Ultrafast Processes in Chemistry
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Lecture # 19
From CW to Pulsed Lasers

Right now we are discussing basics of lasers. And slowly we are on our way to understand how to make pulse lasers in the first place. As we know already. These 3 level systems often give you pulse lasing.

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4 level systems by default would give you continuous lasing, but then you also said that Nd-YAG laser for example, is a well-known four level system, but then we do know about pulsed Nd-YAG lasers. Which means we must be doing something by which the pulses are produced they are not naturally pulsed. Similarly, titanium Sapphire laser, which is the most commonly used laser nowadays for ultrafast studies is intrinsically continuous.

Do something to make them pulse. So what do you do something? What are the factors that is what we want to learn? So we will start our discussion today with continuous wave lasers, and then we will go on to pulsed lasers gradually. And we will see that the same laser under some condition can have continuous operation. And if you create the conditions a little bit, you can get pulses. So to start with, let us talk about a very well known.

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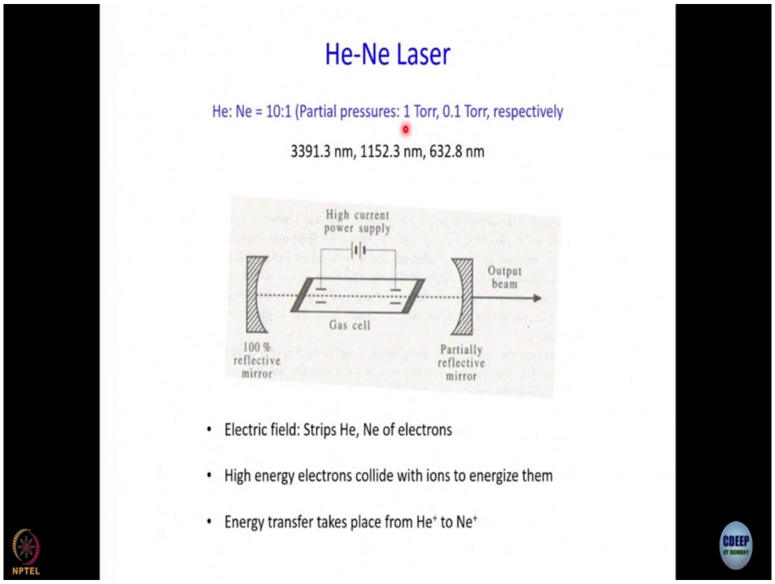

Continuous wave laser a very well-known and a very simple laser is helium neon laser. He-Ne laser as it is commonly called. And I do not know whether you have seen a He-Ne laser yourself because we do not really use it in our lab. But generally whenever alignment is required. He-Ne laser are the default ones that are to be used, where you have used lasers that you have to make and then the high power lasers, you try and switch on the laser, everything might get burned. So what you do is you do the alignment using this laser.

And if you go to our Raman microscope, there, you will see there are 2 lasers, one of the 2 is a He-Ne laser. Now, He-Ne laser what you have is you have this kind of, we know by now that in a laser, you have an active medium or gain media. And you have 2 mirrors. These are this is the simplest way you can build a laser right that is what constitutes a laser cavity. So as usual, you have 1 meter which is a high reflector meter, when reflector is hundred percent, and you have another meter which is partially reflective mirror.

This is called what is it called? What is the partially reflective mirror called in laser? It is called the output coupler. You should also always answer it does not matter. You may be wrong, but that is now what you have here as an active medium is you have a mixture of helium and neon gases.

Why mixture will come to that shortly. But it is important to remember that the ratio of helium to Neon is 10 is to 1.

And for the record, the partial pressures are 1 torr for helium, and 0.1 torr for neon. So why is helium present in 10 times the abundance of neon? We will see shortly. And then you have it inside a gas cell. One more thing I want to draw your attention to without explaining it at the moment we will come to it eventually is look at how the gas cell is drawn. Generally, we when we draw a cell, we like to draw a rectangle here.

What they have drawn is a trapezium, this figure is from McQuarrie and Simon is book. Why is it a trapezium? Why are the ends of this gas cell at an angle that is not a right angle and what is the angle called? There is a hint the angle has a name. So if you try to think of angles which have a particular name in context of optics, you might get the correct answer, not when you can do it in this case, my magic does not always work. In some other angle, it is named after a scientist, it is called Brewster angle.

Why Brewster angle we come to that eventually. And so, here you got the gas cell where these are the windows basically. When I say the ends, the term that is used for them are windows because light has to pass through them. We have all worked with quvettes. And there we know that in a quvette we have 4 windows right? And in case of fluorescence quvette. The windows are all transparent. In case of absorption quvette.

The 2 of the windows are transparent. 2 of them are opaque here we have 2 windows and these windows are at a Brewster angle to the direction of propagation of laser light. And then you have this high current power supply high voltage power supply that is connected to it. So, what happens here, but before that, let me also tell you that you can actually generate different wavelengths, from a He-Ne laser, you can get 3391.3 nanometer, you can get 1152.3 nanometer and the most commonly used He-Ne laser that you will see gives you 632.8 nanometer.

So, that brings us back to the application. I told you that He-Ne is one of the 2 lasers that are present in our Raman microscope. The other laser is Nd-YAG laser, which gives you green light

532 nanometer by now, I think we know very well what the output wavelength of Nd-YAG guess what is the fundamental output of Nd-YAG Glaser 1064 Nanometer please do not forget that 530 nanometer is not the fundamental output of Nd-YAG laser.

We are going to talk about Nd-YAG laser later on, but please remember there is actually an IR laser, you get 532 nanometer by frequency doubling. And this one however, the these are all fundamental emissions 632.8 nanometer which is the highest energy light that I have listed here is also a fundamental light it is not frequency doubled. When I show you the schematics, you'll understand how this is a fundamental light.

And the reason why He-Ne laser is used in Raman spectroscopy Can we say, Can we guess why He-Ne laser is good for Raman spectroscopy? Yes, because high wavelength, high wavelength is correct. So, let is go back to basics of Raman spectroscopy. In Raman spectroscopy you do not want unless you are doing a resonance raman you do not want to have a transition to the next electronic level. Right, you want to promote to a virtual level from which Raman scattering will eventually take place.

So you do not want too much of an energy. Of course, you can say what is the problem with using too much of energy, we might not still have resonance, and sometimes resonance is good. Anyway. The problem with using a blue laser for raman, for example, is that you might have fluorescence that will compete with raman. If you use a long wavelength, then this problem of fluorescence is eliminated. That is why in the raman microscope we have we do have a green laser, it works on many of our samples.

But red laser is the one that is preferable to use those there, you eliminate the problem of fluorescence that can mess up your Raman signal if the fluorescence is strong. All right, but that was a little bit of digression. There has come back to our main point of discussion. He-Ne can give you different wavelengths, but the same He-Ne laser usually would not give you all the wavelengths. If you want a 3391.3 nanometer laser.

You have to make a dedicated 3391.3 nanometer laser a 632 nanometer laser will not give you the other wavelengths. Why is that? So, let us see if you can understand if you can arrive at the answer of this question by the end of this module alright. So, now, the thing is the way it works is that the first thing that this electric field does is it ionizes helium neon it strips the helium and neon atoms of their electrons typically 1 electron.

So, the ions are produced He+ any Ne+ that is what we work with. So, that is the primary preparation of the species that are going to aim it. Secondly, what happens is you produce the electrons you are not really given Electrons just the escape velocity, you have produced high energy electrons that move at very fast speed. So, these electrons collide with ions and then transferred their energy to them alright.

So, remember when we discussed lasers earlier, we said that you can have different kinds of pumping. One way of pumping a laser is we are using another laser optical pumping, here, we are not doing that we are doing electrical pumping. Right. So, it is important to understand the mechanism. So, what you do is you produce high energy electrons, which collide with ions and transfer their energy to them to produce ions in their higher electronic levels.

So the second stage what happens is and energy transfer takes place from helium + to Ne+ and that is why you have to use a mixture of helium and neon. Remember, 2 level system will not give you lasing you need 3 levels, you need to have population inversion. This population inversion is achieved by taking helium in excess, getting it energized, and then getting that energy transferred to neon, which now has energy levels that are suitable to give you wavelengths that we just mentioned here. I will show you the energy level diagram, then hopefully it will become a little more clear.

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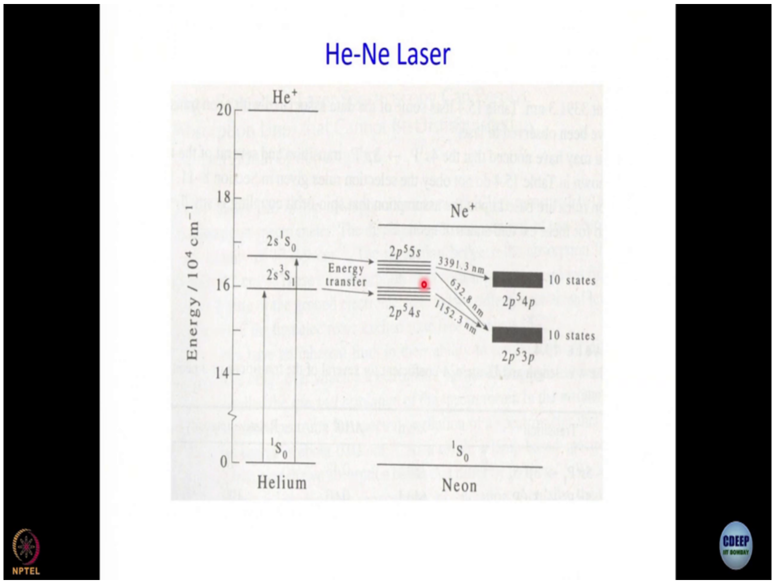

This is once again from my McQuarrie and Simon is book, the energy level diagram of He-Ne laser. See what we have here we have helium, we have neon, this is the grounds electronic state singlet S0 state. This is a triplet S1 state, this is a singlet S state. All right. I do not know why S0 is written there? It should have been written something else but let us not worry about that. Well, this S not really singlet and triplet. This has got to do with this term symbols. So, your triplet state in your singlet state and the meaning of 2s here is that what is the electron configuration of helium 1S2 and helium + would be 1S1.

So, that electron has gone to 2s. So, that way you have produced this. So, now, it is fortuitus is absolute I mean no control over this it is just that it happens that these excited states are closing energy to some excited states of Ne+. This is not by human design. It just happens. So, when the energy gets transferred, it is very easy to populate these levels 2p5 4s and 2p5 5s. What is the meaning of 2p5 4s and 2p5 5s what is the electron configuration of neon + ground state? 2p5 only 1 electron is lost. So, what you see here is that electrons have been promoted to 4s and 5s levels, the high energy transitions.

So, this way what happens is you populate this and then you have other levels nearby and this is why lasing action is so easy to see lasing is not taking place between this place and the ground state that energy would be very high energy difference. Rather, there are many states there are 10 states each have to be 2p5 4p or 2p5 3p you understand what I am saying right. So, now that 1 electron is in 4p or 1 electron is in 3p, these are energetically close to this and these are also higher energy states right, not ground state. So, what will be the population of these 10 states or these 10 states usually zero right.

Very high energy right compared to the ground state, these states are all at very high energy levels. So, population is 0. So, that is why if you have even 1 Ne+ ion in this state population inversion is achieved between this and this or this and this if you have 1 Ne+ in 2p5 4s population inversion is achieved between 2p5 4s and 2p5 3p right and that is where you can get lasing and that is why you get continuously wave lasing right, because the final state to which the system goes as a result of the radiative transition, that state is has a population of 0 almost always.

So this is very much like your four level system. And here you get a CW output so He-Ne lasers that you have are all continuous wave lasers. Similarly, if you now go and see Argon laser, you can understand whether you expect it to be CW or pulse whether you expect 1 line or many lines. If you see Nd-YAG laser energy diagram, I think you will be able to follow after this discussion. So that is why before going into more complicated topics, it is better to discuss He-Ne laser at least once.

So, that is right, because before going there, it is easier for them to have nonradiative deactivation Now, and I mentioned 3 lines, you might see that those 3 energies actually all mentioned here, if it goes from 2p5 5s, to 2p5 4p, these 2 are very close to each other. So, the energy is 3391.3 nanometer 2p5 4s 2p53p, you get 1152.3 nanometer. 2p5 5s to 2p5 3p 6302.8 nanometer. Also there's something else for the lower levels.

This radiative transition is not all that favorite transition moment integral is not does not have a very large value. So, it is to be honest a serendipity that this helium neon mixture has all these properties that allow us to make a laser out of them. But it is important to take the mixture, if you just take neon it may not be so easy. There are many competing pathways perhaps because there is no guarantee that These 2 levels really populated to a very large extent.

If you just take helium, of course it will not work. So it is a little serendipitous, but then it works. So does anybody know when helium neon laser was introduced? Helium neon was 1 of the first lasers to be introduced it 1961 or 62? Something like that long ago. All right, even now, many times you will see that you might think that now diode lasers are there. Why do you want to work with helium because, 1 problem of helium neon laser is that they go bad because you are working with gases and you are working with something like helium.

Which wants to leak out of the vessel all the time. If you do it is really high. So after a while, helium neon lasers cannot be used anymore. Diode lasers have much longer time. So in many applications He-Ne lasers have been replaced by diode lasers however, The 1 good thing about He-Ne laser is that usually the modes are very nice when I say modes I mean transverse modes. That means if you look at the laser on a piece of paper.

It is a perfect circle and the intensity distribution is perfectly also. So, especially for microscopy applications many people still prefer this. There are several other applications as well, but it is usually a low power He-Ne laser you do get high power He-Ne lasers as well. But if you want to go to high power, Nd-YAG would be a better choice. He-Ne is good to give you red or infrared light in moderation. So that is what it is. Now, from here, when we go to pulse lasers 1 thing that happens, other than getting small pulses which are useful anyway, is the amount of energy you pack in to every pulse.

That is a very major difference between pulse lasers and continuous wave lasers. So, before we start talking about how to make pulses, let us do this simple calculation, which I have made up the numbers to suit our titanium Sapphire laser. And since I made them up, it is very possible that I have gone wrong somewhere or the other. So you people would better do the calculation as we go along. But roughly, this is there in McQuarrie and Simon is book for Nd-YAG laser. So what we will do is for our Ti-sapphire laser, I think we can more or less.

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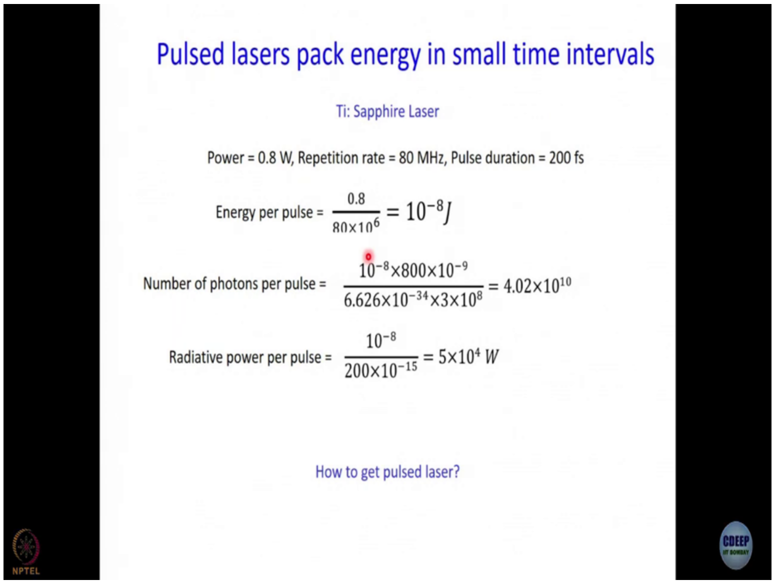

Agree on these parameters. Ti-sapphire tsunami laser that we have in our lab, right, power 0.8 watt, repetition rate is 80 megahertz. Pulse duration is 200 femtosecond. When I say pulse duration 200 femtosecond I do not mean full width half maximum. I mean, 0 to 0. Roughly 0 to 0 and the 0 digital will become important very soon in some other discussion All right. So, this is what it is. Can you calculate the energy per pulse power is given 0.8 watt what is the meaning of 1 watt? Joule per second so all I am asking is you have 0.8 joules per second and how many pulses per second 8 into 10 to the power 6 pulses per second very simple arithmetic.

Total energy per second is known .8 joule. number of pulses per second is 80 into the 10 to the power 6, I am asking you the energy per pulse is which means energy in 1 second divided by number of pulses per second. How much does it come to? Helium cannot be - 8 is it -? This energy per pulsee, energy per pulse is 10 to the power -8 joule. Is that right now I will ask you another question? Can, you tell me what is what is the number of photons per pulse.

What is the energy of 1 photon energy 1 photon? Well, 1 thing I have not written here is which wavelength right let us say 800 nanometer for 800 nanometer photon what is the energy? h nu which is hc by lambda right. So, this is also very simple I know the energy per pulse, if I divided by energy per photon, then I get number of photons per pulse that is us as you will see is going to be a large number. So 10 to the power - 8 divided by h, multiplied by c.

And then in the numerator, you are going to get lambda, which is 800 nanometers. I am asking for number of photos were pulse 10 to the power -8 multiplied by 800 nanometer means 800 into 10 to the power - 9, there is a numerator denominator is going to be what is the value of h 6.626 into 10 to the power - 34 in SI units multiplied by 3 into 10 to the power 8 do not make it 10 to the power 10 like what I did few modules ago, 4 into 10 the power.

How can number of photons be 10 to the power -10. so - + are very important. You do not get them confuced. Very large number of photons, Very, small number. So it comes through. So this is the number of photons you pack into 1 pulse. The reason why we are doing this is that very often we do an experiment or we learn something. But if you do not know the numbers at least once, if you do not work the numbers, at least once.

We do not really get the feel of what we are dealing with. So it is important to get a feel of what we are dealing with. This is what we are dealing with in the laser that we have in our lab and that we have demonstrated during will not open it up yet. Now we are going to do it in a little while, not today, after a few days. So there every pulse we think 200 femtoseconds is such a small time, in that small time. You are packing 4.02 into 10 to the power 10 pulses.

So now think, this light interacting with some matter for a long time, there is nothing then there is invasion within 200 femtosecond this 4 into power 10 number of photons are available to bombard the system over all the molecules that are there. And that is something that can do things that cannot be done using a CW laser. So, what we are depending on here is large number of bombardments in a small amount of time.

So in chemical kinetics, we have hopefully studied things like cage effect and encounters. So what happens is you put things in a cage, then they hit each other many times and the reaction takes place. Here also, what we are doing is we are packing a large number of photons in a small time, so it can actually get things done. So that is the first thing that I did like us to understand today. But it is not over next thing which is perhaps even more impressive, in case we have not got the picture completely it is can we calculate the radiative power per pulse.

We know the power that we measure by power meter as the average power that is 0.8 watt 800 milli watt, right? Not much. Now, what I am saying is that but what you see there is for most of the time nothing is there, you are seeing an average. So, how many pulses are there for how much time I am not reading this but you can work out for how much time do actually have the light on in 1 second.

How many passes are there 8 into 10 to the power 6 and each person saying is 200 femtosecond so what we are for how many seconds within 1 second, is the light actually on 200 into 10 to the power - 15 multiplied by 80 into 10 to the power 6 So, how many times 80 say hundred into 10 to the power? hundred into 10 to the power 6 multiplied by 200 into 10 to the power -15 how much does that come to? Does it come to microseconds so very small right.

So, this is sort of calculating the volume occupied by molecules of an ideal gas right, only occupied by the gases at 22.4 liter if it is 1 mole volume occupied by the molecules is really very small right? Nanometer cube or something. So, the light is actually on for a very small time, but whatever happens within that time. So, now what I am trying to say is, if you now consider that time for which the light is on and leave out the dark period.

Then what is the power that you get per pulse can we do that radiative power pulse energy per pulse is 10 to the power - 8 and time for pulse we are saying 200 femtosecond very easy 10 to the power 4 for what is it? 5 into 10 to the power 4watt? So that is very high is not it? So that is why when you use a femtosecond laser it is very easy to damage your sample , that is why you can do things like laser cutting using this, that is a good thing.

And that is why, if you remember in our FOG experiment, we keep the sample rotating. Why? Because the power that the molecules feel when the light is on is not 800 milli watt. it is 5 into 10 to the power 4 watt, that is a lot. So molecules will get fried very easily. If you do not rotate the sample. So, very often we might not understand this. So, that is why we thought we go through this calculation once I meant to do it in the last module in time did not permit, but at least today we have been able to do it.

So, it is important to understand that when you use a pulsed laser, even though the light itself might not look very strong for the time when it is on the force is I mean the power what is the right word to use here, power is really high. We will not understand it unless we do the statements. That is why I wanted to do it once. But finally, what we have learned is in pulsed laser, we are essentially subjecting our sample to very high power for short periods of time.

And then of course, whatever application is there that comes. Now we come to the question all that is very great, but how do we get pulsed laser, that is what will take in the next module and to do that will need to understand something called longitudinal mode.