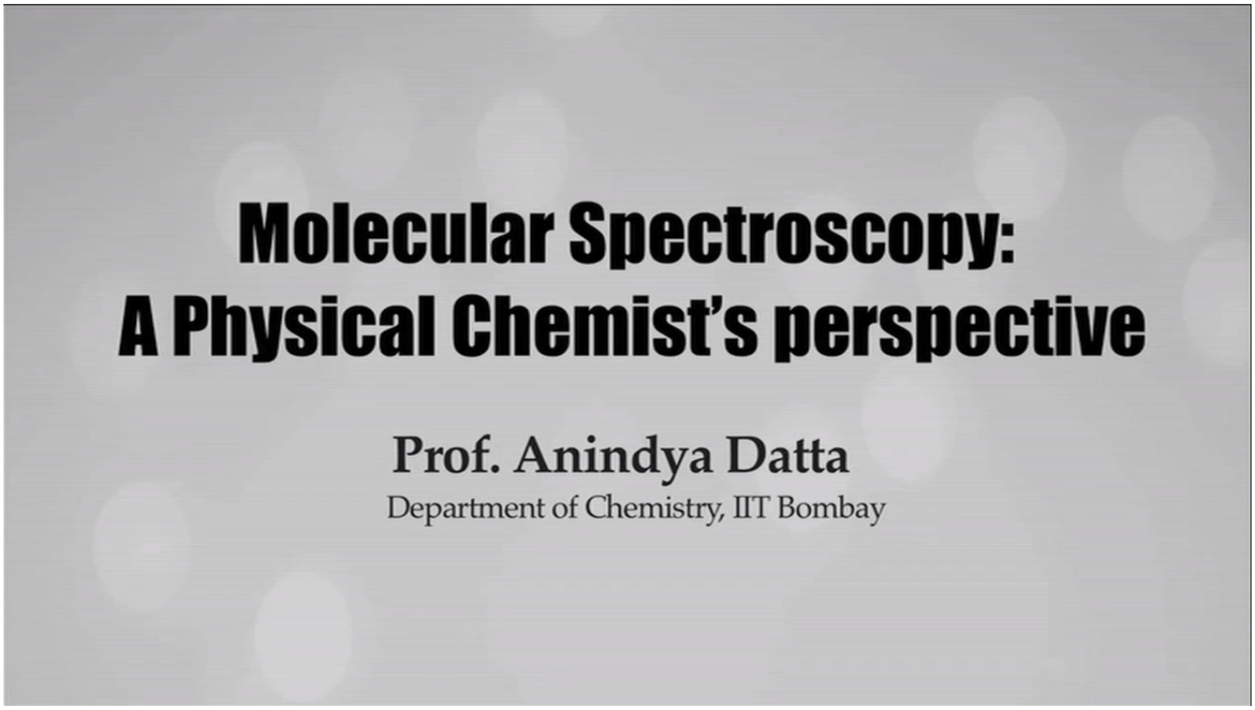

Molecular Spectroscopy: A Physical Chemist's perspective

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Knowledge is Supreme

Lecture No. - 22

Level System: Concluding Remark – II

Anindya Datta: So now we begin the second part of our discussion concluding remarks II for two level system. This is where we got that you must have a population inversion. Population of the higher level must be more than the population of the lower level in order for you to have gain, in order for you to have more number of photons to come out of the system than the number of photons that you put in. and this has direct relevance to something that is now very very familiar to us anyway lasers. I think you told me in one of the earlier classes what is the meaning of LASER, Light Amplification by Stimulated Emission of Radiation. So if I have to have light amplification by stimulated emission then my gain must be more. I should not have a loss. So let us see if that is going to happen. Do I have population inversion in a two level system. That's what we want to know. In order to answer the question what we do is we write once again a rate law kind of expression. Let us write the expression for dNm/ dt. What is Nm? Population of the higher level. That is equal to what? It gets populated by absorption. So the firs term I can write is B rho mu Nl and it gets de-populated by first of stimulated emission, and then your spontaneous emission. Let me write the terms of that. For stimulated emission the term is minus B rho mu Nm minus Anm. Any question about this? Do you understand why B is multiplied by rho but A is not? Why have I not multiplied the last term by rho? Spontaneous emission right. Even though there is no light it's going to take place and that is something that we will come back to in the next part of our discussion.

Now one more thing that I can do here is that in this equation Nl is variable, Nm is also a variable. And it's not so easy to handle both but then the good thing is Nl is simply N minus Nm, isn't it? Where N is the total number of molecules. So I can write this as N minus Nm. Let me collect the terms in Nm on the right hand side. I can write Nm multiplied by everything is minus. So minus B rho mu 2B rho mu Nm, I don't have to write Nm here plus A this whole thing can go into bracket inside brackets Nm, and what is the non-Nm term? B rho mu N. You know what to do. DNm divided by B rho mu N minus 2B rho mu plus A Nm is equal to I can write dt. Now of course I will integrate. I will integrate the right hand side between 0 and t and I will integrate the left hand side also but before I do so let me write this dNm as d of this. So I can write this as d B rho mu N minus 2B rho mu plus A Nm. What do I multiply outside? A numerator or denominator? Denominator minus 1 by 2B rho mu plus A. Is that right? What are the limits? What are the limits of this function? At time t equal to 0 what is Nm? 0. So second term vanishes. First term persists. So the lower limit is B rho mu N and the upper limit is the whole thing. So far so good. Not very difficult I hope.

Then I can write. Yes sir?

Student: [Indiscernible] [00:06:19]

Anindya Datta: Because we are assuming that – sorry?

Student: [Indiscernible] [00:06:27]

Anindya Datta: No. No. But don't forget where we have started from. Actually this Nm is difference in population. We are saying that when you start with the system is completely defined by PsiL. That means Nm has to be equal to 0. Isn't it?

Okay. so what do I get here. I can erase this all thing. Right hand side is very easy. What is the right hand side I can take this up to there minus 2B rho mu plus A multiplied by t. that is very easy. Even left hand side is easy. Lm B rho mu N minus 2B rho mu plus A Nm divided by B rho mu N. Is that right? So lm you know very well what to do. Get rid of lm. This is e to the power minus this thing.

Now what do I get? I get I will write like this. 1 minus 2B rho mu plus A divided by 2B rho mu we can of course simplify this further multiplied by Nm is equal to e to the power minus 2B rho mu plus A into t. So finally I get is equal to I can take this on that side. 1 minus e to the power minus 2B rho mu plus A into t and on this side I have where is Nl, where is N? I forgot to write N here, isn't it? On this side I have let me write like this. That is taken care of anyway. So Nm divided by N will be equal to what? 1 by 1 plus A by 2B rho mu. 2B rho mu divided by A plus 2B rho mu, is that right? Now I will divide I get 1 here, I get 1 here and this is – that is also not required. This is enough actually.

Now this is the expression I get. Now let us see. What is the left hand side? So what is N don't forget. What is N? Right. So Nm by N is the fraction of molecules in the higher level. What is the condition for population inversion? This fraction should be greater than half. What is this value when t is equal to 0? t equal to 0 it is 0. So if I want to plot Nm divided by N against t I start with 0. What is the value if t is equal to infinity. So the curve is going to be something like this. Is that so? There will be a limiting value. So now we come to this question what is this limiting value? Is that limiting value equal to 1? Can it be equal to1? Can it be equal to 1 because then you are left with only this coefficient. Okay can it be half? When will it be half?

Student: [Indiscernible] [00:11:50]

Anindya Datta: Only when A is equal to 0. So that is the limiting value we can think that when so first – so you are asking it can never be 1. it can be half if A is equal to 0. Now let me ask you the question can it A be equal to 0 if B is not equal to 0? remember that we have discussed in one of the previous classes A is some constant multiplied by B. So if B is not equal to 0 then A is not equal to 0 either. So actually A can be much smaller than 0 as we have discussed. What does it depend upon? Ratio of A and B. what does it depend upon? Isn't it something like mu cube by C cube something like that? So when – what happens is when mu becomes large then A gets a chance. A becomes larger. When mu is small then A becomes smaller. But whatever it is it can never be 0. So this limiting value is going to be half and you will never get population inversion in a two level system. That is A, very important take home message that for a two level system you can never achieve population inversion. Therefore you can never get stimulated emission for a two level system and therefore you can never hope to make a laser if a system has only two levels. Did I come to – did I show all you that little too quickly? Okay. let's say it once again.

You agree with me that the limiting value is half. Nm by N limiting value is half and when is this limiting value achieved? Only at t equal to infinity. But then t equal to infinity if you want to go there [Indiscernible] [00:13:48] will be very unhappy because the perturbation theory will not work any more. So you can never go there. You have to restrict yourself here. So for a two level system Nm by N is always less than half which means no population inversion. And if you remember what was the essential condition to get next stimulated emission population inversion. So we see that since there can be no population inversion in a two level system it implies that you cannot make a laser out of this two level system. You cannot get net gain from a two level system. But of course lasers are there. We use lasers in our classroom as well. Everybody has seen a laser show somewhere or the other. Lasers are there everywhere. You have laser printers in labs and homes. So how does one make lasers? Of course you cannot make lasers out of two level system. What you need is you need to add more levels. Next day we are going to discuss how you can get, I am not done yet today. we will discuss something else. But next day we are going to discuss how you can actually get next stimulated emission and therefore how you can actually make lasers out of three level and four level system an we also discussed what is the difference between this three level and four level systems. Once we are done with that we will take a brief walk through of laser spectroscopy. That is the reason why we are doing. Otherwise, laser is optics. Therefore, physics, right? But the reason why we study laser in this course is that we also want to tell you a little bit not too much, about lasers spectroscopy. So that is what we will take up in the next class. The take home message for today so far is that you cannot make lasers out of two level system because it is impossible to have population inversion and therefore impossible to have net gain if your system has only two levels.

When we talk about lasers what we mean is that we must have a net gain. We use the word gain. We must have amplification. That is the point. You can absorb some stimulated emission of course. But you cannot make a laser out of it. To continue this discussion of two level system let us do something. To start this discussion what we had done is we had turned the light on. We said there is no perturbation. System is in PsiL. You turn on the perturbation, turn on light and the state starts mixing you get a sum of these two wave functions.

Now to conclude the discussion let us turn the light off. Now let us say there is no light. What happens then? Of course at the instance when I switch the perturbation off there is some excited state population Nm. So what happens. The moment I switch the perturbation off does all these population [Indiscernible] [00:17:30] do all molecules come down to down state in an instant? Not really. Because don't forget what are the processes that are cut off. We talked about three processes. Stimulated absorption, stimulated emission, spontaneous emission. First two are associate with B, Einstein B. the last one is associated with Einstein A coefficient. First two of course are gone the moment you switch the light off. They are induced processes. What about the third one? It is spontaneous. That will still be operated. So the rate of decay of excited state population if I write dNm/dt that should be in that case minus A into Nm. Do you agree? All we are doing is we are taking the same Einstein treatment but now since the light is off, we have removed the first two terms. We are working only with the third term. Are we clear?

Very simple equation. If I solve it what will I get? But Nm I will just write t explicitly now. T is equal to Nm at time 0, don't forget in this case time 0 is the instance at which I have switched off the light. So there is some population in the excited state . I call that population Nm at time 0 multiplied by what? E to the power minus At. So what do you expect is an exponential decay. Same treatment as what you have done in your chemical kinetics class in class 22 or class 12. We expect an exponential decay in population. It is conventional to write this expression not as in the terms of A but in terms of what is called lifetime. In this case I will call it tau R where tau R is equal to 1 by A it is called radiative lifetime. So the process you have here essentially is [Indiscernible] [00:20:16]. So far so good? Agree?

Now by the time we end this discussion once again what we will do is we will build another bridge between experiment and theory. If you remember in one of the earlier discussions we had simply. We said that you can express A and B in terms of that stylized A. what was stylized A? It was an absorption coefficient. You can easily expression it in terms of epsilon which is an experimentally measurable quantity. We will conclude with something similar today as well. This is lifetime.

Alright. Now let me ask you a question. Is everything emissive? Is everything in the world emissive? I see you are wearing shirts. They are colored usually. Even if they are white they are actually colored. It's all that all colors are present but do they actually give out light? I mean if I turn out the light for sometime are you going to see a glow? Not really. Not usually unless your shirt has some florescent pigment in it. So actually most of the colors substances that we see are not emissive. Why are they non emissive? Is it possible that A is equal to 0 for them? No. You understand the point I am trying to make. For anything and everything A can never be equal to 0. You told me 15 minutes ago. If there is a color that means there is a transition. That means B is non-zero. If B is non-zero A cannot be zero either. Why is it then that we don't see emission from anything and everything? The reason is we have not considered something so far. You have two levels. We have said we have absorption and we have emission. But I think most of you know that it is also possible and in most cases that is the predominant thing that happen is that you can have what is called a non-radiative relaxation. The point is there are several pathways available for the molecule to come down to the relaxed round state without having to give out a photon. I will take a very very simple example. I will just write some arbitrary groups, A, B, C, D. This is a CC double bond. Is it possible to for [Indiscernible] [00:23:13] alkaline with CC double bond to become trans alkaline? No right. [Indiscernible] [00:23:19] is not possible. Why not? Because it's a double bond. Five bond is there but suppose I now do a what is called a π π * excitation or transition then what happens? Now as long as it is in the excited state π π * transition has taken place. So we have one electron in π orbital. One electron in π 8 orbital. What is π [Indiscernible] [00:23:44] in the excited state? 0. That means the excited state this has become a single bond.

Now it can rotate. He moment it rotates that itself is a non-radiative process that happens. Photoisomerization. In fact photoisomerization is taking place within all of us right now in this room because we are seeing each other. Photoisomerization is an important part of vision process. [Indiscernible] [00:24:09] so there are several non-radiative channels that are [Indiscernible] [00:24:13] available for relaxation of excited states for the system to come down to down state. So our discussion is really not complete here. We have defined radiative lifetime. Fine. But if you really want the whole picture then I should write not just A but some other term I choose to write A plus KNR. N for null R for radiative. KNR is a non-radiative rate constant. We will just need two, three more minutes. Please bear with me. So if I do this this expression just gets modified in this way. Now I don't call it tou R I call it tou. So tou is 1 by A plus KNR this is called the excited state lifetime. So lifetime of the excited state is merely the reciprocal of the overall rate constant for B excitation of the state. Any question? Yeah? Okay. tou is equal to 1 by A plus KNR. Do you have any question here? Have you all understood? Can I go ahead? Great. I leave it to you to figure out this is homework, write down. Prove that this tou we call it lifetime. Why do we call it lifetime? It's not half life. If you simply put t equal to tou what do you get? See Nmt divided by Nm at time 0 is equal to e to the power minus t by tou. What happens if you put t equal to tou? Right hand side becomes 1 by e. What is 1 by e? Approximately one third. It won't be 0.69, 0.33. Yeah approximately one third. So it is not half life period. So this is you can say very roughly that time for the excited state population to decay to about one third of its initial value but more importantly it is the average time spent by a molecule in the excited state. So I request you to work it out by yourself. It's there in many book [Indiscernible] [00:27:18] topics in [Indiscernible] [00:27:21] spectroscopy would be a good reference among others. You can also look up photo chemistry books by Rohatgi-Mukherjee or Rohatgi-Mukherjee; that's one name. Rohatgi-Mukherjee. Not minus hyphen. Rohatgi plus Mukherjee that's why it became Rohatgi-Mukherjee. Not minus, Rohatgi-Mukherjee's book or you could see Turro's photochemistry book. Nicolas Turro photochemistry.

Okay. alright. It is the average time spent in the excited state by molecule you can work that out yourself. But what we end our discussion today is this, remember we have talked about steady state some time ago. What is the meaning of steady state? Rate of excitation is equal to rate of I can call it de-excitation. So in steady state what you can write is rate of excitation is your A plus KNR. Will you agree with me? Rate of excitation is A plus KNR because that is your well multiplied by Nm. A plus KNR multiplied by Nm excited state population is the rate of de-excitation of the excited state and here I have considered radiative as well as non-radiative. Everything, All channels. So this is rate of de-excitation at steady state you can equate it to rate of excitation as well.

Now I bring you back to something familiar, something we had written earlier. What is emission quantum mean? Iem by Iabs can I not [Indiscernible] [00:29:33] rate of emission divided by rate of absorption. So rate of absorption I know already. It is A plus KNR or tou you can say. What is this Iem? Not emission quantum mean. It is A into Nm. Rate of emission for rate of emission you have to only look at the emissive channel. You have neglect the non-emissive channel. So ANm divided by A plus KNR Nm. Nm and Nm cancel. What are you left with? You are left with A multiplied by tou. Psiem is equal to A multiplied by tou. What is 1 minus Psi em? You work out for me from here. 1 minus Psi em just do the algebra here. 1 minus A divided A plus KNR what are you left with? KNR by A plus KNR and we know that 1 by A plus KNR is tou. So it is KNR multiplied by tou.

Now see you know how to determine quantum [Indiscernible] [00:31:07] emission quantum [Indiscernible] [00:31:08] you did that last evening. How do you measure lifetime we will discuss it when very briefly when we talk about laser spectroscopy but just believe me for now that it can be done experimentally. So you do these two experiments steady state emission experiment and you measure lifetime experiment what you can find out is you can find out the rate constant for the non-radiative process that de-populates the excited state. So if you are talking about photoisomerization for example I should be able to find out what is the rate constant for this photoisomerization process simply by doing a steady state experiment and measurement of lifetime. Last point, absolutely last point is how do find A. you don't have to do it experimentally. Isn't it? Remember A is related to B and that is related to epsilon. So if you have experimentally – suppose you have done an absorption experiment from there you can find out what is epsilon. From epsilon you can find out what is stylized A, from there you can determine A. So once again we finish in a situation where you have a nice correlation between experimental and theoretical quantities. You do an experiment you can find out the value of this theoretical quantity. You determine the value of the quantity theoretically you can try and predict what your experimental results are going to be. We stop here today. Next day we start talking a little more about lasers and laser spectroscopy.