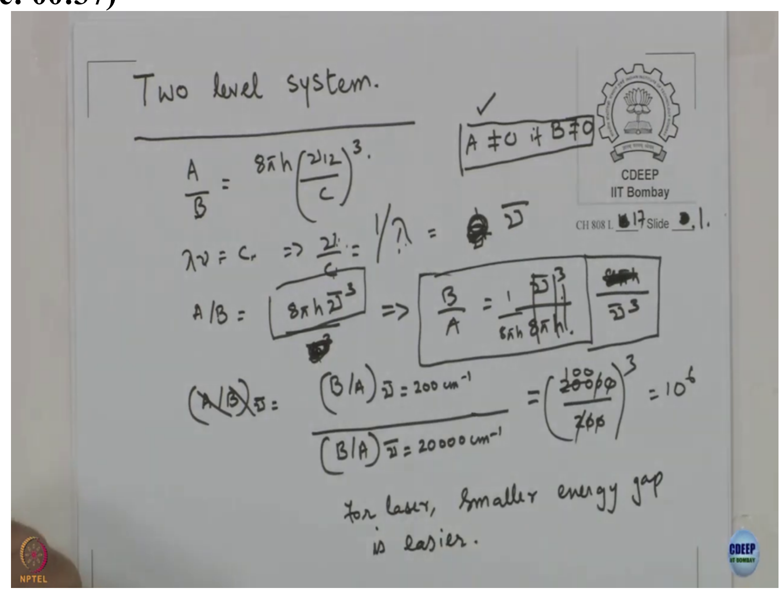
Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture No. 17
Two Level System

So now we want to continue our discussion on 2 levels systems. But what we would like to do is, well, we are continuing the discussion so there is no but anyway, we will go back and write down the expression that we had arrived at the end of the last module.

(Refer Slide Time: 00:37)



And that is A / B will be equal to 8 pi h nu 12 divided by C whole cube. What does nu 12 stand for once again? The frequency nu 12, what does it denote? It depens on the energy gap so from this expression, what can we say about the relative propensity? I do not want to use the term probability now, relative propensity of spontaneous emission and you are stimulated emission.

First thing that we have to recognize is that A is never equal to 0. If B is not 0 very simple. There is A some constant multiplied by B and that constant is not 0. So if B is not 0, then it cannot be 0. And B is zero then what does it mean? That means even absorption will not take place. We just proved that B is the same no matter whether it is absorption or stimulated emission. So that means if B zero the transition is forbidden, in our spectroscopy course because we have worked out the relationship between Einstein's B coefficient and the square of transition moment integral. So that is equal to 0.

So transition is not even there, if transition is not there, what are we talking about? So in all this discussion, we talk about situations where at least B is not equal to zero, is it a B to zero then again we can go home. So that is the first thing sounds very simple. But actually, this is what vindicates Einstein treatment. It is important and this is something that is going to come handy in our discussion towards the end of this module. A is never equal to 0, if B is not zero, seemingly simple, straightforward, might seem obvious.

But extremely important profound second thing is this is A / B ratio. When is A / B ratio more when is A / B less on the right hand side will eight is a number pi is h is a constant c is a constant nu 12 is the only thing that you have any control. So, if nu 12 is large, then A/B ratio is large. That means spontaneous emission takes preference over stimulated emission. So, now see, you remember when you want to make a laser, you want to you want stimulated emission to happen.

Not spontaneous emission, so if energy gap is very large, then spontaneous emission is favourable. So that is not a happy situation for making a laser that is important to understand. So smaller the energy gap. Better is it is if you are talking about making a laser, and that is why the first laser that was ever made was actually a maser. Not measure, what is laser instead of light, it is microwave that is all microwave, and first laser that was made was in microwave domain.

And that is where nonlinear optics become very important, because in most of our applications, as we discussed already, you want blue laser, you want ultraviolet laser, and you cannot make them. So your only hope is to somehow make a laser in infrared. And keep on adding those photons performing second harmonic generation third harmonic generation or fourth hermonic generation, sum frequency generation produce the light produce light of frequency required.

This is important to understand smaller the energy gap, better chance it has for your spontaneous emission, and to establish this point, I want to do some calculation. And as you know in calculations I often go wrong. So you better be careful and do the calculation yourself. Before starting since I already moved once on the speed of light, I do not want to eliminate speed of light and do that what it uses lambda nu equal to C we know that.

So, nu / C is equal to lambda. So, we can substitute and write this in terms of lambda. In fact, I will go one step forward and write 1 / nu bar. For the simple reason, that I remember the wave number of microwave, I do not remember the wavelength, you can do it in whichever way you like, but the point is you can use any one of these. So, you can write A / B in terms of frequency or wavelength or wave number or whatever energy anything see, we are trying to make a laser that s is for stimulated emission.

So, if you want to make a laser, then we have to promote stimulated emission and not spontaneous emission. So, it is better to work in smaller energy gap you have said spontaneous I made a mistake again, are you clear now, sorry for confusing. Now, let us slide this here so, what I get is A / B is equal to 8 pi h divided by nu bar cube. So, if I write A / B, for some nu bar 1, so I write for, nu bar equal to, or maybe I will write it in terms of B / A.

Because the thing is we want to promote stimulated emission, why keep it in the denominator? Better keep it in the numerator so we write something like this. B / A equal to nu bar cube divided by 8 pi h. And even if I missed out some constant in the process, it does not matter. So let us see what will be the B / A ratio for nu bar equal to say, I am making a mistake here, am I not? I am surely making a mistake here, is not it? This cannot be because a nu and nu bar would be in the same place.

So let us see where I have gone wrong lambda nu is equal to C. So nu / C is equal to lambda and this equal to nu bar cube. So why have I written it here? It should have come here. So in fact, B / A is equal to 8 pi h divided by nu bar cube you have made a mistake here. So I will just go back once A / B equal to 8 pi h, multiplied by nu bar cube by C whole cube. So now then I said I do not want lambda, I do not want nu I want nu bar. So I said lambda nu is equal to C, therefore nu / C which is a quantity here that is equal to 1 by lambda which is equal to nu bar.

So as I told you, please be careful and correct me wherever I go wrong. Otherwise we learn things that are reciprocal of the correct picture. So B / A is equal to 8 pi h divided by nu bar whole cube. So B / A for nu bar equal to say 200 centimeter inverse divided by B / A for nu bar equal to 20,000 centimeter inverse B by equal to everything is in the denominator. Yes, this is a mess. Eight pi h. So, because here it is 8 phi h nu bar cube, but well, it does not matter because I wanted a ratio all ratios.

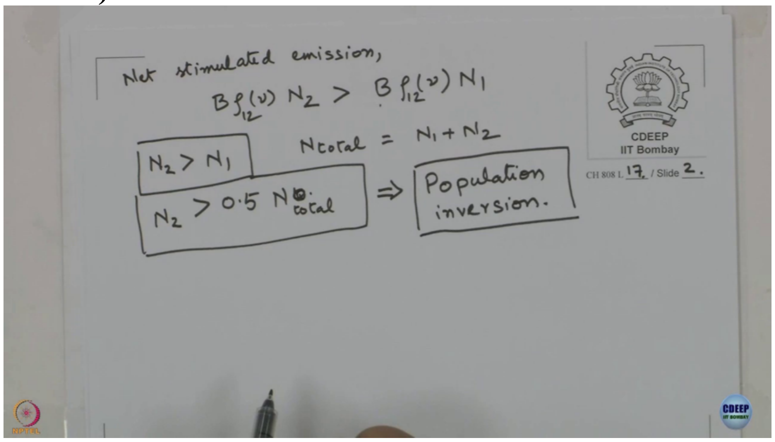
What is this going to be? 200 centimeter inverse. What is it? Is it microwave? Is it IR? Is it terahertz? What is 200 centimeter inverse what kind of light is it definitely not visible is 200 centimeter inverse 20,000 centimeter inverse what is, bluer UV and this is well something that is not exactly microwave still IR here so let us take them now I think the answer is very clear right? I put cube and here I write 200 here I write 20,000.

What is the answer? 10 to the power of 6 so, if you go if you want to make a laser, who is wave number is 200 centimeter inverse and a laser whose wavenumber is 20000 centimeter inverse which one will be easier? Definitely the 200 centimeter inverse one because the B / A ratio there is 10 to the power 6 times that of the B / A ratio for 20,000 centimeter inverse. If you just want to work out the value of A value of B might be a little confusing. So B / A ratio is something that allows us to understand what exactly the situation is right here.

So, the take home message here is first of all, is never equal to 0. Second one is for laser smaller energy gap is easier. So the discussion of 2 levels system has actually given us some very important information what we learned in the last module is we learned how to get a relationship between A and B. And what we have done so far in this module is that we have seen what is the ratio for the different kinds of energy gaps?

So, now, let us ask the question, what is the final I want to make a laser so, I want simulated emission as you said as well as you saw, when light comes in and is impinged 2 levels system, then you can have either upward transition or downward transition. So, if you want a laser, what you want is more photons should come out then what is going in otherwise how you will have light amplification.

(Refer Slide Time: 12:55)

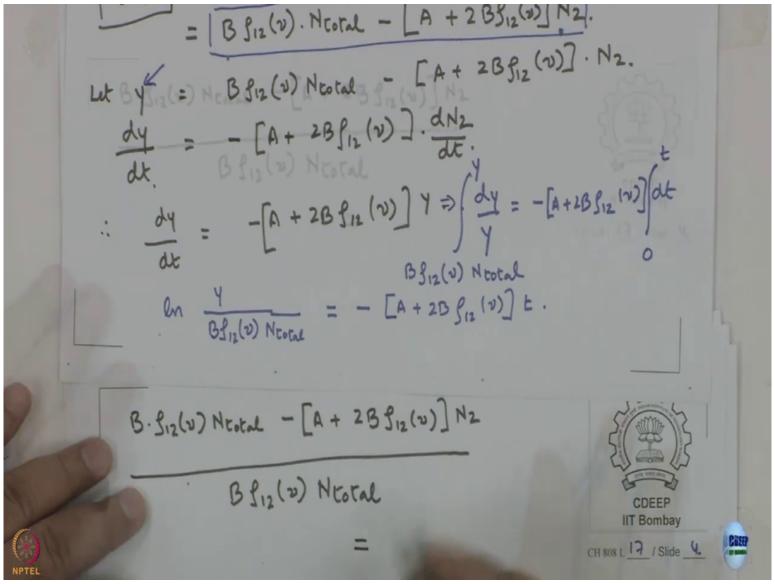


So, in order to have net stimulated emission the rate of downward transition must be greater than the rate of upward transition not writing one to any more data. Here I should write left hand side is rate of downward transition N2 right hand side is rate of upward transition because it has N1. And we already established that Bs are the same energy density the same anyway. So finally, what it boils down to is N2 has to be greater than N1.

And since we are talking about a 2 level system, we can right N total is equal to N1 plus N2 where N total is the total number of molecules that are there. So molecules can either be in state 1 or state 2 so when we add up the populations of state molecules in state 1 and molecules state 2 you should get N total. So, another way of writing N2 should be greater than N1 is N2 should be greater than half of N total.

And if you put it in words, then what we will say is that a population inversion is an essential condition. So that we get more light coming out then going in. So, population inversion is an essential condition without which you cannot get stimulated emission and therefore, you cannot get lasers. So, now the question is, is it possible to get population inversion in a 2 level system that is what will prove. I think most of us know the answer that is not possible but we will go ahead and prove it.

(Refer Slide Time: 15:09)



Now what I do is I write the rate equation. What is what is this term rate of which process B row 12 of nu into N1 it is induced absorption. Next time I will right is B row 12 of nu N2 what is this? Stimulated emission, does it populate or depopulate energy level two it depopulates. So what will be the sign plus or minus the first one populates N2 sign will be plus and second one depopulates N2 sign will be minus what is the third term spontaneous emission and it will also minus because it de populates depletes energy level 2 minus A N2.

And right here of course, there are 2 things to understand is the dN2 / dt is equal to 0 only steady state. But if you start if you have a situation where initially or nothing then light the light is switched on, then until saturation is reached the N1 and N2 values will change and N1 will keep decreasing and N2 will keep increasing. Now it remains to be seen, saturation of value of n two has to be there because you are not producing molecules.

So best case scenario is if at all molecule will go to N2 state and I'm not saying it is possible, but it is I am not saying it happens, but that would be the best case scenario. Initially when you start everything is that in N1 no N2 and then after some time, all molecules are in the high energy level that is the best kind of population inversion you could have of course, as we will see that is not achievable.

As you said already, even population inversion is not possible. I mean, dN2 is never half of it, but then the point I am trying to make is that it is the dN2 / dt is not zero until that steady state is achieved. And right now we are talking about a non-steady state situation. Now here of course, N2 changes with time and N1also changes with time N1 decreases from the initial value and N2 increases from 0.

So, two variables 1 equation will be difficult, but then we know already that I can write like this N1 is equal to, N total minus N2 in this equation which are the time dependent quantities? is N total time dependent. No it is a constant N1 and N2 are our time dependent, they are variables, but they of course correlated to each other. So, what I can do very conveniently is that I can write, I can replace N1 by N total minus N2 that way it becomes an equation in N2 and we are in a comfortable situation we can try to solve it.

So, that is right quickly rest of it is quite simple algebra and very little calculus. dN2/dt is equal to B row 12 of nu N total minus N2 minus B rho 12 of nu N2 minus A into N2. To formulate it makes sense to collect all the terms in N2. In fact, out of all the terms that you get, only one does not have N2 is not it? The first one so that is the only term B rho 12 of nu multiplied by N total is there a constant with respect to time this term, that is a constant and all the other terms are variable.

Not only that, the only variable there is N2 everything has minus in front so I can happily take this minus out, and I will take N2 out at the end. So what do I get? I will write a first and then see, this one is B into row into N2 with the minus sign. This one is also B into row into N2 with the minus sign. So it will be A plus 2B row 12 of nu, into N2. If you are good in calculus, you can actually write the solution right away. But since I am not good anymore, I will do it step by step.

Let me say y equal to right hand side. B row 12 of nu in total, minus A plus 2 B, row 12 of new into N2 what is then dy/dt at first time is constant. So, that goes second down I can write like this minus A plus 2 B rho 12 of nu into dN2/dt so what is then dy / dt. So, instead of this dN2 / dt I can write dy / dt divided by minus A plus 2 B row 12 nu and then on the right hand side I can write why is it? Therefore, I can write like this dy / dt is equal to minus A plus 2 B row 12 nu into Y this is dN2/dt equation. This one, I have said this whole thing to be Y.

Now it is not very difficult anymore. I hope that I can write something like this dy / Y. And everybody knows what the integral of the Y is, equal to minus A plus 2 B rho 12 of nu dt. What do I do I integrate? Only one trick I mean not trick. One pitfall is there, when I integrate, I am going to do it definite integration will integrate from zero to time t. So, right hand side is quite simple left hand side is also quite simple is going to be lnY, but we cannot forget what Y is upper limit is Y I just write Y for the upper limit.

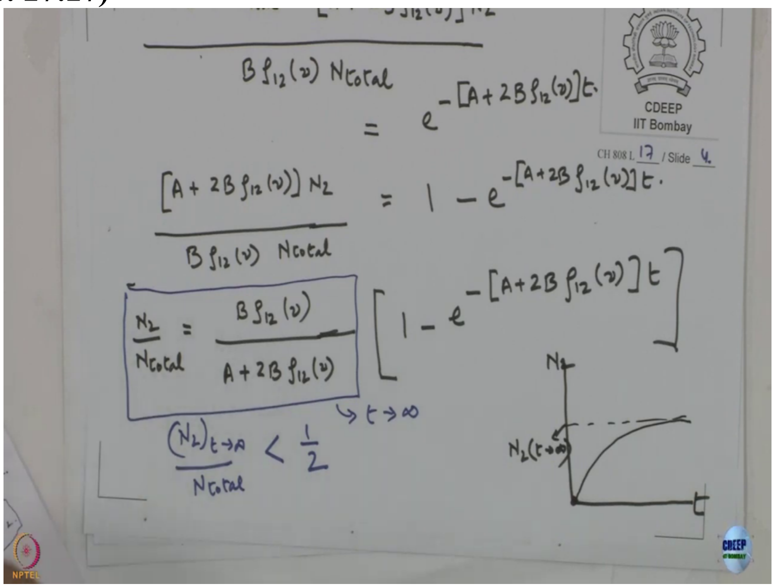
If you want you can write y dash, it does not matter, then you would like to share what is the lower limit? What is the value of why when the equal to zero? Go back to the definition of why at equal to 0, the second term is 0 was into right? There is no molecule in the second level is what we are working with, even though there is a little bit of a problem with that, but we can write it for now. We are talking about Y.

So my question is what is the value of y at t equal to 0? Second term will be equal to zero. So y will be equal to B into row 12 of nu multiplied by N total that is a constant. So that is the limit is important. B rho 12 of nu N total this is simple. Now just write the result, left hand side will be lny. I will still keep it that y, but then we will change later on, divided by B rho 12 of nu N total is equal to minus A plus 2 B rho 12 of nu t, see if you are convinced with this next step is very simple. Raise both sides to each find the analog right hand side will be e to the power minus A plus 2 B row 12 into t left hand side.

Numerator will replace Y by B into row 12 into Ntotal minus A plus 2 B row 12 into N2, but not yet because right now, left hand side is an ln, so when I take antilog, the left hand side ln will vanish, right hand side will be raised to the power of e. So I have not done that yet I am going to do so, let me keep it in such a way that you can still see it, there is a solution to a problem. Of course, the thing that you cannot see still is what is why we need that also. So what I can write is now l'llt try and explain you understood why I am doing this in both sides.

And taking anti log right? And let us not forget what is Y. So what will the left hand side we ln vanish. So why I am writing this expression that is all it is a little long, not difficult. B into rho 12 of nu N total minus A plus 2 B row 12 of nu into N2 divided by B row 12 of nu N total even before I write the right hand side, do you see the beauty of this expression, if I expand the first term is one second term has N2 by Ntotal N2 by Ntotal is what we are looking for so we are getting there is equal to is equal to e to the power minus A plus 2 B row 12 of nu t.

(Refer Slide Time: 27:27)



So now simplify a little bit, so, left hand side you can see, right, it is one minus this thing divided by this. So, can I jump a step? I just take the second term to right hand side so, that minus sign we will go. I will take one to the other side. Are you okay with that? So then what I have is A plus 2 B, row 12 nu N2 divided by B, row 12 nu N total. I have taken this to the right hand side. So on the left hand side, I have one and I am taking this actually to the left hand side. So minus e to the power minus A plus 2 B row 12 of nu t.

Now, climax is there N2 by N total is equal to B rho 12 of nu divided by A plus 2 B row 12 nu multiplied by 1 minus e to the power minus A plus 2 B rho 12 of nu t. This is the expression for N2 of N total. My job now is to see, is it ever possible for this ratio to be more than half. Because if it is if that happens then population in inversion is going to happen. Let us see let me plot I think we chemists understand pictures better than numbers.

So, let me plot N2 verses time as we discussed already N2 at time t equal to zero is zero what is N2 at time t equal to infinity this is a monotonic function at time t equal to infinity what will happen? This will become 0 the exponential term because e to the power minus so, take it in the denominator will become a large number, so, it is going to be 0 and then you are left with one. So, what we get is that we get a monotonic increase like this to saturation and what is the saturation value? I can write N2 at time t tending to infinity.

What will that be? Well actually Ntotal should we hear them? What will that e what will enter N2 it will be so this thing is gone. So, N2 by N total value maximum value at time equal to infinity turns out to B into row divided by A plus 2 into B into row. So this is actually the best possible value, saturation value t tends to infinity of course, when I say infinity, I did not mean real infinity it can be really small time but its saturation value that is now see, now, remember, we said that A being non zero is going to be useful, here it is useful.

See if A would be equal to 0, then the best then it would have been half. So population, not exactly inversion. But actually, at least population equal equalization would have happened but what you said is that A is never 0 is B is not equal to the 0 that means that this ratio N2 at time t tends to infinity by end total will always be less than half have I been able to make the point? So, this is why population inversion can never be achieved in a 2 stage system the best possible value is still a little less than half and half is not good enough.

Actually looking more than half is what is required for population inversion that is never achieved even half is not achieved. So, this 2 level system which has given us all the important quantities that are relevant to lasing to lasers. Unfortunately, cannot give us an actual lasers. If we want to make a laser stimulated emission will be there, we have to add at least 1 or 2 more levels. So that is what we study in the next module.

We will talk about 3 level and 4 level system. And then maybe I think we will have time for it. We will do a little bit of calculation on our own laser to get an idea of some of the numbers associated with it.