Ultrafast Processes in Chemistry

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Lecture # 18
3 & 4 Level Systems

We learned in the previous modules that this 2 level system that is so useful in developing the concept of stimulated emission and spontaneous emission is actually useless as far as making lasers in real life are concerned. So, what we will see in this module is what happens when we have more levels than 2, but before going there, let me ask a question about 2 level system. See, the way we introduced it was that when you perform the semi classical treatment, using perturbation theory, time dependent perturbation theory.

Then you get an idea about absorption and stimulated emission. And then we said that it was the genius of Einstein that brought in the spontaneous emission term in the kinetic equations he wrote, because it is there it is real, but I hope you are not forgotten that we also made a passing comment that even then the picture is not complete. Can you tell me why we made the statement? why is the picture not complete for even a 2 stage system.

Even if you consider absorption, stimulated emission and spontaneous emission, what have we missed out on? Yes, so, we missed out on something that is actually the focus of our research entirely. We missed out on the non-radiative rated relaxation, even an Einstein statement, non radiative relaxation was not there. So that comes in as another yet another term in the kinetic equations and when you bring it in then you get all those relations were written earlier.

The rate constant of non-radiative processes quantum yield and lifetime the right 1 – phi_f divided by tau_f. So, that is where that comes from, but in the discussion that we are doing so far, we are pretending as if there is no non radiative relaxation, which of course is not correct and it does not give you a complete picture. But in the discussion that we are going to do now, we are going to invoke rather non-radiative processes to understand the situation, all with qualitatively.

I mean, one can go and do a lot more kinetic equations, and convince ourselves what the situation really is for a 3 level and 4 level system. But once you have done two level system, rest of it is just an extension. You can do it yourself. So, not try to do it in the course. I will draw the picture perform a qualitative discussion and then move further ahead so, 2 level system

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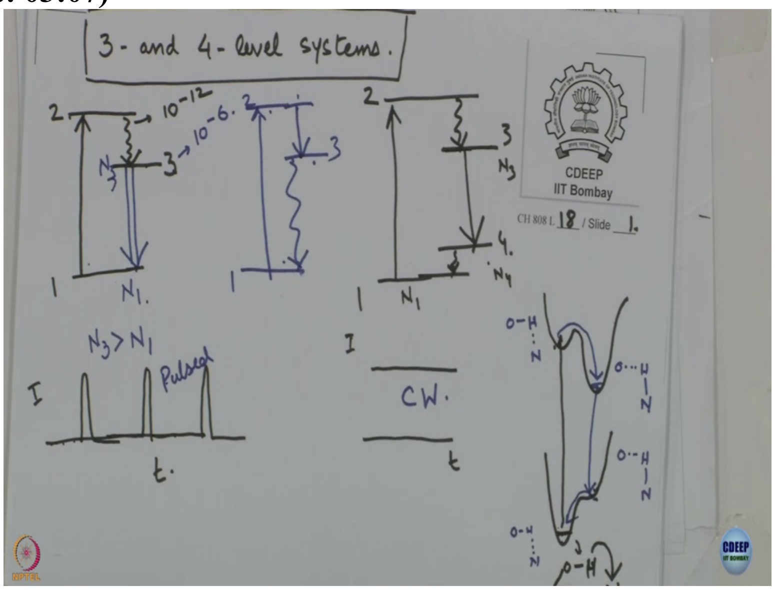

As we said is not good enough to give you next spontaneous stimulated emission, what about a 3 level system? Suppose I have another energy level 3 and acid, we are going to perform a qualitative this description here and the situation is this that you promote the molecule from energy level 1 to energy level 2 and let us say that there is some efficient non-radiative relaxation pathway that quickly brings the system down to level number 3.

If you read textbooks on laser in many cases, they have not used non related the discussion of non-radiative path they have stuck to discussion of radiative path and it might as well be there may be a radiative transition from 2 to 3, the only condition is that it has to be fast. Then what happens? And let us say so, an example that we will all understand is, let us say that state 1 is S0 ground singlet state, state 2 is a S1 excited singlet state, state 3 is a triplet state.

So in that is this nonradiative process would be an ISC and as you know, ISC can actually be promoted by using heavy atoms and all. There are mechanisms by which you can actually make ISC very efficient. Of course, purists would say that in that case, the state number 3 is no longer a triplet. Because when you invoke heavy atom effect, then what you have is your spin orbit coupling. And it is no longer a pure triplet state.

But that is fine. I mean, we can still work with the fact remains that it is not so easy for the system to come back from 3 to 1 anyway. So as we know, triplets have a long lifetime is sort of a quasi-permanent state right then what will happen? Let us say that this process takes place in a few femtosecond or few picosecond let us say and let us say that this state number 3 has a lifetime of let us say microsecond, microsecond is enough.

How many picoseconds are there in a microsecond? 2 picoseconds are there in 1 microsecond. Please come back to the linear world. So, can we try again? How many picosecond are there in microsecond 10 to the power 6 right 10 to the power 6. So what I am trying to say is that before a molecule can come down from 3 to 1, this is a lifetime is large population of 3 can actually be built.

If this process 2 to 3 radiative or non-radiative are whatever takes place in picosecond timescale, and if lifetime of this is microsecond also, then before a molecule that goes here, can come down to the ground state. This 2 to 3 conversion will take place maybe 10 to the power 6 times. And 10 to the power 6 is a large number. So what is happening for sufficiently long lifetime of this state number 3 is population will build up N3 and N1 will keep decreasing that right.

So what you are doing essentially is that you are pumping population from state 1 to state 3 through state 2 and in this 2 to 3 relaxation is fast enough and if stage 3 is sufficiently long lived, then you can achieve a situation can reach a situation where N3 can become greater than N1 and then you can get spontaneous emission between 3 and 1. Is that right? Have you understood what is going on so, for what we have discussed now N2 is populated from N1 we can say instantaneously.

Time for transition is attoseconds, from 2 to 3, that population takes place very efficiently femtosecond process let us say, what you are saying is 3 is very, very long lived, if all the numbers work out nicely and that is you can get an actual feel of the numbers if you work out the differential equations then you can hope to achieve population inversion between 3 and 1. And once that is achieved, you can have lasing has everybody understood.

And that brings us to something that is very, relevant to our core discussion. That have a pulsed laser. Let me see. As long as so initially think of times 0 population of stage 3, level 3 is 0, population of level 1 is almost in total. Now think of say 1 nanosecond after your started, light is shining, right? The pumping light 1 to 2 that is shiny. What N3 is building but still perhaps it has not reached population inversion.

So for the first 1 nanosecond, there is no lasing, for 2 nanosecond also maybe there is no lasing maybe after 500 nanosecond or 1 microsecond or 5 microseconds provided lifetime of 3 is long enough population inversion will be achieved. So, if you think of the output of the laser, there is no lasing for a long time right, but when population version is achieved, this is the important part. Then all the population will want to get depleted by stimulated emission at 1 go. So, the output will get will be something like this. And then again, if this 1 to 2 radiation is on, population of N3 will keep building up and the laser will be silent x axis is time y axis we can say is intensity is going great then after the required amount of time, once again there will be a burst of light. And this will go on provided you keep the pumping or so, for a 3 level system like this where 2 to 3 transition is ultra-fast and 3 is ultra-long lived. You are going to get pulsed output.

Case in point, ruby laser. So, this is 1 situation. Now, we will come back to Level 3 also level 3 once again, but let us just talk about full level system first. Let us say I have a situation like this 1 2 then let us say this 3 and 4 and situation is like this direct transition is possible between 1 and 2 from 2 to 3, you have an efficient non-radiative pathway from 4 to 1 also you have an efficient non-radiative pathway can you actually have a system like this.

Well, suppose you have intramolecular, proton transfer, excited state intramolecular proton transfer. Then it is possible, then if you look at the energy profile, then most likely it is going to be like this. So I will draw schematic molecule some OH is there. And a nitrogen atom is there. I am not even drawing the rest of the molecule here. So what I am saying is, this is the ground state corresponding to it, then you excite and an excited state proton gets transferred to nitrogen excited state intramolecular proton transfer.

So, even if we are going there, if ground state this is the situation, what I am saying is that nitrogen mean protonated that is not an energetically favorable situation. So, that is when you have this asymmetric double well potential y axis potential energy what is the x axis, you can say bond length for now, or the reaction coordinate. So your asymmetric double well potential. What happens when you excite as we might have discussed in this course, acids are more acidic, bases or more basic in the excited state.

OH is an acidic group, and N is a basic group, the excited state due to change in acidity and basicity proton gets transferred. So, now this locally excited state for this 1 is no longer energetically stable. So, next site then you are going to reach a state that is actually energetically less stable. So, excited state potential energy surface you can expect something like this this state is OH double bonded to N, this excited state is also OH not double bonded hydrogen bonded to N, then proton transfer is taking place this is hydrogen is covalently bonded to hydrogen bonded to oxygen, this is the corresponding ground state.

So if proton transfer is sufficiently facile What will happen you excite immediately proton transfer will take place and then whatever emission takes this will be from here to here, but then since this is energetically not favorable, the moment it has any population, it will come back to this 4 level system. So, that is why a ESIPT molecules have been touted for a long time as good candidates for making lasers because they are actually 4 level system.

But now see what kind of output will get this like when you start population of N 1 of 1 is N1. What is population of 2, 0. This is 0 this is zero, a little while later, so N1 equals to N total, you start from that a little while later, what happens? This decreases a little bit. population of N2 is still 0 because there is an efficient non-radiative pathway to level number 3, level number 3, let us say has some life time, whatever.

So N3 population is there what about N4? What we are saying is if you look at this diagram, the moment level 4 is populated, it goes back to 1. So, N4 population is maintained to close to 0 at all times is important to understand here, if the rate constants are such that N4 concentration is held to be near zero at all times, then what will happen? Population inversion is already achieved between third level and fourth level.

Because even if there is like 2 molecules in N3, population of fourth level is 0. So, in this case, what kind of an output you will get there might be any Initial induction time and if you neglect that, you get a continuous output. So, this is an example of and the first 1 third level 3 level system is an example of an intrinsically pulsed laser. This is an example of an intrinsically continuous wave laser.

So, I told you an example of a 3 level system that is actually, something like this. Does anybody know an example of a 4 level system something is very, very common and not necessarily an ultra-fast as I do not exactly know it must be diode laser? So, most likely yes Nd-YAG laser is what I had in my mind. Nd-YAG laser is perhaps the most celebrated example of a 4 level laser supposed to be continuous right.

So, you see that Nd-YAG lasers are there that are that have continuous wave output And then you see Nd-YAG lasers that are fast. So, we are trying to say is Nd-YAG lasers are actually intrinsically not fast, intrinsically there CW lasers, if you want to make them pulsed if you want to get pulses out of them, then you have to do something yourself and that doing something yourself is either q switching or mode locking.

So, that is what we are going to learn in the subsequent modules. Maybe not very sure whether it will be exactly in the next module or not made up my mind yet, how much I want to talk about gain and loss and Q factor. Perhaps we should do a little bit but eventually we are going to talk about mode locking. So remember something that is intrinsically CW can perforce we made to give you a pulsed output. And it is not very difficult to understand as well.

So the light is coming from that lamp is CW? And the director I have my eye. So I keep it shut, I do not see it, then you open it for a small time and close it again. So that way the detector that I have actually gets pulse light out of a CW source? Or I could use the shutter will eyelid is a shatter. But here I cheated a little bit because I talked about shattering the detector rather than the laser itself. What I can do is, maybe I can keep it off for some day turn on the switch, only for a short time.

If you do it that may not be a very good thing to do, because it might spoil it. But there are other ways we can use different kinds of shutters by which is CW light can be made pulsed. And that is what we learn in detail because that is, that is really something that is very important to our course of study. But before we leave this discussion, if we talk about another kind of 3 level system, and I say another kind, 3 level system has to have 3 levels, you cannot really help there. what I could cannot really do much, much about 2 to 3 also.

But suppose now, I have something in which this 2 to 3 conversion is radiative and 2 has a long lifetime. 3 to 1 is non radiative and fast. Of course, there is a catch here. the catche is, what about 2 to 1 emission will come to that, but for the moment you tell me if this is a situation then what will happen what kind of laser do I get? First of all, this is where the lasing will take place then between 2 and 3 will it be CW will it be pulsed it will be CW.

So, you can have 3 level systems in which the output is continuous wave it is not necessary that whenever you have 3 level system, the output is going to be pulsed. It all depends on the relative rate constants. But now, what who will take care of the 2 to 1, 1 to 2 absorption is taking place. So 2 to 1 can also take place and I am trying to have induced emission. So, do I have some way in which I can force the system to give me lasing into 2 to 3 and not 2 to 1 yes, energy density matters right do not forget energy density is another factor here.

So, if the energy density of new 2 1 is very low and energy density of 2 to 3 is high, we introduced some photons from somewhere of that energy, then you can make a laser emitting in that particular frequency and this is actually discussed in McQuarrie and Simon's book, in my edition.

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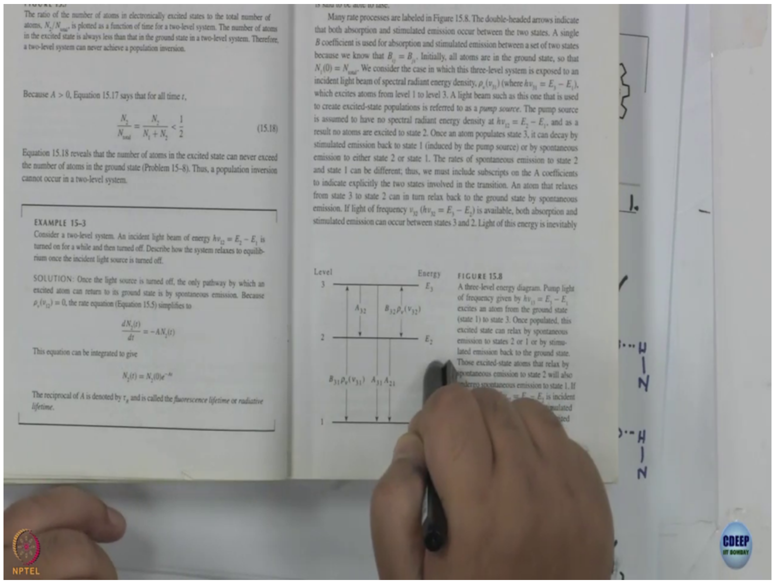

The page number is 603 here they have talked about 3 level system. And you see they have considered all kinds of as if you look carefully, there is no non-radiative transition here. It is radiative all the way but they have set the conditions in such a way that you have a 3 level system where the lasing is between 3 and 2 and the output is continuous wave. So I would advise you to try and work out this problems you see finally get an expression of N3 by N2 into and so on and so forth.

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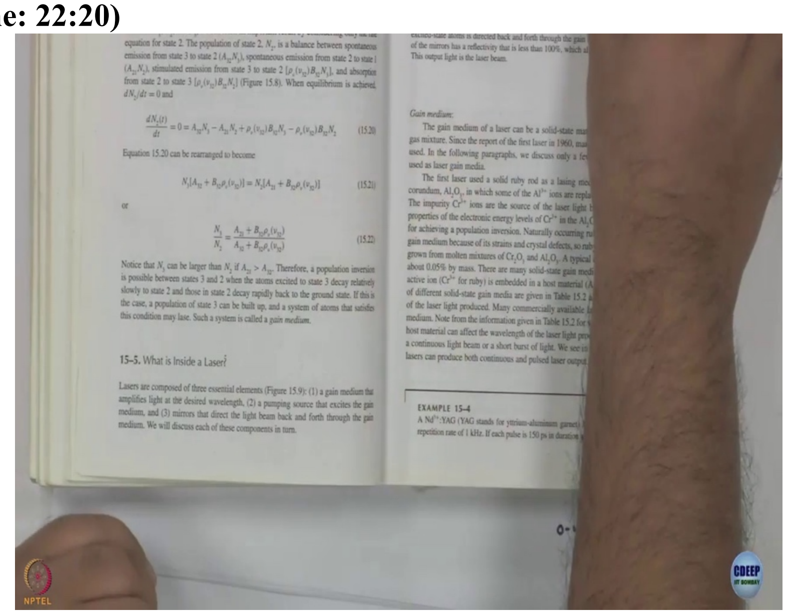

So, do it yourself and satisfy yourself that this is actually the case. We will move on a little bit and give you a quick glimpse of what is to come.

And let us let me show you since I have the book open instead of drawing, let me show you the diagram. This is what we have inside a laser. I think this is something that all of us know. How do you make a laser? How do you get amplification? What you do is first of all, you need some pumps source you have to create that appropriate excited state pumping can be done either optically or electrically, you can have some light source.

So, if you see older Nd-YAG lasers, they use flash lamp to excite. So in the laser that I use as a PhD student had this Nd-YAG rod about this big. And on 2 sides, there are 2 flash lamps. So the arrangement was like this parallel, you can think that the blue pen, you better look at the position then you will see blue pen is the YAG rod. And let us say the black pen is flash lamp and you have another flash tap on the other side. And we had this parabolic mirror.

So light from here would be focused on to the YAG rod. Of course. Anyway, 30 years ago, things were much more primitive than what they are today. And there is always this problem of heating. You have this flash lamp on all the time and it is pumping. So the things would get heated. How do you dissipate the heat does this actually very nice if a little cumbersome design where this whole thing was immersed in a tub of water on tub is about this big the whole thing was in water.

So of course, that water had to be this distilled water and then constant temperature had to be went into the secondary cooling and all but you know, if you use a bulb sometime or the other it goes bad. And if you are unlucky, the flash lamps instead of just dying on you would burst and then whether the burst or not to change the flash lamp, we had to take out a 12-13 screws, drain the water completely.

Then salvage broken pieces or the unbroken flash lamp from there and change it. Those are more interesting days. So that is one way of pumping what we do now In a diode pump solid state lasers is that your diode bank, which gives you light, which is directed by photodiode on to the YAG laser. And whoever used that laser would know that there is a chiller that provides cooling, but things are not as messy as it used to be earlier.

Now, it is not necessarily that you always do optical pump and you can do electrical pumping as well. But let me decide whether you want to talk more about that later. And then you have this, I do not know if you can read the projection.

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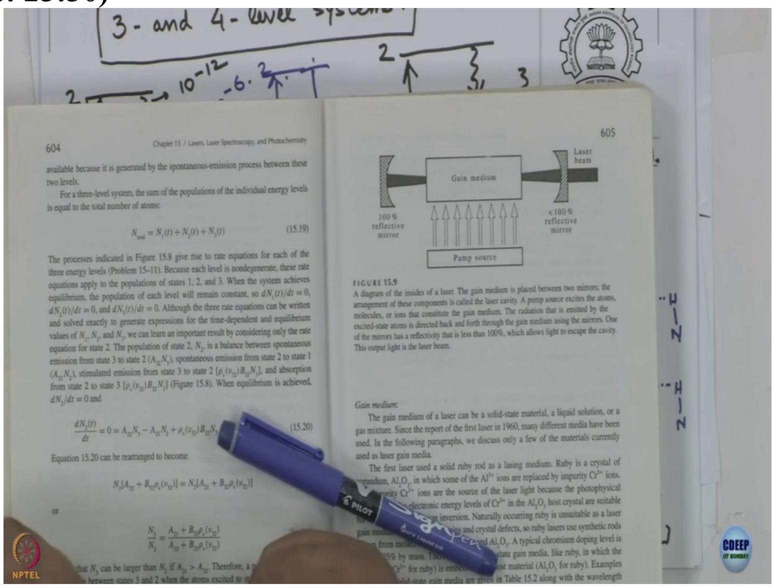

here then you have this gain medium, or active medium, that is the molecule or material or ion, which actually gives the emission so we are talking about Ruby laser. Again, medium contains to be what is Ruby. We will come to that a little later. I will show you if you can read and then what you do is all emission takes place and that emission photon that there are the 2 mirrors on 2 sides. So, for photons that go to this mirror and typically have curved mirror, because you want to focus here so that you high density of photons.

So, let us think of 1 photon which has gone here hit this mirror comeback and when this photon passes through the game medium is going to experience other ions or other molecules or other material that is excited already by the pump source. You get my point. First think of it like this pump source, let us think of it as excitation light 1 to 2 excitation. I have done that and some emission has taken place. Let us see the stimulated it is spontaneous emission does not matter. It can take place in all directions, but we are talking about this mirror.

So a photon that goes and hits this mirror comes back retraces its path now, when the photon comes back to the gain medium, it is going to find other molecules or other ions whatever the gain medium is in excited state, who has taken them to excited state the pump source it is a pump source that is exciting the components of the game medium. The job of the photon that is initially emitted and has come back is to cause either promotion of unexcited molecules or de excitation of already excited molecules is finds both.

And that is where this discussion of gain and loss and all that comes in. Maybe we will do it later. So, think of this photon comes depopulates 1 ion or 1 atom or 1 molecule in the excited state through stimulated emission, the important thing to understand is what we are drawn at the beginning of the 18 17 16, whatever it is called 16 module 16th lecture. Remember, the photon that comes in is not absorbed, it goes out itself.

But it de excites a molecule and causes the emission of a second photon. So, now if you think like this photon goes out by whatever mechanism of emission comes back causes stimulated emission. Now, 2 photons come here, hit this mirror, come back, and they cause 2 more photons to come out. So, in every round trip, the number sort of doubles. In the best case scenario, it does not always double it will always be less than 2 actually the factor but it increases.

So in a very short time, how much time does a round trip take? Let us say let us do a simple calculation. Let us say this length is 1 meter. So roundtrip would take how much? Start from here? Go here, and come back later say complete round trip. It is traveling 2 meter in that case, let us set the meter. Let us say 1.5 is the cavity lane, then it us easier, then now trip distance is 3 meter, what is the speed of light 3 into 10 the power 8 meters per second this time we have not made a mistake.

So we can calculate how much time it takes very small, right. So if you are talking about some seconds, in a few seconds, this is huge amount, a huge number of photons that is produced. And that is called gain, increasing number of photons. But now, what is the point I mean, if you are a miser, you work very hard. Earn a lot of money, keep everything in an iron box, and then when the time in the earth is over of what uses that money to you have to spend it also, if you are going to make a laser, it is not enough.

We just have a lot of gain. We also need to have a little bit of loss I mean light should come out. And the easiest way in which it is done is that on one side, you have a highly reflective mirror reflectance 100 percent. On the other side, you are partially reflecting mirror so say 95, 99% reflecting mirror, 1 percent will come out. This is called the output coupler. We will discuss these terms again in more detail.

Then what will happen? So initially when number of photons is small, you hardly see any output because say 1% of light is coming out let us say, and being a little stringent here. But when there is a lot of gain, there is a buildup, then 1% of that amount is also good enough. Then you get laser light coming out from this side. This is the simplest way in which you can depict a laser. Now we will get into more complication what happens? What should a cavity length be? I arbitrarily said 1 and then I said 1.5 is it arbitrary.

Can I have any laser light even for CW and if I want pulsed light, what is the more stringent condition that comes? These are things that will slowly get into, but let me complete this discussion by showing you another page of McQuarrie. If you cannot read here, please go back and read in you are home.

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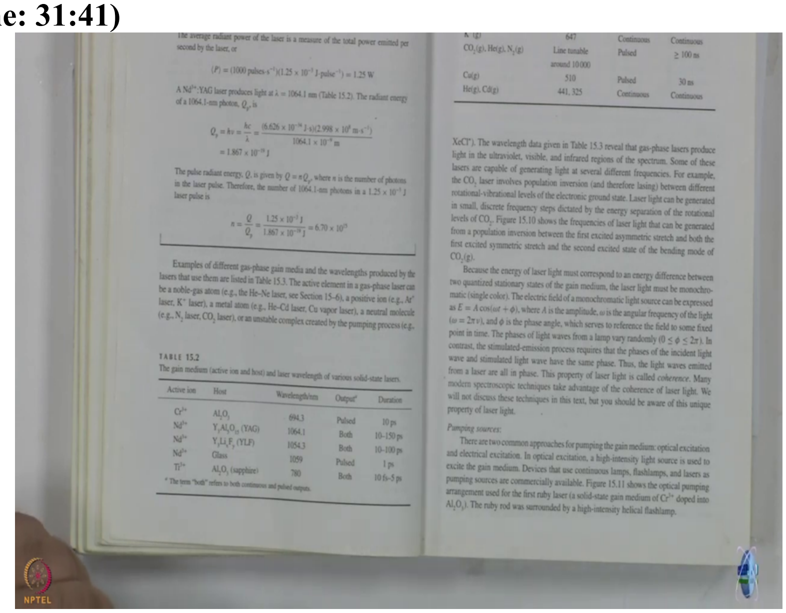

The average radiant power of the laser is a measure of the total power emitted per second by the laser, or

$$\langle P\rangle = (1000\ \text{pulses}\cdot s^{-1})(1.25\times10^{-3}\ J\cdot\text{pulse}^{-1}) = 1.25\ W$$

A Nd^{3+}:YAG laser produces light at $\lambda = 1064.1$ nm (Table 15.2). The radiant energy of a 1064.1-nm photon, Q_p, is

$$Q_p = h\nu = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ J\cdot s)(2.998\times10^{8}\ m\cdot s^{-1})}{1064.1\times10^{-9}\ m} = 1.867\times10^{-19}\ J$$

The pulse radiant energy, Q, is given by $Q = nQ_p$, where n is the number of photons in the laser pulse. Therefore, the number of 1064.1-nm photons in a 1.25×10^{-3} J laser pulse is

$$n = \frac{Q}{Q_p} = \frac{1.25\times10^{-3}\ J}{1.867\times10^{-19}\ J} = 6.70\times10^{15}$$

Examples of different gas-phase gain media and the wavelengths produced by the lasers that use them are listed in Table 15.3. The active element in a gas-phase laser can be a noble-gas atom (e.g., the He–Ne laser, see Section 15-6), a positive ion (e.g., Ar^+ laser, K^+ laser), a metal atom (e.g., He–Cd laser, Cu vapor laser), a neutral molecule (e.g., N_2 laser, CO_2 laser), or an unstable complex created by the pumping process (e.g.,

TABLE 15.2
The gain medium (active ion and host) and laser wavelength of various solid-state lasers.

Active ion	Host	Wavelength/nm	Output*	Duration
Cr^{3+}	Al_2O_3	694.3	Pulsed	10 ps
Nd^{3+}	$Y_3Al_5O_{15}$ (YAG)	1064.1	Both	10–150 ps
Nd^{3+}	$Y_3Li_3F_4$ (YLF)	1054.3	Both	10–100 ps
Nd^{3+}	Glass	1059	Pulsed	1 ps
Ti^{3+}	Al_2O_3 (sapphire)	780	Both	10 fs–5 ps

* The term "both" refers to both continuous and pulsed outputs.

[illegible]	647	Continuous	Continuous
$CO_2(g)$, He(g), $N_2(g)$	Line tunable around 10 000	Pulsed	≥ 100 ns
Cu(g)	510	Pulsed	30 ns
He(g), Cd(g)	441, 325	Continuous	Continuous

$XeCl^*$). The wavelength data given in Table 15.3 reveal that gas-phase lasers produce light in the ultraviolet, visible, and infrared regions of the spectrum. Some of these lasers are capable of generating light at several different frequencies. For example, the CO_2 laser involves population inversion (and therefore lasing) between different rotational-vibrational levels of the electronic ground state. Laser light can be generated in small, discrete frequency steps dictated by the energy separation of the rotational levels of CO_2. Figure 15.10 shows the frequencies of laser light that can be generated from a population inversion between the first excited asymmetric stretch and both the first excited symmetric stretch and the second excited state of the bending mode of $CO_2(g)$.

Because the energy of laser light must correspond to an energy difference between two quantized stationary states of the gain medium, the laser light must be monochromatic (single color). The electric field of a monochromatic light source can be expressed as $E = A\cos(\omega t + \phi)$, where A is the amplitude, ω is the angular frequency of the light ($\omega = 2\pi\nu$), and ϕ is the phase angle, which serves to reference the field to some fixed point in time. The phases of light waves from a lamp vary randomly ($0 \le \phi \le 2\pi$). In contrast, the stimulated-emission process requires that the phases of the incident light wave and stimulated light wave have the same phase. Thus, the light waves emitted from a laser are all in phase. This property of laser light is called *coherence*. Many modern spectroscopic techniques take advantage of the coherence of laser light. We will not discuss these techniques in this text, but you should be aware of this unique property of laser light.

Pumping sources:

There are two common approaches for pumping the gain medium: optical excitation and electrical excitation. In optical excitation, a high-intensity light source is used to excite the gain medium. Devices that use continuous lamps, flashlamps, and lasers as pumping sources are commercially available. Figure 15.11 shows the optical pumping arrangement used for the first ruby laser (a solid-state gain medium of Cr^{3+} doped into Al_2O_3). The ruby rod was surrounded by a high-intensity helical flashlamp.

This table 15.2 in McQuarrie and Simon provides you a compendium of some solid state lasers. And what you see is chromium. So, it is important to understand what this is. We always say Nd-YAG laser and forget about it. It is important to remember what is the role of what the role of Nd is and what is what the role of YAG is. what is YAG yttrium aluminum Garnett and what is that?

It is actually Al_5O_{15}. Ok $Y_3Al_5O_{15}$. Have you heard the word Garnet in any other context is a precious stone jewelry? Yes.

Have you heard of Ruby in some other context? Of course you have. So all these precious stones are precious to us. Not because we want to wear earrings, I mean not all of us but because they actually make good gain medium. But it is important to understand that it is the DuPont the ion. That is actually truly the emissive species, the role of YAG or YAL or glass, all that is to provide a support. In fact, we will talk about Ruby laser, natural Ruby does not give you good laser,

Ruby laser invariably has synthetic Ruby which is grown so, that the crystal structure is good enough. Natural Ruby is not very easy to make use of laser material. So, here the last example that is discussed is our good old titanium sapphire laser here the Ti 3+ iron that is what gives you the emission and Sapphire, again another precious stone is Al2O3 that is the matrix. More than important. Titanium in some of the matrix may not be as stable as titanium Sapphire.

So, good thing Why are precious stones precious? I mean, let us see mixed no sodium chloride crystal of sodium carbonate I can call it a stone right? It is not going to be very precious calcium carbonate that is actually valued stone. Why is it that calcium carbonate is not so precious as Ruby? Because the answer is same as if I asked you why is gold precious? As gold does not react. You make very nice jewelry out of iron and then eventually they rust and it is not there anymore.

In a silver gets black but not as bad as iron. Gold does not react that is why gold is so precious. Platinum is precious. So here also the good this precious stones are precious because they are so stable. They do not react to the slightest by moisture some of the guests that are present that is why you want to make these a support material. This is what you Titanium sapphire laser actually is and you can also have it gases as gain media, you can He-Ne laser Is it something that you might have heard before the advent of diode lasers He-Ne lasers were ubiquitous especially where alignment was involved.

Now, in many cases they have been replaced by diode lasers because now you have good quality diode lasers which give you nice transverse mode and all, but that will be discussed sometime later. The point I am trying to make here is that your gain medium can be many different things can be solid can be liquid can be gas. But it has to satisfy certain properties three level or four level at least. And stability is an issue.

Do you know of any laser where the game medium is liquid? Well, it is a liquid I mean a solution. Go to the next lab. You will see dye lasers. So what they do is they dissolve something like Rhodamine 6G methanol and keep it in quvette excite using a green laser and make a laser out of it. Again as PhD student I use what is called a synchronous pump dye laser we will discuss what synchronous pumping is there we used to flow the dye that I wanted to use picosecond resolution you cannot use a quvette.

So, you actually flow the dye and you have a jet of dye coming out and it is caught by what is called the catcher tube and that takes it back to the reserver. And the green laser was focused on to the jet of the die in no medium, so, it does not become broad. There was also Rhodamine 6G but not dissolved in methanol, it dissolved in some viscous solvent so that the jet is good. So we will come to those 1 by 1. I wanted to do a calculation today, but maybe we will leave it for a little later when we actually discussed Ti-sapphire laser. So, next day onwards, we talk a little more about lasers and finally we are going to arrive at pulsed lasers.