Quantum Mechanics and Molecular Spectroscopy

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Lecture – 21
Spontaneous Emission Lifetime

Hello, welcome to the lecture number 21 of the course quantum mechanics and molecular spectroscopy. We will have a quick recap of the previous lecture and proceed with the present lecture. In the last lecture, I was talking about rates of emission and absorption and their coefficients okay.

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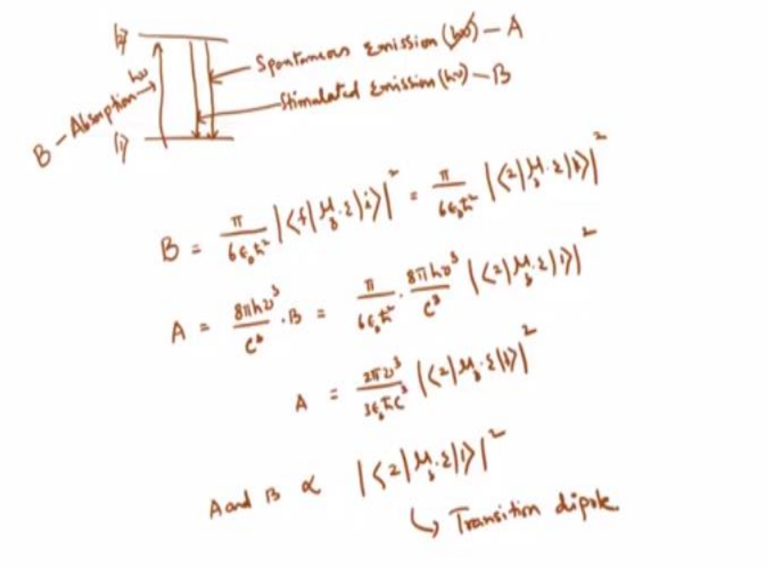

$$B = \frac{\pi}{6\epsilon_0\hbar^2}\left|\langle f|\mu_z \cdot E_z|i\rangle\right|^2 = \frac{\pi}{6\epsilon_0\hbar^2}\left|\langle 2|\mu_z \cdot E_z|1\rangle\right|^2$$

$$A = \frac{8\pi h\nu^3}{c^3} \cdot B = \frac{\pi}{6\epsilon_0\hbar^2} \cdot \frac{8\pi h\nu^3}{c^3}\left|\langle 2|\mu_z \cdot E_z|1\rangle\right|^2$$

$$A = \frac{2\pi\nu^3}{3\epsilon_0\hbar c^3}\left|\langle 2|\mu_z \cdot E_z|1\rangle\right|^2$$

$$A \text{ and } B \propto \left|\langle 2|\mu_z \cdot E_z|1\rangle\right|^2$$

↳ Transition dipole

So when you have state 1 and 2 okay, there is an absorption and absorption happens in the presence of a h nu and there are 2 kinds of emission okay, one that happens in the presence of h nu is called stimulated emission okay, one this happens in presence of h nu and there is a spontaneous emission which happens in the absence of h nu okay. Now we have the coefficients or rate constants and this is called B, this is also called B and this is A.

And using our transition moment integral or transition dipole moment, we figured out the relationship between A, B and also A and the transition moment integral. So the final equations that we came in the last lecture was a B = pi by 6 epsilon 0 h bar square transition moment integral f mu mu z dot electric field along the z axis i or this could square or equivalently one could write pi 6 epsilon 0 h bar square 2 mu z.

Along the electric field of 1 whole square and A was nothing but 8 pi h nu cube C cube into B. So this will turn out to be pi by 6 epsilon 0 h bar square into 8 pi h nu cube by C cube into 2 mu z along some electric vector 1 whole square. Now this is nothing but 2 pi nu cube divided by 3 epsilon 0 h bar C cube mod plus of 2 mu z electric field vector 1 whole square, so which is A.

Now we also said that both A and B are proportional to this transition dipole okay. Now one of the most interesting point of spectroscopy using this methodology is that you can get both A and B theoretically as well as experimentally okay. One can measure A and B experimentally and calculate theoretically and one can compare okay the experiment and theory and that is a real test of quantum mechanics okay.

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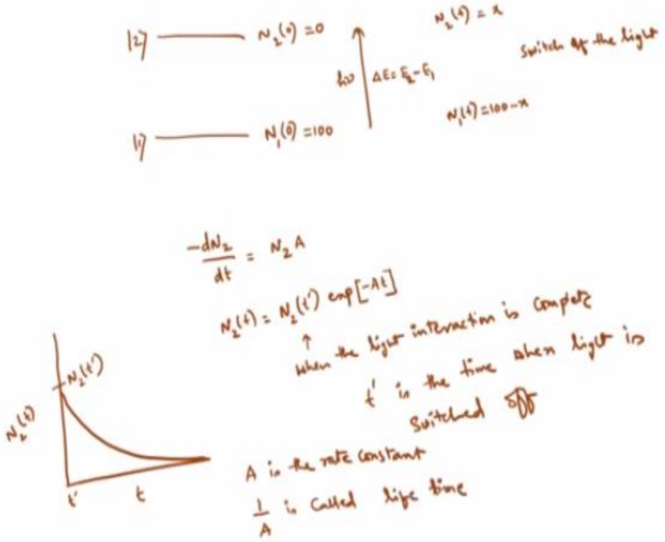

Now for example let us suppose there are 2 states 1 and 2, initially the population of N 1 at time t = 0 okay, something I do not know, some value and there is N 2 at time t = 0, but if you start with a separation of very large separation of 1 and 2, then you can see that N 2 0 will be equal to 0 and let us call this as 100% okay and 0% something like that okay and then what you do is you shine light, at some point of time you shine light h nu corresponding to delta E that is equal to E 2 – E 1.

Then what will happen? It will transfer some population okay, let us say some population x percent has been moved to the excite state, so what you get is at time t, this will be 100 - x and N 2 of t will be equal to x okay. Now after that you switch off the light. Now of course, the molecules will not be able to stay there in N 2 for all the while because thermodynamically N 1 is the most stable state.

So the molecules must return to N 1 state. So the kinetics of that will be -dN 2 by dt is going to be proportional to N 2 and this is happening in the absence of any light, so the proportionality constant must be equal to the A coefficient, so that is A okay. So, I can rewrite this equation okay and it turns out that N 2 of t, it is a simple first order differential equation which you can solve and you get that N 2 of t = 0 = N 2 at, now I am going to use N 2 at t prime okay exponential -A times t.

Now what is N 2 a t prime? N 2 at t prime is actually equal to x that is when the light interaction is complete. So if you switch on the light and wait for a while and t prime is the state when you switch off the light or interaction is complete or when you switch off the light, t prime is the time when light is switched off okay. So what you will get is this equation okay. Now this is an exponential, you can see this, so what it does is the following.

So you can think of it like this time and N 2 of t, so it will have some value and then it exponentially decays okay. Now that is this value will be nothing but N 2 of t prime okay. It starts at t prime because that is when it goes to infinity and this is asymptotically going to 0 okay. Now if you have that this is a first order equation, so your rate constant will be, so A is the rate constant okay. If A is rate constants, 1 by A is called lifetime okay, we will just come to that.

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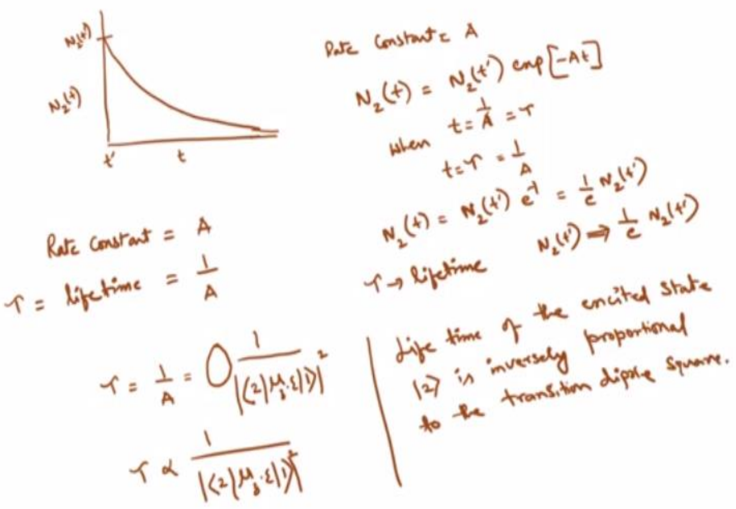

So let just look at the first order kinetics okay. So if you have a population that decays exponentially okay, so let us say this is N 2 of t versus t and this is N 2 of t prime and I am starting time at t prime okay. Now if is exponentially decay, I told you that the rate constant is equal to A and the equation is this N 2 of t = N 2 of t prime exponentials -A. Now let us assume one thing. So when t equals to say 1 by A okay, t = 1 by A and this I will call it as tau.

So, when t = tau okay, its value is 1 by A. Then what happens then you will have N 2 into t = N 2 t prime okay, this will become A into 1 by A, so that will become -1. So this will be e to the power of -1. So this is equal to 1 by A okay. So this is called lifetime. Lifetime is when, tau is called lifetime and lifetime is a time when initial population N 2 into of t prime okay decreases to 1 over e of N 2 of t prime okay.

So if you look at that so for a given exponential the lifetime is fixed, that is 1 over e okay and the rate constant in this case the rate constant is equal to A, therefore lifetime will be equal to 1 over A okay. So it is also called radiative lifetime tau, so tau now equals to 1 by A, this is equal to, now what is A equal to? A was equal to some constants multiplied by the transition moment integral or transition dipole square okay.

So some constants okay multiplied by 1 over 2 mu z1 whole square. So one can think of the radiative lifetime tau is proportional to because these are all constants 1 over 2 muz1 square okay. So what is that? So lifetime of the excited state in this case that is 2 is inversely proportional to the transition dipole square okay. So what does it really mean?

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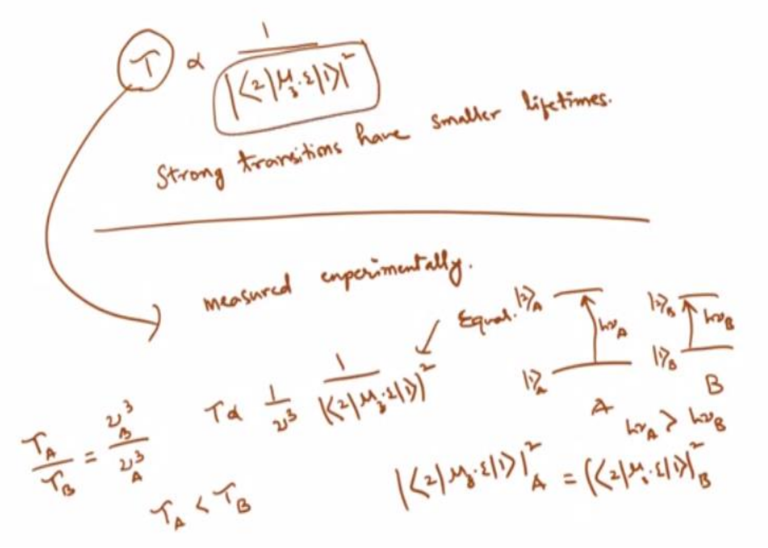

It means that if you measure the lifetime tau that is inversely proportional to 1 over 2 that means if this number is large, this number will be small. So lifetime is inversely proportional transition dipole moment. So if there is strong transitions strong transitions have smaller lifetime okay. So something absorbs very strongly will have a shorter lifetime okay. This is something that now if you quickly remember in the chemistry there is something called potassium dichromate.

It is very strongly absorbing okay because the extinction coefficient is much stronger. So if you excite potassium dichromate, it must decay much faster that is what it means okay. Now this kind of tells you that once you, but by the way the tau, this value can be independently measured, can be measured experimentally. This is measured experimentally, which means now this tau of course is multiplied by lot of constants okay.

But there is another factor that is also important is that A has this nu cube. So tau is also proportional to 1 over nu cube okay, 1 over nu cube into 2 mu z epsilon 1 square. Now if this value is equal, let us say there are 2 transitions on molecule A and molecule B such that ok so that okay, so that I will call it as 1A, 2A, 1B, 2B and you see this the way I have drawn is this, this is h nu A and this is h nu B such that h nu A is greater than h nu B.

And it so happens that this integral okay 2 mu z 1 square of A is equal to modulus of 2 mu z 1 of square of B. If the transition dipole square in both cases in A and B if they are equal okay, let us assume a scenario when these two are equal then what happens is that then your lifetime will depend on 1 over nu cube. That means larger separation; the decay will be the faster okay.

So the tau is 1 over nu cube because nu is larger in the case of A with respect to B, 1 over nu cube will be smaller. Therefore tau, so based on this one can write tau A will be smaller than tau B and the ratio of tau A to tau B will be equal to nu B cube by nu A cube okay. So, that is only when these two transition dipoles are equal. Of course if they are not equal, then it will be complex mixture of the ratio of the transition dipole squares and the nu cube okay.

So this is kind of a way one can estimate. So t tau can be experimentally measured, then depending on where you have excited what is the nu, then one can actually experimentally calculate or estimate transition dipole okay.

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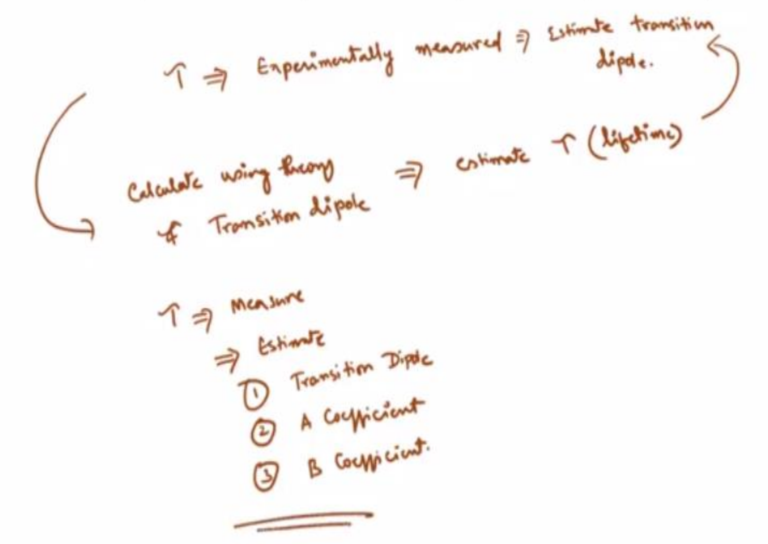

$\tau \Rightarrow$ Experimentally measured $\Rightarrow$ Estimate transition dipole.

Calculate using theory of Transition dipole $\Rightarrow$ estimate τ (lifetime)

$\tau \Rightarrow$ Measure

$\Rightarrow$ Estimate

① Transition Dipole
② A Coefficient
③ B Coefficient.

Now what I am trying to say if tau is experimentally measured, then from this one can estimate transition dipole or other way around if you can calculate using theory transition dipole, then from here one can estimate tau and then of course this tau is lifetime. So, one can go back and forth okay. If you can measure one, then you can estimate the other one or if you can calculate the transition dipole you can estimate the tau.

And one can go back and forth and see whether you have done it in a very consistent manner okay. So both experimentally and theoretically, the transition dipole and the lifetimes can be measured or estimated, so that is the connection between the transition dipole and the lifetime and this comes via the Einstein coefficient A, but once you know that Einstein coefficient A, you also know Einstein coefficient B because A and B are connected.

So, it just takes one experiment to estimate all the values okay. So if I can measure the lifetime, if I can measure tau, then I can measure, then I can estimate 1 transition dipole, 2 A coefficient, and 3 B coefficient okay. So, I am going to stop it here and we will continue in the next lecture. Thank you.