Ultrafast Processes in Chemistry
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Lecture # 16
Stimulated Emission

Ok, so now today onwards we start discussing laser basics. And laser as we know is light amplification by stimulated emission of radiation and stimulated emission of radiation is what we want to start with. So we start talking about something that is very fundamental. We have discussed it in our spectroscopy course as well. And I am sure most of you would have studied it in you are MSc curriculum at least.

But still will revise it in case first of all we need to remind ourselves and secondly in case we add any lacuna and understanding that hopefully will get sorted out now. So stimulated emission is what we want to start talking about. And the reason why we do not want to talk about lasers is that it is central to any study of ultra-fast dynamics it is central that you use a pulse laser as light source. So before we go to the pulse part of it. We should at least know our laser works, then only when we talk about how pulsing is done and all it will start making sense.

So what we are doing now is actually like the part before times zero in our transient absorption or upconversion measurement, we are going back to the very basics. And the next couple of modules of the models will be about that. And for this, actually, one can read from something as fundamental as a McQuarrie and Simons book, physical chemistry and molecular approach by McQuarrie and Simon.

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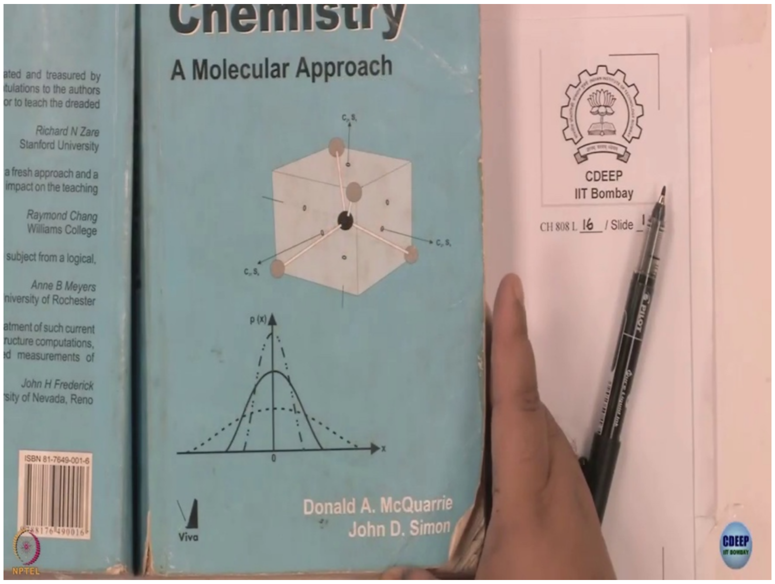

So this is a standard book for undergraduate and level MSc classes as well. The discussion here should be enough for the next couple of modules and then we move on to more sophisticated books. So what is stimulated emission those of you who have studied the interaction radiation of matter. From a quantum chemical perspective, at least a semi classical treatment of it, at least might remember that.

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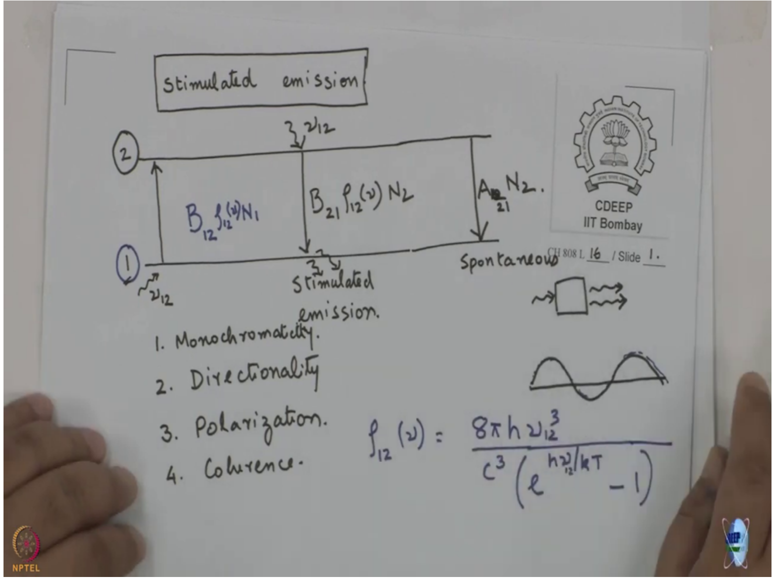

Stimulated emission

1. Monochromaticity.
2. Directionality
3. Polarization.
4. Coherence.

$$\rho_{12}(\nu) = \frac{8\pi h \nu_{12}^3}{c^3\left(e^{h\nu_{12}/kT} - 1\right)}$$

The way it was done is that you consider 2 energy levels. Let us call them 1 and 2. 1 is the lower one, 2 is the higher one. And we said we asked a question, what happens when a photon of appropriate frequency is incident on this system? Actually, 2 things can happen. What is very clear to us is this photon might come and cause an upward transition. This I think everybody understands is an absorption process. Now, what is the condition for the photon to be absorbed, it must satisfy the Bohr resonance condition $h\nu_{12}$ let us say this frequencies

I am writing 1 2, specifically because I want to highlight the fact that the frequency of the photon is such that it's energy matches exactly the energy gap between the two states involved. So, when nu(ν) 1 2 is incident photon of new ν_{12} is incident on the system, we understand very clearly that absorption is going to take place. What we might not understand to start with is that the opposite phenomenon might also be brought about by a photon.

This is an emission, but it is not an emission by itself. This is called a stimulated emission. This is absorption. Why is it that a photon would cause an emission of another photon? Because if you go back to the formulation of the problem in semi classical limits, the light here actually I should not even say photons if you I am talking in semi classical terms, because they are the molecule is model using quantum mechanics light is modeled as a wave that is where it is called a semi classical treatment in the first place.

So, let us think like this light which is a wave acts as a perturbation here, we have two energy levels, you have some population distribution between them. What light does is that it disturbs the level and causes of mixing. So, when I say mixing N 1 has to be mixed with N2 can also be mixed within N1 mixing of states in quantum mechanics is equivalent to a transition in spectroscopy. So, here when light comes and causes the transition, it can do it both ways.

To put it very qualitatively, this is stimulated emission. And this stimulated emission takes place the light that comes out a look a write like to curly arrows first of all, it is important to understand that light that came in is actually conserved and some more light comes out. Now, I have no option but to go back to photons, if 1 photon causes the transition, then 2 photons come out if there is stimulated emission.

And if there is no other loss in some other way. So, this gives you a multiplication of number of photons, this is very important to understand. And not only that, the light that comes out is correlated with the light that caused the downward transition. That is why there are several properties that are associated with light that comes out as a result of stimulated emission may not always be there for spontaneous emission.

But we are not even talked about spontaneous emission yet. So, let us see what kind of correlations there will be between light that comes out and light that goes in, a stimulating emission process. First of all, the frequency of the light that comes out exactly the same nu 1 2 right. So, you get monochromatically secondly, then this is a curious property, let us say this is your sample here light comes in from this direction.

Original light goes in goes out in this direction, the light that is that comes out as a result of stimulated emission we follow the same path. So, in stimulated emission, you get directionality unlike light that comes out from regular light sources for example, right, generally that light sources that we have or fluorescent molecules and all that we have they are going to aim it in all directions if it is spontaneous, you know, there is nothing to drive the direction.

Here, the emission is actually driven by the light that comes in the light that produces a perturbation. We are not doing the math here. But there is something called transition dipole moment. That ensures that not only is it directional, but also something else is that polarization of the light is maintained. If you put in vertically polarized like and if there is no rotation at all, then stimulated emission light that comes out is also vertically polarized. And another important property is coherence.

coherence means not only are the 2 light waves, monochromatic, monochromatic means what exactly same wavelength polarized that means the oscillations are in the same plane, that is not enough, what happens is that they are instead light that comes out as a stimulated emission is exactly in phase with the light that causes it. And these are the properties that make stimulated emission, a suitable candidate for light amplification. And obtaining lasers with the properties that we know that most lasers have.

And this is the simple formulation. But there is something else that we need to discuss here, which might sound a little off topic, but actually, it is not as you will see by the time we are done. Einstein did a kinetic treatment of this process. It was something that is obvious here is that we are not discussing the whole thing. If you only talk about induced photoinduced processes, induced absorption if you want to emphasize in this part of it induced emission or stimulated emission.

Then one thing that you are definitely leaving out is spontaneous emission. But Einstein said that that is not practical, because spontaneous emission does take place, we see it all the time all around us, we cannot say that only stimulated emission takes place, even though in realm of semi classical treatment using time dependent perturbation theory, you only consider induced processes induced absorption induced emission.

So, what Einstein did was that he brought in this thought process, which might actually be more obvious to us than stimulated emission, he brought in spontaneous emission. So, the way I have drawn it here, in the way that I have drawn a spontaneous emission is stimulated emission, actually at the same wavelength, because I have only 2 energy levels and nothing else, but properties that will not be seen stimulated in spontaneous evolution, what will be seen in a stimulated emission are those that we have written here 234.

Of course, this is a discussion that was performed several decades ago. Nowadays people are working on how to get directional spontaneous emission. So, if you read work by Lakowicz, they have made some progress in it. There is something called I just told you that for amplification stimulated emission is a good candidate, but actually we are going to discuss later when you try to make a laser and try to get amplification of spontaneous emission.

One big problem that shows up is ASE. And again that term ASE might be a little confusing because ASE is there in laser as well. You just take out the L and take out the R what you are left with is ASE, but when we say ASE generally we mean amplification of spontaneous emission actually we have to kill amplification of spontaneous emission, if you are going to get a good laser, if you work with homemade lasers.

And if you try to actually get the lasing done, their ASE can turn out to be a threat. And the reason why it can turn out to be a threat will come too shortly, but let us do Einstein is formulation here.

What Einstein did was a very simplistic kinetic formulation all of us have studied chemical kinetics, I hope at least in 11 and 12 so, there what we know is we know how to write differential equations. What is it what is read it is something like dx dt.

So we will write the rate equation and to start with will not even write the dx dt part will only write with w the right hand side without w will only write the RHS. So, let us say, we consider the first process absorption. See, absorption is sort of like an element biomolecular reaction. You can think it is a reaction between a photon and molecule. So if it is biomolecular, then it is rate will depend on the product of concentration of the molecule in state 1 and concentration of light.

So what will the rate of upward transition be? It will be N1 where what is N1? N1 is the population, one rather the number of molecules in state 1, multiplied by 2 multiplied by concentration of photons. That is usually given by something called energy density. I will write it like this. Rho 1, 2 nu. It is a little bit of an overall here, because the moment I say nu, it appears that 1 2 is taken care of actually it is not energy density rho.

Everybody knows its density, just to emphasize that it is a density of energy and not of matter. We write nu in brackets and one two subscript is there to denote what is the energy gap ok is there any other thing here for the rate concentrations of both taken care of concentration of light concentration of molecule, the only thing that is left is the rate constant. And Einstein for whatever reason wrote this rate constant has B I can write 1 2.

So, B12 is the rate constant for absorption, it is called Einstein is B coefficient, where what we can come to that later rhw 2 3 nu is the energy density. Can anybody does anybody remember where we encountered energy density in some very highly celebrated blackbody radiation, right? The blackbody radiation we had studied energy density and there is an expression for it right? From Planck theory.

So, I like that expression here so that we can use Later on the next question is and also you might want to write it down because this is going to be useful I can write like this row 1 2 of nu is equal to 8 pi h by C cube nu 1 2 cube e to the power divided by e to the power h nu by KT, this K is not rate constant, this k is Boltzmann constant - 1 this expression for energy density is going to come extremely handy in the next 5-10 minutes.

So, this is energy density that is known, number of molecules in state 1 is N1 and the rate constant is beyond 2. So, this is the rate of formation of from N2 from N1 rate of absorption What about this process again and now I can start writing from the beginning because we know basically what it is again, it is sort of a biomolecular reaction between energy and matter. So there will be some rate constant.

And again I will write B and this time this is the 1 2 I write 2 1 of course I will have rho 1 2 nu there is no point in writing rho 2 1 nu because energy density or particular frequency will be the same with that is a property of light actually, and then multiplied by N2 or N1 N2 what is N2 is the number of molecules in state 2. Now, what about this spontaneous emission process? That is like an elementary unimolecular reaction.

Because no light is there molecule has been excited fine, but it has been excited by the absorption process. When it emits it emits on its own, so here, the only quantity that will be important is N2 and the rate constant here is written as A12 Einstein's coefficient for spontaneous emission. So here we have three Einstein's coefficient, A12 is Einstein's coefficient of spontaneous ambition. A21, as you will see in a while, it will not matter.

A12 is Einstein's coefficient of spontaneous emission B21 is Einstein's coefficient of stimulated emission, B12 is Einstein's coefficient of you can see stimulated absorption. So this is the formulation of Einstein problem. Now, we will go and actually write the rate equation, but again, we are going to use something that we have studied in chemical kinetics. And that is a steady state approximation.

Remember steady state approximation when you have something like a reactant going to a product P through an intermediate I, what is steady state approximation? D[i] / dt = 0 I in third bracket, of course, concentration of the intermediate is 0. Now, what will happen? How do you get that concentration equal to 0? Because what you say essentially is that the rate of formation is equal to the rate of well.

Deformation would sound strange rate of breakdown. So, here we can say that its steady state rate of formation of 2 = rate of depopulation of 2, which means B12 row 1 2 of nu into N1 should be equal to a sum of B21 row 1 2 nu, into N2 multiplied by, + inside brackets, A21 N2. Let me write it. What I am saying is at steady state that d N2 dt = 0.

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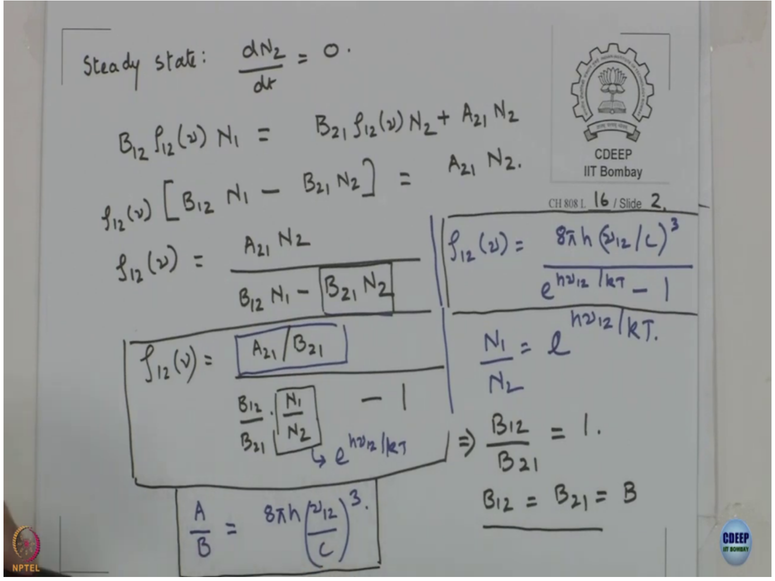

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Steady state: $\frac{dN_2}{dt} = 0.$

$$B_{12}\rho_{12}(\nu) N_1 = B_{21}\rho_{12}(\nu) N_2 + A_{21} N_2$$

$$\rho_{12}(\nu)\left[B_{12} N_1 - B_{21} N_2\right] = A_{21} N_2.$$

$$\rho_{12}(\nu) = \frac{A_{21} N_2}{B_{12} N_1 - \boxed{B_{21} N_2}}$$

$$\rho_{12}(\nu) = \frac{\boxed{A_{21}/B_{21}}}{\frac{B_{12}}{B_{21}} \cdot \underbrace{\boxed{\frac{N_1}{N_2}}}_{\hookrightarrow e^{h\nu_{12}/kT}} - 1}$$

$$\boxed{\frac{A}{B} = 8\pi h\left(\frac{\nu_{12}}{c}\right)^3.}$$

$$\rho_{12}(\nu) = \frac{8\pi h(\nu_{12}/c)^3}{e^{h\nu_{12}/kT} - 1}$$

$$\frac{N_1}{N_2} = e^{h\nu_{12}/kT.}$$

$$\Rightarrow \frac{B_{12}}{B_{21}} = 1.$$

$$B_{12} = B_{21} = B$$

Now let me write the expression for dN2/dt. B12 rho 1 2 of nu N1. Then I should write if I am going to follow from here I should write – B21 row 1 2 of nu N2 – A21 N2 = 0. I stepped jump a little bit and write something like this. B12 row 2 row 1 2 nu into N1 = B21 row 1 2 of nu multiplied by N2 + A21 into N2 clear. Now, we go ahead try to find a solution for this 1 will try to find a solution means what we will do is we already know the expression for rho 12 right. We will try to find the expression for rho 1 2 and from there, we will try to get an idea of what A is and what B is to the maximum extent possible.

So what I want to do is I want to collect the terms in rho 1 2. So whatever is there in the 1 2 we can bring 2 left hand side so let us proceed. Rho 1 2 of nu multiplied by B12 N1 – B21 N2 = A21 N2 simple. So write, row 1 2 nu = A21 N2 by B12 N1 – B21 N2 is this correct. Now is a good time to write the other expression once again and start comparing what was Planck’s expression Rho 1 2 at nu = 8 by h nu 1 2 by C whole cube divided by e to the power h 1 2 by KT - 1.

So what we will try to do is I will try to write this expression in black in such a way that will look more or less like the expression in blue. And then we will just compare the terms. How do I do that? Second term has to be 1 - is already there. How do I get second term = 1, if I just divide numerator and denominator by the second term? Then I will get 1. So that is a good seems to be a good starting point. So I can write A21.

Well, N2 by N2 = 1 so I will not write that divided by B21. That is what I have in the numerator. What I am doing I am dividing numerator as well as denominator by this and in the denominator I know the second term is very easy that is - 1, what is the first term? First term is B12 by B21 multiplied by N1 by N2. Now see, we have 2 energy levels, 1 is lower and energy lower energy 2 is higher in energy.

So, we actually know what this N1 by N2 is, do not we. Boltzmann distribution, what does N1 by N2? Remember N1 is lower energy N2 N1 is the population of lower energy level, increase the population of higher energy level. So it will be e to the power h nu12 divided by KT. We are more used to writing the higher energy 1 in the numerator that is why you get e to the power - h nu by KT here we have written the lower energy population at the top so and then you see it is falling unfolding in front of your eyes.

This N1 by N2 turns out to e to the power h nu 1 2 divided by KT. Now compare this expression with this expression what is the first thing we get? First thing we get is that this B12 by B21 has to be = 0. So let us to get the right denominator. So first thing we learn is one so decide B12 by B21 ye if it is 0 then we can go home = 1 or I can write like this, B12 = B21, I do not need 1 or 2 anymore I can just write it as B.

So, this is your Einstein coefficient and the messages carries after such a simple exercise is profound. What you are saying is that for an induced process, for a given two two level system, rate constants for the upward and downward processes are actually the same. And this is something it can remind you of what we have discussed earlier. Remember we had said sometime that you are quantum yield Fluoresence quantum field is related to epsilon right epsilon is something that you measure from absorption spectrum.

So, and that is an intrinsic quantity it has got to do with probability of transition from lower state to higher state emission quantum yield talks about probability of transition from higher state to lower state. I hope you are not forgotten that we had said these 2 are correlated. If epsilon is high for a molecule, then quantum yield is also expected to be high. The reason why I say expected to be and not is will come to that shortly. But do you understand that they are expected to be high why because of this because B12 and B21 rate constants.

They essentially are measures of probability of transition from 1 to 2 and from 2 to 1. So what we are saying is for induced processes, the probabilities are the same, no matter whether it is an upward transition or downward transition. That is why your emission quantum field and epsilon should be correlated and not seeing equal correlated proportion. Has everybody understood? Is everybody comfortable with this? I am not comfortable. Because, if you remember, all the emission that we have talked about earlier, is spontaneous emission.

And what we have shown here is that b12 = B21 here the process of emission that we are talking about this stimulated emission. So if I am going to say what I just said, then I better establish some kind of a linear relationship between stimulated emission and spontaneous emission as well. Of course for that, I do not have to go very far. It is right there in front of our eyes. Look at the numerator here, look at the numerator here.

What you see from here is, now there is no need to write 1 and 2, so I will just write A. So I see that A by B is = 8 by h nu 1 2 I will keep by C whole cube. So A is actually proportional to B. So it is if I am talking about spontaneous emission as well, because after all, spontaneous emission, well rate constant of spontaneous emission Einstein’s A coefficient varies linearly with Einstein’s B coefficient, so there is no problem. Well, there is more that we want to say about this A and B business. But let us do that in the next video.