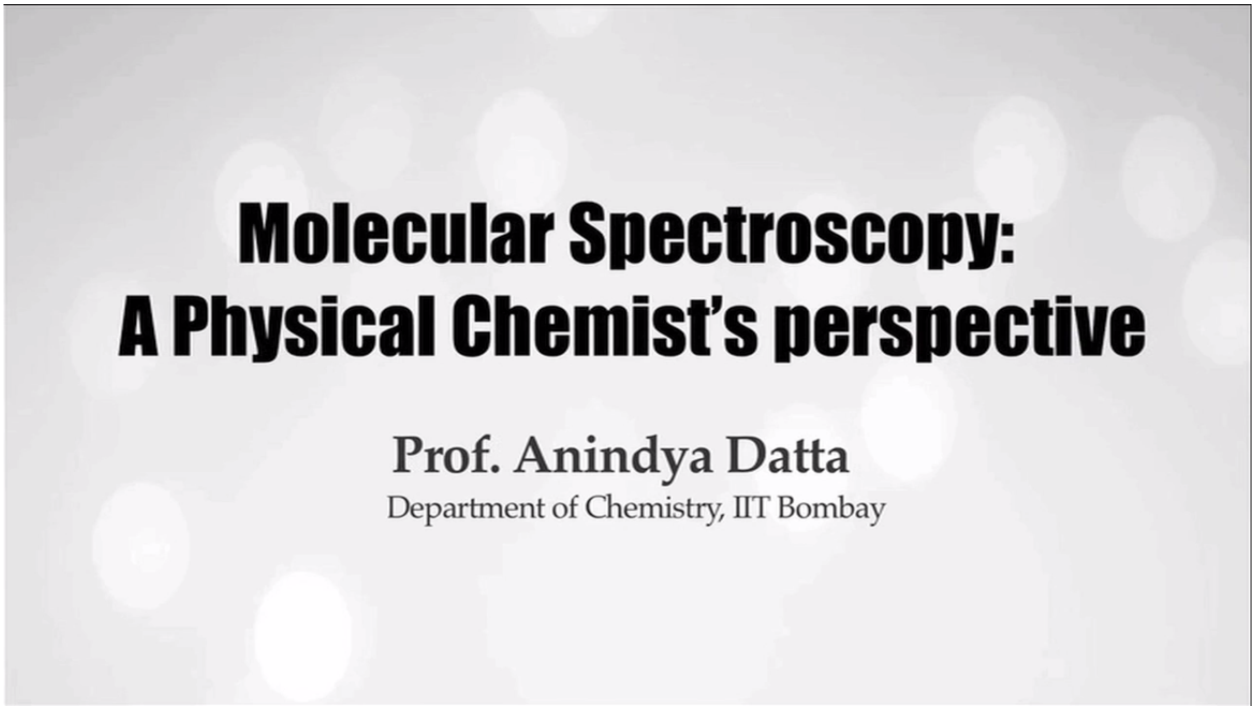

# Molecular Spectroscopy: A Physical Chemist's perspective

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Knowledge is supreme.

Anindya Datta: This of course is a continuation of what we have been discussing in the last few classes. Time dependent perturbation theoretical treatment of semi classical – semi classical treatment of interaction of radiation with matter and to keep things simple we are working with two state system. One is designated L, one is designated M and now I can write L lower and M higher with confidence because we have already seen that we have eliminated the other possibility where L is higher. Essentially L means the level from which the transition begins. M is the destination level where the transition terminates. So if L is below M in energy then we are talking about an absorption. As we have said since we are using perturbation theory what we do is we write the Hamiltonian like this. Hamiltonian of these two states system is [Indiscernible] [00:01:32] Hamiltonian plus a first order perturbation term and this first order perturbation term as we have already is minus µ x into Ex. You are working in x direction only. µx is the x component of dipole moment. Ex is the x component of the electric field associated with light and so once again please don't forget when we formulate the Hamiltonian in the [Indiscernible] [00:02:10] treatment all our formulations are actually classic in nature. We are considering a classical electrostatic interaction between the dipole and the field. That's all.

So this Ex we [Indiscernible] [00:02:23] to Ex 0 cos 2 pie µt and then this boils down to minus µx Ex0 e to the power 2 pie I µt slash e to the power minus 2 pie I µt. Is that right? Right. So this was the formulation of the perturbation. What about the weight function? We said the time and space dependent rate function side of the two state system is given as a linear combination of [Indiscernible] [00:03:18] functions of the two states. And it is very important to remember that this coefficient Cl and Cn are time dependent at initial times we said Cl tends to 1, Cm tends to 0. of course they are not exactly equal to 1, not exactly equal to 0 at any time after [Indiscernible] [00:03:51]. 0 time is the time when we switch the perturbation on. And since the question was asked once, the perturbation remains on. It's not that the perturbation goes off. If perturbation goes off then you have what is called relaxation. That's a different ball game altogether.

Okay. From here I think so far we have reached here. Cm I will just write Cm for now actually it is absolute value of Cm. Cm has turned out to be Ex0 multiplied by psi m µx psi l integrated over all space. Now this psi and this psi what kind of functions are these? Yeah? I cannot hear you. What is the difference between this psi and say this psi? The statistical psi is space dependent as well as time dependent. Actually it's a product of the space dependent, time dependent part. This is only the space dependent part. It is – I have said it five times already in this course, or more but I am saying so many times because it's important that we do not have any confusion here.

This integral is only in terms of space [Indiscernible] [00:05:15]. It's very important that you understand that. What happened to the temporal coordinate? The temporal coordinate has come out here like this. For absorption process, we have got the temporal – we have got this term to be denominator is Em minus El minus hµ. What is the nominator? E to the power what happened? You are telling me the answer is it? No what is it? Right. I am skipping the exponential. I keep forgetting that 1. 1 minus exponential 2 pie I by h into Em minus El minus hµ into t. is the expression complete or is there anything else? Yeah. Minus will neglect or not. Okay. thus inside later on when we do an integration the limits are between minus infinity to plus infinity. That will be get reverse. So that minus sign will come from there.

So for now we will just write the absolute result. Is it complete? I am not missing any h, 2 pie those are the things I always miss while writing an expression. This is complete? Okay.

Now what we will do is we will start from here. This is our starting point for today. And don't forget we are only talking about an absorption process. This kind of situation. Okay. So what I want to do now is I want to find what is Cm [Indiscernible] [00:07:19] multiplied by Cm because as you know naught square of the coefficient gives you the probability. Probability of that wave function in the combined wave function. If you have any doubt about that with this [Indiscernible] [00:07:36] sheets that I am going to share today it is worth. You can have a look at that. Okay. Well I forgot this. So what I will do is I will simplify this a little bit. Let me write A is equal to Em minus El minus hµ. I will simplify a little bit. Multiplied by pie by h into t. why did I write this change expression all of a sudden because the change expression is there. I have tried to simplify this exponential term. It is just that I have not – I have let the two outside and I have left I outside. Except for that see pie by h multiplied by Em minus El minus hµ divided by 2. Yes. Okay. That's all. I am going to write it in terms of A. Nothing else.

Now why have I left the two outside and why [Indiscernible] [00:09:00] taken two inside. I have written the two outside because I have the benefit of hindsight. We are not the first ones in the world to be working this out today. It has been worked out not 100 maybe 80-90 years ago. So we already know that if we leave the two outside our next step is going to be little simpler. Otherwise you could have just taken it. It doesn't matter. So what we will do is what is the denominator then? What is the denominator? Em minus El minus h µ that will be equal to hA divided by pie t isn't it? HA divided by pie t. So what I will do is I will write this expression as hA [Indiscernible] [00:09:55] A here I might write pie by ht somewhere here. Okay. understand what's going on? I am just writing this in terms of A nothing else. What is the numerator? Instead of 1 minus exponential all this what can I write? 1 minus e to the power A upto A, 2A. 2Y so this becomes much smaller. This becomes 1 minus e to the power 2iA divided by A. So first so good. Okay. clear. Now what do I want? In fact I will need this later on anyway. So let me write something else also. And let me put it here in the recap section. What is d μ? d μ in terms of I will need dA later on very soon I have to integrate over μ. So it makes sense to write these d μ and dA that expression also. So I may write like this. DA is equal to minus pie t d μ. Is that right? Right? Where is h? H and h will cancel. H and h cancels, isn't it. This h and this h they will cancel. Okay.

In fact, I have written it in a little, I will write it here. I want to keep that portion of the board. [Indiscernible] [00:11:53] A is equal to pie by h Em minus El minus h μ t. Now we have a clean expression.

Now what I want to write is Cn star into Cn what is that? Of course, let's do the easy part first. Well everything is easy here. Y square t square by h square then multiply buy square of the transition moment integral divided by A square. Don't forget we have a complex number here. So we have to multiply it by its complex conjugate. So 1 minus e to the power 2iA multiplied by 1 minus e to the power minus 2iA. That turns out to be pie square t square h square. In fact what we have written already has load of information but let us just complete it and we will discuss once. [Indiscernible] [00:13:24] what is that? T is not square. Why? And where is X? What are you saying. T or Ex 0. Ex square is what I missed here right. This already has some very important information but let's wait a little bit. Let's just get done with that little bit of math and then we will talk about it. pie square t square by h square multiplied by Ex0 whole square. Square of transition moment integral multiplied by well divided by A square 1 then this into this is what? Minus e to the power 2iA multiplied by minus e to the power minus 2iA that is plus 1 right. Right? Minus into minus is minus and then sorry minus into minus is plus unless you are education minister in some Indian state. And then you have plus 1 anyway.

Okay. Then minus e to the power maybe I will write it in bracket for our so that we see it better. E to the power 2iA plus e to the power minus 2iA. Write it a little bit simpler pie square, t square by h square Ex0 square, square of transition moment integral. Why have I written [Indiscernible] [00:15:16] plus 2 into 1 minus what is this e to the power 2iA plus e to the power minus 2iA? 2 cos 2A right. So I will take that two outside and write 1 minus cos2A divided by A square. Everybody know what 1 minus cos2A is. What is it? What I always remember is cos square A minus sin square A but then cos square A is 1 minus sin square A. So what will it be? 1 minus 1 sin square A. Right or wrong? Any doubt about that? So what I will do is instead of minus cos2A I will write 1 minus 2sin square A. Now the numerator has been cleaned up very nicely. 1 minus 1 that is 0. So you are left with pie square, t square by h square Ex0 whole square square of your transition moment integral multiplied by maybe I will write 4 here. Is that right? Is the expression correct? Is it okay. 4 pie square t square divided by 4 square into Ex0 square multiplied by transition moment integral. Yeah sin square A divided by A square, yeah this is right.

Now what is this? This is probability of transition. Yes.

Student: [Indiscernible] [00:17:28]

Anindya Datta: Why do we say probability [Indiscernible] [00:17:33]

Student: [Indiscernible] [00:17:33]

Anindya Datta: Hold down I am coming to the integration. Now let us discuss this expression in a little more detail. What do we see here? First of all you see that probability of transition is proportional to square of transition moment integral. We have been saying all along that if transition moment integral is equal to 0 then the probability is – then the transition is not allowed. Now we have a little more quantitative way of saying the same thing. We can say that probability of transition is actually equal to square of transition moment integral. Alright.

Now if I go back to those classes on experiments that we had initially. We are talking about absorption. For absorption what is the experimental parameter of probability of transition. Experiment. What we are doing now is theory. Remember Spectroscopy after all is an experimental science. And if you remember the initial discussion we had in this course we talked about this time domain measurement, frequency domain measurement and we had talked about an empirical law that everybody knows. Beer–Lambert's law right. So from Beer–Lambert's law what can you say is the measure of probability of transition. Epsilon right. Absorption is equal to epsilon Cl. Now see what is C? C is concentration. That's an intrinsic parameter. Good force. Increase the concentration absorption increases. Length is an intrinsic quantity. Increasing the length that means your light encounters more molecules in its path. That's all. But if you talk about one molecule and you think of [Indiscernible] [00:19:40] transition epsilon is the parameter.

So now what we learned is that that epsilon that we talked about initially must have some relationship with square of transition moment integral and that is what we are going to learn in the next class. Not today. We will actually write down an expression which relates epsilon absorption coefficient and transition moment integral square. [Indiscernible] [00:20:06] that story for another day. What we learn for now is that probability of transition is directly proportional to square of transition moment integral. Where does the square of transition moment integral come from? Which part of the wave function? Special or temporal? Special. What is it that we get from the temporal part of the wave function. This is constant. This is the special part. Where is the temporal part? This t square multiplied by sin square A by A square. Remember the sin square A by A square came from all these exponential terms. Where did the exponential terms come from? From the phase. From this e to the power I something t that kind of a part of the wave function. So that time dependent part of the wave function. So the special part gives us this probability fine. But the transition – what the time dependent part tells us is that it is Sin square A divided by A square. If I plot Sin square A by A square what do I get.

Yeah so sin A into Sin A I am not sure how to Sin square. We get this kind of a function. In fact if you plug in the numbers you will see that the width is not too much. But there is a finite width nevertheless. So from the time dependent part of the wave function we learned that even for – don't forget what kind of a system it is. This is a system. Two states. L and M. We don't have many states. We only have two states. We are not accounted for any sub-levels or such thing. Even when you have a pure two state system what we get from the time dependent part is that you can never get a delta function. You know what delta function is. A function that has some value for one particular value of the independent variable and it is 0 for all other values. So you will never have a delta function. You will never have a line with 0 width. That is the line shape that you always get even if you neglect all other line [Indiscernible] [00:22:14]. This line width that you get from here is called the natural line width. Natural line width. No matter what you do you cannot change the wave function so it is the wave function that tells you that you are going to have at least this kind of a line shape at least this amount of line width in this [Indiscernible] [00:22:35]. This is something that is in my opinion a very very important observation. Yes?

Student: [Indiscernible] [00:22:46]

Anindya Datta: Square is also there of course but then when I taught this I only did Sin square A but you can multiply that by t square. It doesn't matter. So if you just increase t square okay, well that is another aspect of the story. If you increase t square what will happen? It will just be more. C star Cm will be more. The whole function get multiplied by what amount of time it is. So that is the third important thing that we learn from here. If you keep the perturbation longer you get a greater mixing of space. You will get a greater amount of transition. But before going there do you understand this? Where does this come from? The time dependent part.

Now it is actually a direct consequence of uncertainty principle. Uncertainty principle you know delta into delta t that has to have some value. Now what happens is this if this is your system when you have two states, the ground state has lifetime of infinity. If you don't disturb the system it will be in the ground state forever. But excited state doesn't have an infinite lifetime. It has a finite lifetime. If you promote the molecule to excited state what will happen is that it has to come back sooner or later. The average time it spends in the excited state is called the lifetime.

So now see what is the uncertainty in time associated with the ground state? It can actually be infinity because it's always there if you don't disturb it. What is the maximum allowed uncertainty associated with the excited state? That cannot be more than the lifetime, isn't it? If I say my height is five feet plus minus 30 feet. Does that make any sense? If I say my height is five feet plus minus five feet that also doesn't make sense unless I am a quantum mechanical object. We are dealing with quantum mechanical objects here so maximum allowed uncertainty is of the same model as what the value is.

So always there is an uncertainty in time and that brings in a uncertainty in energy as well. So what I have drawn is one line is really an [Indiscernible] [00:25:09] states with small maybe but finite distribution of energy. So correct picture here really is something like this. There is an uncertainty in energy of the excited state that is what brings in natural line width. Are we clear so far because what we have discussed so far is actually profound. Are we clear? Any question? Can I go ahead?

Let's do that. Now if this is the case, then when I want to talk about the probability of transition I am faced with the dilemma. What do I define as the probability of transition? I can say it is a probability here. But then in that case I will be neglecting this and this and this and that. Even if you come here there is a small but finite probability, isn't it? So the correct way of handling this is to talk about a probability that as somebody was saying that is integrated over the bend. If I integrate it then the probability that I get is the probability of that transition. Once again, let us be very very careful here. The reason why I want to be careful is that you have done experiments in electronic spectroscopy and you are associated with broad bands. When you do [Indiscernible] [00:26:46] measurement don't you get a broad band? We are not talking about that kind of a broad band. That broad band arises because there are actually many states. It is not two state system at all. That's a different issue altogether. We are talking about the situation where there is no other line [Indiscernible] broadening mechanism. We have two states. Whatever uncertainty in energy is there, that is the only contributed to the line width.

In that case what we talk about then is we should talk about a probability that is integrated over the band. For the records let me say once again that this line width is not too much. It is small or it is not [Indiscernible] [00:27:22].

Okay. Yes.

Student: [Indiscernible] [00:27:26]

Anindya Datta: Yes.

Student: [Indiscernible] [00:27:34]

Anindya Datta: So it signifies the periodicity of comparatively higher probability of transition to some state. So as I said there is a distribution of states. But then the thing is the distribution comes out of the periodic function. So that's why the probability is also periodic. Whereas some transition which have a little higher probability for example this transition has a little higher probability than this one. And definitely higher probability than this one but it dies off with it. So this arises out of the periodic nature of the wave function itself. Can I go ahead? Great.

Now I am going to need this. What we want to talk about then let me define this probability of transition, I will write it as P l to m as integral Cm*Cm d μ. That is the integral – that probability integrated over the band. Don't forget the band is for a single l to m transition. What will it be? That will be equal to – I will just write the constants outside and integration is our μ so I take Ps constant. That's not a problem. But what I have to do is I have to since this thing is written in terms of A instead of d μ I will write this. This d μ becomes minus pie t into dA. Minus dA by pie t and what I will do is I will neglect this minus also. We have not ignored minus earlier, isn't it. Remember we got a minus and that is where – that is this is the reason of the deviation we had from the textbook. They have not written any of the minus signs. Since we have followed that convention and omitted the minus sign earlier I will omit this one as well. So this I will write as dA by pie t then this becomes this is what it is 4 pie square by pie so this is the pie t square by t so this is t divided by h square into Ex0 whole square square of transition moment integral. Have I written everything? Integral sin square A divided by A square dA. What are the limits of the integral? Minus infinity to plus infinity. Minus infinity to plus infinity considering there is no other transition. Okay that doesn't matter anyway.

Is it okay? Done? Sure?

Now what is the next step? Next step is work out the integral. What we will do is we will do the standard integral. This minus infinity to plus infinity integral we will look up a table and that table will tell us that this value is actually pie. Minus infinity to plus infinity is a standard integral right. Sin square by A square that turns out to be pie. So then what does it become? That is a pie so this becomes 4 pie square t divided by h square multiplied by Ex0 square maybe I will write this t here at the end. Multiplied by square of the transition moment integral. Yes.

Student: [Indiscernible] [00:32:04]

Anindya Datta: Yes. That's right. But now we will deviate from there. We have considered it at a time t at particular time t after perturbation. So we don't have to integrate over it. Now the thing is this this is the [Indiscernible] [00:32:23] step of what we are trying to get. The ultimate step is we are talking about intensity. Remember when we talked about the experimental part of the spectroscopy we are talking about intensity of [Indiscernible] [00:32:35] intensity of emission. What is the definition of intensity?

Student: [Indiscernible] [00:32:44]

Anindya Datta: It's not high probability or anything. I said intensity. I didn't say high intensity or low intensity. Last bench. What is the definition of intensity?

Student: [Indiscernible] [00:32:55]

Anindya Datta: Answer has come from third bench. Anyway but at least we have your attention. You are right. Per unit time. It's basically rate. It's a rate. So what we will do is we will convert this to per unit time as well and we write it as dP l to m dt is equal to 4 pie square divided by h square Ex0 whole square transition moment integral square that's it. This is your expression for rate of transition. Will you agree with me that this rate of transition is the one that is directly correlated with intensity of absorption? Intensity of light absorbed. Rate of transition. So the part second is already there.

Okay. Now let us write it in [Indiscernible] [00:34:00] of something else [Indiscernible] [00:34:04] two substitution in this expression. First is so far we have been working with µ x. now it is time that we write it in terms of µ. So for an isotropic radiation. For what happens is that you can just write µ x as µ divided by 3. So I can write that as µ by 3 that will take us a little closer to the expression that we are trying to get and this is the general expression for transition moment integral, don't forget. And we will do another thing generally when you talk about light of course this is something that you are – unless you have taken a course in optics this is one part where you will have to just believe me what I am going to say right now. What we generally want to work with when you talk about light is not Ex0 but this. Rho of µ. Have you encountered rho of µ somewhere? Yeah? Never? Rho of µ is energy density. Yes black body radiation. So in black body radiation [Indiscernible] [00:35:19] so when we talked about [Indiscernible] [00:35:21] law and all that rho µ. Rho of µ is something that is more familiar and now you just have to believe me that in the system that we are using here it is equal to Ex0 square divided by 2 pie.

Of course in the exam I have to give it to you. I cannot just expect you to remember this. So let us substitute that also. I will write rho of µ here. And I will divide it by 2 pie so this becomes a 2, this becomes a pie. 2 pie divided by 3 h square. Is this right? I am going wrong somewhere. Where did I go wrong? So what should I write in place of Ex0 square? I should write 2 pie right. So actually 2 pie goes here. 8 pie. 8 pie cube divided by 3 h square. I made silly mistake that's all. Rho of µ equal to Ex0 square by 2 pie. So you substitute Ex0. So Ex0 square has to be substituted by 2 pie into rho µ and that's what you get. So this is a rather important equation, rather important rule you can say, it is called Fermi's golden rule. And as I think I have told you earlier Fermi's golden rule was not derived by [Indiscernible] [00:37:29] and said oh man it's such a great rule. It's a golden rule. And then it took the name Fermi's golden rule.

Now why is it that Fermi was so impressed when he saw this? Does it look impressive? It doesn't. It's like any other expression. So why is it golden rule? It's a golden rule because first of all it brings in an idea of [Indiscernible] [00:37:56]. It's a rate on the left hand side. Secondly if you look at the right hand side you have a constant multiplied by an intrinsic quantity probability. Intrinsic quantity here multiplied by an extrinsic quantity. Energy density of light. And that kind of opens up the field where we can discuss lot of things now. That's why it's called a golden rule. And it's important to remember that. This Fermi's golden rule essentially is an expression of the rate of transition as a product of two factors one which is intrinsic to the system, the transition moment integral square and the other that is actually a property of the I was little wrong there. A property of light [Indiscernible] [00:38:52]. So now you can model this transition like a chemical system that molecules react. You can think that this is one kind of concentration which is related to concentration of – which is related to the system. This another kind of concentration energy density. So kind of concentration of photons you can think. So now that opens up the possibility of expressing this radiation matter interaction as a sort of bi-molecular reaction between molecule and light. Matter and light. And whenever we have that then we [Indiscernible] [00:39:42] because this is then if you look at it carefully it's like a rate equation, rate of reaction, rate equation of you can say second [Indiscernible] [00:39:52]. It's something like you are familiar with this kind of a reaction, say A plus B forms product it is not necessary that the rate will also always be a concentration of A and multiplied by concentration of B but suppose it is then what is it? Then you can write dp/dt is equal to some constant K multiplied by concentration of A multiplied by concentration of B which is exactly similar in form to your Fermi's golden rule. So Fermi's golden rule now lets us move towards the territory where you can do some very easy kinetic treatment and get some idea about the transition. And that is what Eisenstein did.

What Eisenstein did is that he set up this kinetic treatment of the two body problem. He considered two levels like what we have done. He considered that there are three possibilities actually. One is induced absorption. One is induce emission. I hope you have not forgotten that when we talk about emission so far it is always induced emission because light is involved. Third thing that is not something we have considered so far is spontaneous emission. Actually we are more comfortable with the idea of spontaneous emission because we know about nuclear decays and all. You leave something in excited state it just decays by itself. It doesn't need any help from anything. But then in the treatment that we have done so far spontaneous emission has not come at all. So what Eisenstein did was that he kind of used this as one of the terms and he setup a rate equation involving two states. First term was for absorption, population of the excited state by absorption. Second term was for de-population of the excited state by stimulated emission. Third term was the de-population of excited state by spontaneous emission. So the first two terms are you can say of second order. Third term is first order. And hence he took us to an interesting discussion of when do you have stimulated emission, when do you have spontaneous emission as the measure radiative deactivation pathway. And that eventually takes us to a very useful discussion of lasers and lasers spectroscopy. So tomorrow we are going to at least begin with Einstein kinetic treatment and then let's see where we get.