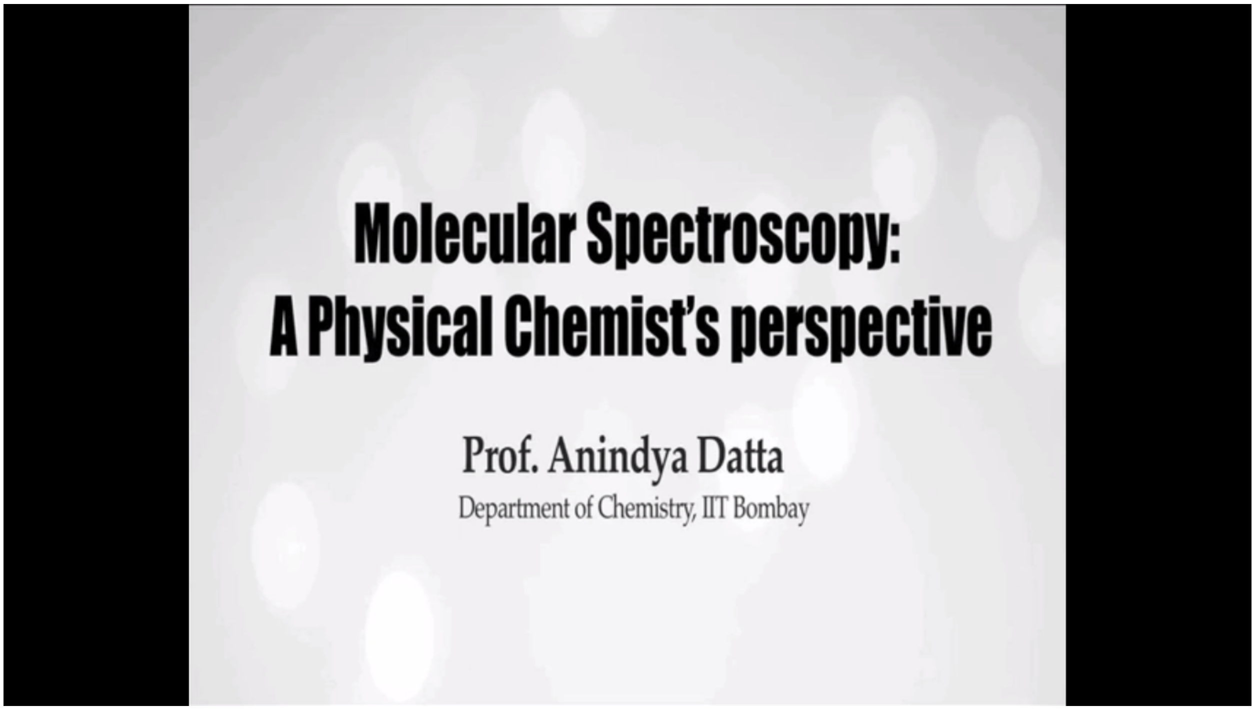

Molecular Spectroscopy:
A Physical Chemist's perspective

Prof. Anindya Datta
Department of Chemistry, IIT Bombay

Knowledge is supreme.

Lecture No. - 20

Relationship between Theoretical and Experimental Quantities

Anindya Datta: So so far what we have done is this. At the beginning of the course, we have discussed how to actually record spectrum and in doing that we came up with two important intrinsic parameters that we have to use in spectroscopy all the time if it absorption we talk about epsilon. The absorption coefficient. If it is emission then we talk about emission quantum with [Indiscernible] [00:01:10]. Then we took a break from this discussion of experiments and performed a completely theoretical treatment semi classical treatment based on time dependent perturbation theory whereby we have arrived at certain quantities that tell us not only whether a transition will take place or not but also if the transition takes place the extend to which the transition will take place. So first of this quantity is worth your transition moment integral. Then after Einstein treatment we found Einstein's A coefficient and Einstein's B coefficient.

For the sake of continuity let us write down what are the expressions for A and B. B is written here anywhere. 8 π cube divided by 3 h square mod lm square that is your Einstein's B coefficient. What is the relationship between A coefficient and B coefficient that we had worked out? A is equal to help me with this, 8 π h μ lm cube B, c in the denominator otherwise C should have been very different. C cube. Of course, it is very easy for you to take this expression plug it here and determine what is the relationship between A and transition moment integral. That is not very difficult. So we have a complete co-relation between your Einstein's A coefficient and transition moment integral. The question is how are these related to experimental quantities. Let us say absorption coefficient. So while doing absorption coefficient we will nto actually go up to epsilon but it is very easy. Let us see.

So what ever we have learned so far from golden rule what is the probability of a single transition. What is the probability of a single transition? Single molecule single transition. This we are talking about absorption right now. For absorption well rate of change of probability of transition dplm dt that is given by this. I will write that once again. 8 π cube divided by 3h square mod μ lm square rho μ. Now if this is what it is then in a single transition let us say, what are we trying to do we are trying to now get an expression that looks something like where we started from when we derived Lambert-Beer's law. Remember the derivation of Lambert-Beer's law. How did we begin? We said minus di is proportional to i then concentration and the length segment bl. And from there we integrated. Here we don't even have to integrate. We want an expression where on the left hand side where minus di divided by i on the right hand side if possible we want bl multiplied by cm multiplied by something else. Whatever soemthing else will be there that should be equal to your absorption coefficient. Not epsilon but alpha. Actually not even alpha we will see what it is.

That's what we are trying to do. This is probability let us say per unit time. Probability of transition per unit time. Why is that per unit time important? Remember what is the definition of intensity? There also there is per unit time. So you can see it is not very difficult to go from here to intensity. We will get there. What is the energy of transition, each transition? L and m h μ lm. So probability of transition multiplied by h μ lm that is your energy removed per transition. Alright. Now let us say N dash is the number of molecules per centimeter cube. What will be the relationship between N dash and Cm molar concentration? Molar concentration? What is molar concentration? Number of moles per decimeter cube. So if I want to go to centimeter cube first of all I have to divided by 1000. So this is basically moles per centimeter cube. If I want molecules from moles what do I do? Multiply by Avogadro's number. That's all. Na. Na Cm divided by 1000. I multiple this. Na Cm divided by 1000.

Now if I take unit cross section and a length of dl multiply this by dl that gives me volume. Concentration multiplied by volume, that is the number. Now last thing that I want to do is this, what is the relationship between rho and intensity since you want to write it in terms of intensity anyway? What is the relationship between rho of μ and intensity? I equal to C into rho μ. Just we can take this [Indiscernible] [00:07:53] if required in the exam and all I will provided. I equal to C into rho μ wher C is not concentration or anything C of course is speed of light. So what is rho of μ? I by C. So what I can do is here I can write I by C. What is this equal to? Will you agree with me if I write this is equal to minus dI? See I have from light with intensity I impinging on a surface in the sample. Probability of transition is given by this multiplied by I by C. Energy removed per transition is h μ lm. That is the amount of energy that is removed from this beam of light that is passing through the sample. I multiplied it by this number of molecules per centimeter cube and I multiplied that by volume as well keeping unit cross section. That should be decrease in intensity of the light that falls on this segment. Agree. So see now I already have what I wanted. I have something like minus dI divided by I is equal to let us simplify this a little bit 8 π cube μ lm divided by 3 there is an h here and h there so h goes. So 3h actually I can write

3000h and since this is an universal constant I will write this here Na multiplied by μ em multiplied by Cm multiplied by dl. What was the starting point for derivation of Lambert-Beer's law? Minus dI by I is equal to alpha μ Cm dl. Isn't it? This is where we had started from where alpha μ was the coefficient. Just one thing that we want to emphasize here is that when we did this we pretended as if we are working with one single frequency. But in our time dependent perturbation theoretical treatment we have learned that actually the band has some width. And that reminds me when I wrote the [Indiscernible] [00:10:46] that perhaps could have been a little confusing for some of us because there was a question last class and where [Indiscernible] [00:10:53] asked to do suppose to remind me today but did not. So if you remember that plot of the Cm Cm* against something was there. So the question was that what is the minus? μ cannot be minus. Don't forget this X-axis was something like delta e minus μ. So that can be minus. There is no problem with that. So that was a small point that I wanted to make first. The second thing is here I should not use alpha μ as such. What I should really use is this stylized A which is equal to integral of alpha of μ over the entire band. Which band am I talking about? I am talking about this one. This is what we studied in last day's class. So the thing is if you remember we worked with the integrated coefficient. We integrated the whole thing and worked with the area. So here also what we will do is we will just write this is stylized A which is called the integrated absorption coefficient. I will leave it to you to work out the relationship between the stylized A and epsilon. And when I say I leave it to you it means that it is highly probably that I will ask you to do it in one of the exams. So please work it out by yourself. You can work it out now or you can work it out for the first time in the exam there is no problem. But I hope it's not very difficult to understand that this A can be related to epsilon because when you integrate it will be lm you have to go from lm to locked to the base end and so on and so forth. But the other thing that we are – the point that we are really trying to make now is take out this Cm into dl left hand sides are the same. So you are left with integrated absorption coefficient is equal to 8 π cube Na μ em what am I missing? What am I missing? Who will write this? Without that it becomes constant for everything. μ em mod square of transition moment integral divided by 3000h. Is there a C? There is C here, right. Yes. Yeah.

So now we have achieved what we wanted to do. On left hand side we have an experimentally determinable quantity something that is some constant multiplied by your epsilon. On the right hand side I have a purely theoretical quantity. So this is the relationship between your experimental and theoretical quantities and as you see square of transition moment integral is proportional to epsilon.

So if I somehow know if I can calculate I can calculate the epsilon value theoretically using the wave functions. Or what I can do is from the epsilon value I can try and find out what is the value of transition moment integral. So from experiment you can get an idea of what the theoretical quantity should be. From theory you can make an estimate of what the experimental quantity is going to be. This part is there in your [Indiscernible] [00:15:23] book. You can study this from [Indiscernible] [00:15:25] book but I find it easier to follow the logic of an ancient book by Gordon Barrow. The most recent edition of Gordon Barrow's book I think was published in 1964 where all of us were perhaps in our previous birth but the thing is it's good enough. So this is what we have achieved.

Now once I know this I can do whatever I want. From here the relationship I have is between your integrated absorption coefficient and transition moment integral. If I ask you to find the relationship between integrated absorption coefficient and A coefficient. Can you not do it? Einstein A coefficient. You know what is the expression for Einstein coefficient. It is written in terms of B. substitute the value of B here you get it in terms of your transition moment integral and you can work it out. So this is your homework. Please try and find out all the inter-relationship that are possible. Relationship of stylized A with Einstein A and stylized A with Einstein B. And finally, the important thing that we learn from here is this, let me ask you a little different question. Is it possible to have a situation where I have only spontaneous emission and no stimulated emission? When? How can I create that situation? The energy gap is very high. Then A becomes well it never is larger than B as you saw.

Student: [Indiscernible] [00:17:22]

Anindya Datta: Even for UV it is still much smaller. Actually you are the one who said that it is too small when we calculated it.

Student: [Indiscernible] [00:17:32]

Anindya Datta: You can actually try and see. Well that is one part of the story. I agree with you. But there is something else that you could do. Don't forget your stimulated emission is analogous to A bimolecular reaction. B is the property of molecule. Molecule is only half the story. What is the other half of the story? Radiation, light. So if I work at a low value of rho then what happens? Then I can pressures the rate of stimulated emission. Is that right or wrong? I can play around with the energy density. I can play around with the intensity of light. So if I have a small intensity of light then your stimulated emission can be suppressed. So yeah [Indiscernible] [00:18:32] of course it will suppress absorption but what absorption is there when the stimulated emission take place then well the [Indiscernible] [00:18:42] take place stimulated emission will be not there. There is something else that can happen. Do you people have in many cases recorded absorption and emission spectra, right? So sometimes that emission spectrum is largely rate shifted, isn't it? So suppose there is a big energy difference between absorption and emission then what happens. You have this energy density of the excitation light. It's a blue light. But you don't have so much of red light coming in. whatever red light is there is a result of the light that is emitted. That's not so much. There also you can create a situation where you have predominately, sorry, spontaneous emission.

So next day what we will do is we will first discuss this part. What happens when there is only one kind of emission? And from there we are going to talk about what is called radiative lifetime and excited lifetime. We will talk a little bit about non-radiative processes. Hence after that we will go over to our discussion for lasers.