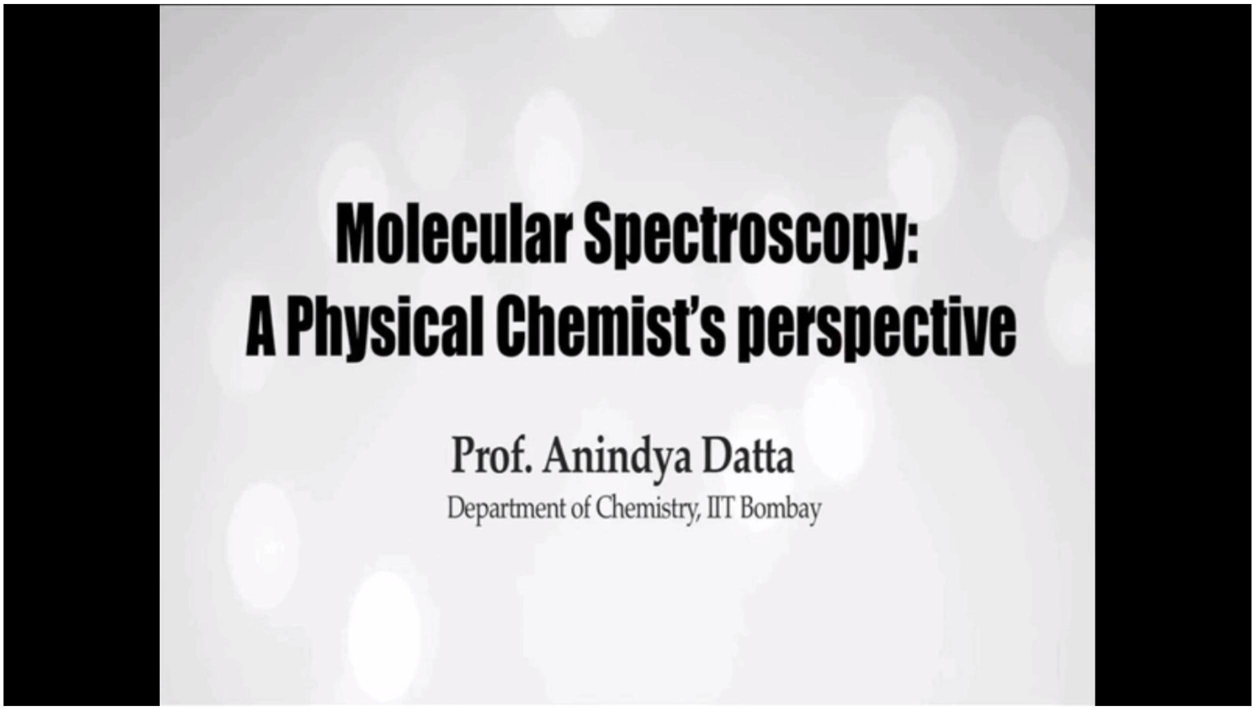

Molecular Spectroscopy: A Physical Chemist's perspective

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Knowledge is supreme.

Lecture No. - 19

Einstein Treatment

Anindya Datta: Today we are going to discuss Einstein treatment. Well when you take Einstein's name what comes to your mind is relativity. And as you know he got his Nobel Prize not for relativity but for photoelectric effect. So that is [Indiscernible] [00:00:58] connection with this photoelectric effect also has to do with light. Today what we talk about is A, rather simplistic approach that Einstein has developed which enables us to as you see co-relate experimental and theoretical quantities eventually.

So before we embark on that let us remind ourselves what we have studied so far. First of all we have studied that transition moment integral has to be non-zero. This has been said many many times. What I will do is I will just write this in a little different way today for the sake of gravity. This is our transition moment integral. Let's write it as µ lm mod µ lm something like that. You will see why.

So what we have done so far is that we have arrived that this golden rule what is this golden rule, what is there on the left hand side? DP l to m dt. Rate of change of probability. You can say. That is equal to 8 please remind me because I don't really remember expressions very well. 8 π cue divided by 3 h square multiplied by we can write μ lm mod square anything else, into rho μ. What is rho μ? Rho μ is energy density. And let us see who can tell me the expression for energy density that we have from Planck's law.

I remember the denominator so I will write it. Denominator is e to the power h μ lm. What is μ lm?μ lm is the frequency that gives measurements for the energy gap that is there divided by kT minus 1. This much I remember. In the numerator if I remember correctly there is 8 there is π. What else is there? I think it is μ lm cue divided by C cube. But I will just check because I am not all that good. 8 π h cube lm cube divided by C cube divided by, whole thing divided by e to the power h μ lm divided by kT minus 1. is that what I have written? Great. I am proud of myself. Numerator, 8 π is there. Yeah h is what I had missed. So this is what we have.

With this we are sufficiently equipped to [Indiscernible] [00:04:22] path of Einstein. What Einstein did was this. He considered the same two levels system that we are talking about. Lower level is l. upper level is m. Now first of all we face two paths that we have discussed already. This arrow means what? Light has come in and has caused an induced absorption. For induced absorption what should I write? B multiplied by rho μ, this whole thing is constant. So Einstein wrote it as Blm, l is the level of origin. m is the destination level. So this is called Einstein's coefficient for induced absorption. This Blm is called Einstein coefficient of induced absorption. So this rate of transition for a single molecule from golden rule would be Blm multiplied by rho μ. What is the other process we have studied? Light comes. There is some excited state population here. This causes this to come down. This would be Bml rho μ. What is Bml. I think you can guess it is Einstein coefficient for induced emission.

In principle you should be able to find out an expression from Bml as well from this perturbation theory type of treatment that we have already done. But as you will see we don't need to. The answer that comes out is fairly simple.

Now this is the probability for one molecule. Now if I consider that ml and lm are the populations of level l and level m respectively, then what can I do, if I just multiply this by Nm where Nm is the number of molecules in m level, I multiply this by Nl which is the number of molecules in l level. What is that? That is first we have the probability. So one molecule. Then we multiply by population. What do you get? See this expression that we have golden rule that is dpdt. Probability. So that is so one molecule. I am multiplying by population. What do I get then? You think total number of transition.

Now then Einstein induced something that was not there in our discussion so far. It is important to remember that light comes in and goes out as well. Einstein said there is always some spontaneous emission. And he said let Aml be this coefficient for spontaneous emission. Of course, he didn't call it Einstein coefficient for spontaneous emission. Other people have added his name to it. So Aml is the coefficient of spontaneous emission. What do I have to multiply Aml by this to get this rate of transition from m to l by this spontaneous emission pathway? Should I multiply by rho? What should I multiply by? Nm. See this what do I write? Let me write S for system, S plus light forming S* or maybe I can just write l and m. this is the first kind of if you can think of, the first kind of reaction that we have. The other reaction this one is m plus h μ forms l. The last one is essentially m forms l. I am not writing the plus h μ in the last two. So this you can think is biomolecular reaction. This is a uni-molecular reaction. So there is no scope of writing rho there. There is no need of writing rho there. Are we clear with this?

Then we use something that we have studied in classes of chemical kinetics long long ago. We used what is called steady state approximation. Before I write that can you tell me what is steady state? What is the meaning of steady state? What is an example of steady state? Let me rephrase the question. What is the difference between steady state and equilirbrium? As chemist we are all familiar with the term equilibrium, checmical equilibrium but chemical equilibrium and steady state are not one and the same. And perhaps you have studied long ago this example where you have this tank, tap at the top, drain at the bottom. And the tap and the drain are adjusted in such a way that the level doesn't change. Is that a steady state or is that an equilibrium? It's a steady state. Why is it a steady state?

Student: [Indiscernible] [00:10:44]

Anindya Datta: Not really. When you talk about equilibrium you mean a closed system. When you talk about steady state you mean an open system. This system as you see is not really closed because light is coming from outside. Light is going out. So it's an open system but what you can think is at steady state rate of absorption should be equal to rate of emission. So at steady state I can say that rate of population of m should be equal to rate of de-population of m. question?

Student: [Indiscernible] [00:11:29]

Anindya Datta: Okay. what is that process? Absorption. So absorption as I did but I have erased now, absorption is like reaction between molecule in the l state and light. So if I think of rate of that reaction, rate of that process, so that should be a product of concentration of molecules in m state that is Nm, number of molecules in m state and concentration of light. So one way of writing concentration of light is energy density. I have written it wrong. You are right. You are right. So sorry if I confused you. It is Nl here and Nm here of course. So you are right. Are we clear now or do we have become more problematic? Yeah?

Student: [Indiscernible] [00:12:23]

Anindya Datta: Is it okay? Not okay. Yes or no. Yes. So again please use that convention. This is not yes. This is no. Okay so far. So at steady state what will happen? At steady state Blm multiplied by rho μ multiplied by Nl should be equal to Bml multiplied by rho μ multiplied by Nm plus Aml multiplied by Nm. The rate of upward and downard transition should be equal to each other. That's all.

Now what will I do? See I already know an expression for rho μ. So if I try and rearrange that equation and make rho of μ the subject of formula then perhaps I can compare the right hand side of that equation and the right hand side of Planck's law and get some information about how the A and Bs are related. That is essentially what we are trying to do. So let's try and do that. Rho μ multiplied by Blm Nl minus Bml Nm is equal to Aml Nm and hence I can write, I will write here, if I make rho of μ the subject of formula that should be equal to Aml multiplied by Nm divided by Blm Nl minus Bml Nm. What am I doing?

I am back calculating. Are we okay so far? Now what do I want, I want something like this. I want the second term to be minus 1. Minus is already there. I want to make it one so I will just divide by your I will divide by Bml Nm. So if I do that what do I get? Aml divided by Bml this becomes 1 and what does this become? Divided by Bml Nm. Is it okay?

Now we can use something else that we know already specically those of you who are studying stastical thermodynamic course right now, yes I have two levels populations are Nl by Nm, you know very well what is Nm by Nl or what is Nl by Nm. What is Nl by Nm? To keep things simple let us consider degeneracy be 1. actually degeneracy also has a role to play here but let's just put it to be equal to 1. What will Nl by Nm be equal to exponential Nl by Nm. Nl is a lower level. So it is actually h µ lm divided by kT. H µ lm is the energy gap. Nl is the lower level that's why. Otherwise, if I wrote Nm divided by Nl it would have been e to the power minus h µ lm by kT that's all. And see it's nice because here also I have e to the power h µ lm.

So I will write it here minus 1 e to the power h µ lm divided by kT. Now my job is done. What do I learn from here? First thing that I learn is that if you compare this expression with Planck's law, what do I learn, Blm by Bml equal to 1. Is that right?

First thing I learn is that Bml equal to Blm so since they are equal to each other I don't have to bother about m and l what is the order I just write it as B. so Einstein coefficient of induced absorption is the same as Einstein coefficient of induced emission. This is a rather profound very important result. Are we clear so far?

What is the second thing that I learn? What is the second thing that I learned? Now I am not going to write ml at all. I will just write A and B. From denominator you get A by B is equal to 8 π h µ lm cube divided by C cube. So we get a very convenient relationship between Einstein's A coefficient and B coefficient. And that again leads us to some very important result. First, in the treatment that we have performed earlier did we consider spontaneous emission. The treatment that we did upto last class, did we consider spontaneous emission at all? We did not. What does Einstein treatment tell us that spontaneous emission is always there.

If B is there see, if B is zero, let us say B is equal to zero then A will be equal to zero, no problem. But then if B is equal to zero that means transition between l and m is not even allowed. So if there is no absorption what emission are we talking about? So it's important to understand that B tells me actually how allowed the transition is. So if B is zero then only A is zero. If B is non-zero, A is also non-zero. So first thing that you learn is that you cannot ignore spontaneous emission. It is always there.

Second thing that comes is when does it become important and when is it not important? As you see we write like this this here is the factor. And even with this this is the only thing that can change depending on the system. 8 is a number, π is a constant, h is universal constant, C is universal constant.

Let us see what this constant turns out to be. 8 into 3.142 , help me with the value of h, 6.6 into 10 to the power -39 unit 34 unit, okay. What is C in that case? 3 into 10 to the power 8, not 10. Okay. So what do I get here? 8 multiplied by 3.14 multiplied by 6.6 by 3, right, ,who is going to – this is actually cube, right. What is the number can somebody calculate quickly and tell me? It is approximately something like 20 right. Yeah. 8 by not 20, not 20. this is not 9. This is 27. 8 multiplied by 3.142 multiplied by 6.62 divided by 3 cube. What is 3 cube? 27. What is it? 56 something like that. Something. So well the point I am trying to make is 10 to the power 0 so 6.1 multiplied by 10 to the power how much, 10 to the power minus 58 actually it's a very small number. But let us think what µ is. What is a typical value of µ for say microwave. What is the frequency of microwave? Frequency? Say 5 centimeter inverse. 10 centimeter. Microwave right.

So how much should it be? What is the frequency? So what did I say 5 centimeter inverse. That is your μ bar. That is 1 by lambda but in centimeter. Don't forget.

So I want μ. What is the relationship between lambda and μ? Lambda μ equal to C, right.

Student: [Indiscernible] [00:22:47]

Anindya Datta: Wait. Let me work it out. Lambda μ is equal to C is that right? So your μ is basically C μ bar. So 3 into 10 to the power 10 if I do it in centimeter multiplied by we are saying 5 centimeter inverse. How much does it come to? Is it right? Is that in hertz? Right or wrong? Right. So it is 15 into 10 to the power 10. I will take that 15 to be 10 so 10 to the power 11 or something like that. So 10 to the power 11 cube, how much is that? 33. right. 10 to the power 11 is 33. So minus 58 plus 33 that's a very small number. What does that mean? That means in microwave regime, you have very little spontaneous emission. So microwave spontaneous emission is not too much. So if you look at emission in microwave it is predominately stimulated emission. Contribution of spontaneous as we said cannot be – we can never say it is zero but it is very small.

Let us go to UV. UV rays. That is I remember μ bar is 10 to the power 5. 5 or 4, 10 to the power 4 actually. 10,000. 10,000, 20,000 that is your UV visible regime. 18,000 is red I think and 24,000 or something is blue. So basically 10 to the power 4, so if this is 10 to the power 4 μ bar then what is μ? The μ will be 3 into 10 to the power 10 into 10 to the power 4 that becomes 10 to the power 14. Cube of that how much is it? 42.

Now see 58 minus 42 well much better than microwave. Much better than microwave right. And in fact that is the problem. What we realize is that as the energy gap increases contribution of spontaneous emission also increases compared to stimulated emission. That is the problem when you want some application that is based on stimulated emission and the application that is most relevant to spectroscopy is laser. We are going to discuss lasers from next class onwards. So when you want to make a laser you want to amplify the stimulated emission and at that time you do want de-population of the excited state to take place by spontaneous emission.

So it turns out that it is very easy to make a laser in microwave. In fact the first laser that was invented was maser. Maser means microwave amplification by stimulated emission of radiation and till date a UV laser remains illusive. We do not have a laser that gives you ultraviolet light directly. You do get ultraviolet laser light but invariably that is infrared or maybe visible photons which are added up to give you higher energy. We will talk about it a little more when we discuss lasers next day, not today. But for today for until now the message that we have is this we have discussed Einstein's kinetic treatment of this two level problem and we have learned two things Einstein coefficient for absorption is equal to the Einstein coefficient of stimulated emission. Number two, we have learned that your spontaneous emission is never zero. A can never be zero is B is non-zero. But A makes a relatively higher contribution when the energy gap is higher. When frequency is higher. It makes relatively lower contribution when the energy gap is lower, frequency is lower. And that has profound implications on applications based on stimulated emission. Okay. That is the end of this part of the discussion.