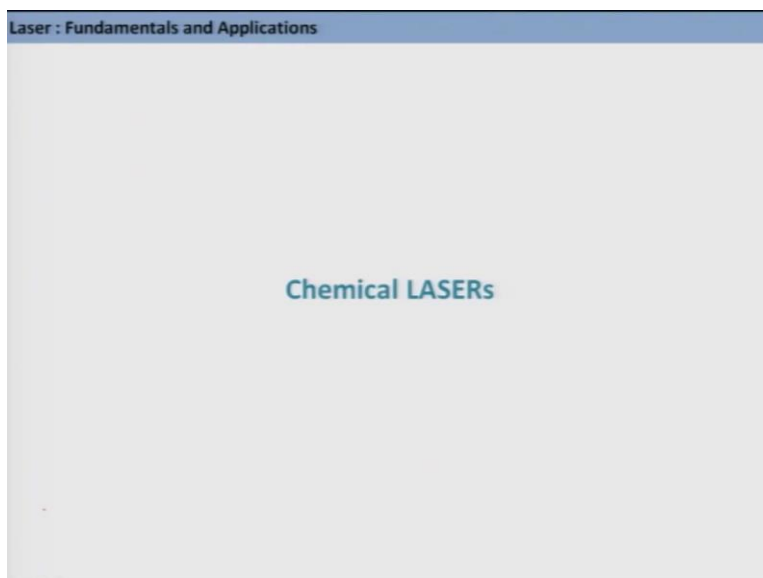


Laser: Fundamentals and Applications
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Lecture – 27
Chemical and Dye LASERs

Hello and welcome today is the second day of the sixth week of this course and we were discussing about different types of lasers and today we are going to start with chemical lasers.

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So, as a name suggests chemical laser, it deals with some chemical reactions which ultimately leads to some products which provides the states that ultimately can give laser action. So, two different types of chemical lasers we will discuss; one is iodine laser and the second one we will talk about an excimer laser. So, let us start with iodine laser. So, first let us look at the you know the system. So, iodine laser it deals with you know the energy levels of iodine atoms. Now getting only iodine atom is difficult. So, you have to do something that you produced iodine and then you exploit the energy states of that iodine atom that is produced in either excited or ground state whatever and then get your lasing out laser output. So, this is what it is done.

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Iodine LASER

- Population inversion is created directly through an exothermic chemical reaction or other chemical means.
- The driving principle involved in the iodine laser, is the photolysis of iodohydrocarbon or iodofluorocarbon gas by ultraviolet light from a flash lamp.

$$C_3F_7I + h\nu_p \rightarrow C_3F_7 + I^*$$

Excited state level in atom

$$I^* \rightarrow I + h\nu_l$$

C-I bond dissociation

$$C_3F_7 + I + M \rightarrow C_3F_7I + M$$

$h\nu_p$ = pump photon
 $h\nu_l$ = laser emission photon

$C-I$
 \downarrow
 $C \quad I$

C_3F_7I , is stored in an ampoule and introduced into the silica laser tube at a pressure of between 30 and 300 mbar.

So, the propagation inversion in this case is created directly through an exothermic chemical reaction or you know or it can be any other chemical mean. So, what do you do? You take a you know a compound containing iodine. So, for example, here we have taken C 3 F 7 I. So, for that matter you can take fluoro iodo carbon or you know iodohydrocarbon. Now this molecule you have to excite, so that it gets dissociated. So, your aim is finally, is to have the C I bond dissociation. So, you have to go from here to C and I. So, this C F 3 sorry C 3 F 7 I is excited by some photon.

So, that is shown here $h\nu_p$ is the pump photon and this pumping will give rise to the dissociation of this molecule and it will create two different species C 3 F 7 and I star. And if you look at the energy level diagram you will see that that first you know absorption of light it takes the molecule beyond the dissociation limit and when I talk about this dissociation limit essentially I am talking about C I bond dissociation limit. So, you know C F bond can dissociate C F also, but that requires totally different amount of energy. So, the energy that is provided it will break only the C I bond because C F bond needs much much different energy compared to C I. So, once this C I bond is broken then the iodine atoms that can be produced either in its ground state or in excited state. So, here this you know P 3 by 2 is the ground state while P half is the excited state, this picture is not very clear. So, I apologize for that, but this is the P half system and ground state is P 3 by 2.

Now the iodine can produce can be produced in either of the states, most of the time you will not be able to control it like you know control the quantum yield of I star. So, the iodine in the excited state is written as I star. So, this is the excited state iodine atom corresponding to P 3 by 2 sorry P half. So, you cannot control how much P half or P 3 by 2 will be produced, but you know different molecules will produce adding atom due to C I bond dissociation with different quantum mean. So, you will choose a particular molecule which has a very high quantum will for I star.

So one of such molecule is C 3 F 7 I which gives this I star in high you know proportion at least decent proportion. Now this I star is a metastable state. So, the you know initial pumping will create this iodine molecule in the excited state that is it will form I star and more and more I star will keep accumulating. So, if you know consider these two levels this level will keep hosting I star molecule, while this level is you know nearly an unoccupied.

Now this P 3 by 2 level that is the ground state iodine, it decays to this level through the combination. So, you break the C I bond. So, the other fragment is also there and this guy is also there. So, they are within the system right. So, they can again meet and recombine. So, the moment they recombine what they will do? They will come down to this state right. So, they can you know you know absorbed the you know, so this particular transition will give me my laser output and the wavelength corresponding to this laser output is 1.315 micron.

So, this is the whole procedure given in this reaction scheme. So, you essentially have this one, this particular step responsible for the laser action. Now some practical consideration this molecule C 3 F 7 I is stored in some small ampule and it introduced to the laser in front of laser and the pressure is kept between 30 to 300 milli bar and you ultimately achieve the you know lasing action.

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- Laser action takes place between excited metastable $^2P_{1/2}$ state and the ground $^2P_{3/2}$ state of atomic iodine this results in narrow linewidth output at a wavelength of 1.315 μm .
- An important advantage of the iodine laser is the fact that the active medium is comparatively cheap and, hence, available in large quantities.

So, I have already discussed this part. Now what is the advantage of iodine laser? So, the advantage is the fact is in the fact that the active medium is comparatively cheap right. So, this halides are quite abundant. So, compared to this in that gaseous, it is lot easier to get this molecule and so therefore, it is you know it can be cheap compared to other active mediums that we deal with. The next that we are going to talk about is excimer laser. So, this excimer laser or for that matter this excimer, what is this excimer? If I expand this term excimer it says, excited state timer. If it is like dimerization of the two same unit then it is an excimer.

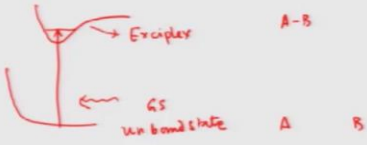
If the two components are different then this is like a complex formation at excited state. So, this is called excited state complex or excite plex. So, an excimer is an excite plex essentially, only thing is that the constituents are same and in excimer laser, this exciplex is the active medium. Now this is excite plex is excited state complex; that means, that it does not exist in ground state. So, this complex is formed only when this components are excited, then they do reaction and then they form the complex, but in the ground state they are you know not together they do not have any bond between them. So, if I look in to the energy a potential energy diagram then it will look like the ground state, there is no bond.

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Excimer LASER

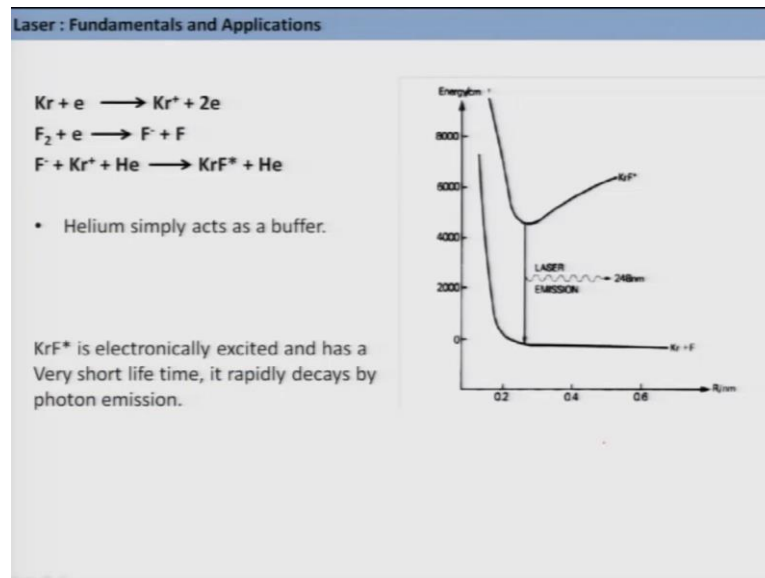
- The active medium is an *exciplex*, or excited diatomic complex.
- The crucial feature of an exciplex is that only when it is electronically excited, it exists in a bound state with a well-defined potential energy minimum.
- The exciplex is generally formed by chemical reaction between inert gas and halide ions produced by an electrical discharge.



So, if there is no bond then the ground state is not a bound state right. So, the you know it will be it will look like a dissociative state or unbound state and unbound state looks like this.

So, this is my ground state for this system and when I excite them. So, I bring in a photon and the molecules here, they get excited and there they form the complex; that means, the moment they are forming complex; that means, they have a bound state and that is given by this. So, this corresponds to my exciplex, it can be excimer also and this is ground state which is unbound state which means two constituent A and B; they are two separate entity here you have A B. So, this is the concept of exciplex. So, how this exciplex can be formed? Exciplex can be formed by giving electrical discharge. So, suppose I have two different gases and I you know put electrical discharge then this two molecules will be you know excited and form a you know a complex and that is my exciplex.

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So, let us look at this problem a little bit in detail taking some example. So, let us take an example of a system comprising of krypton and fluorine. So, krypton and fluorine they do not react in the ground state, but when they are excited. So, when they are bombarded with this electron. So, due to electron impact the krypton becomes krypton plus and fluorine becomes F minus. Now this F minus and K r plus they are excited state and at that condition they are forming this complex K r F and this is you know shown in in this diagram.

So, this is the energy level diagram of the ground state of krypton and fluorine where they are not interacting while, there they are forming and forming a complex and they are already at an excited state. Now this excitation was created by electric discharge right. So, due to electron impact this is formed. Now they will not be stable here right that is not in stable geometry, it is not a ground state there is an excited state. So, they will come back, when they come back they again are dissociated and when coming back they will emit the photon and that is my laser output and that corresponds to 248 nanometer which falls in the ultraviolet region.

So, this excimer laser particularly this krypton fluoride laser is a good source of UV light. Now in krypton fluoride laser you also find helium, now helium in this particular case does not play any role like you have seen earlier helium neon laser. So, there you know helium and neon both are playing some role, but here helium acts just as a buffer.

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- Since this is an unbound state, hence the force between the atoms is always repulsive, the exciplex molecule then immediately dissociates into its constituent atoms.
- This state never attains a large population, and a population inversion, therefore exists between it and the higher energy bound exciplex state. In the case of KrF the krypton and fluorine gas is regenerated.

$$\text{KrF}^* \longrightarrow \text{Kr} + \text{F} + h\nu_l$$
$$\text{F} + \text{F} \longrightarrow \text{F}_2$$

- The laser can be operated continuously without direct consumption of the active medium.
- Excimer lasers are superradiant and produce pulsed radiation with pulse durations of 10-20 ns and pulse repetition frequencies generally in the 1 to 500 Hz range.
- Pulse energies can be up to 1 J, with peak pulse power in the megawatt region and average power between 20 and 100 W.

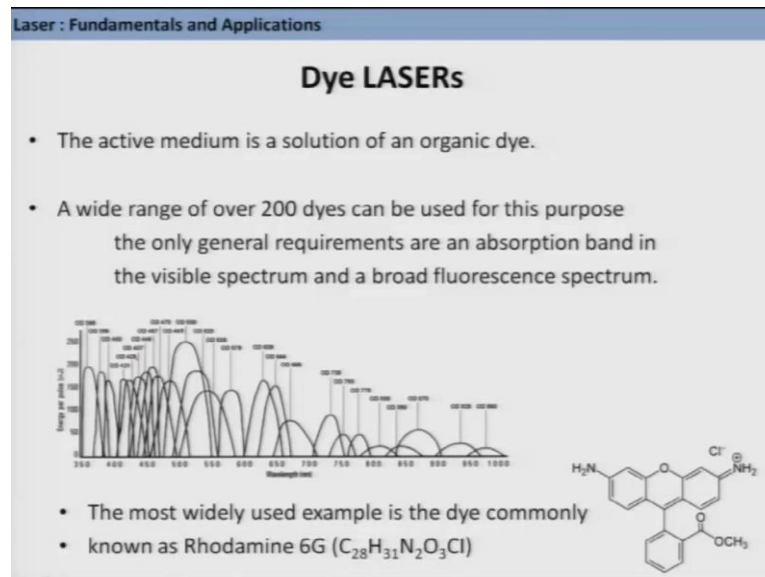
So this part we have already discussed, now a few important aspects of this krypton fluoride excimer laser that this laser can be operated continuously without direct consumption of any active medium; that is probably an unique thing. So, far whatever we have discussed all the time I have been drawing like you know a cavity and putting an active medium here you do not have an active medium to start with. You create an active medium by giving electric discharge which automatically you know breaks down giving a laser output and this excimer lasers are super radiant and they produce pulse radiation with a duration of 10 to 20 nanosecond and repeat can be 1 to 500 hertz and the pulse energies can be up to a joule and the peak power can be a megawatt and the average power can be 20 to 100 watt.

Now these are not very large number, but if you think about a source giving ultraviolet laser photons these numbers are quite good because the UV radiations are already highly energetic frequencies right. So, the next thing that we will discuss is one of the most important lasers which is Dye Laser and in the in a very you know first class while you started discussing about this different types of laser which you know put this laser in a different category. Now Dye Laser as the name suggests the active medium is constituted by a solution of an organic dye.

So, which particular dye you use? The good thing is that there are you know many many dyes that you can use for this purpose and how many? I mean it is like 200 or even much

more than that actually with every passing day you get you know a newer time which has certain properties which are better than their you know predecessors. So, you can have different dyes fulfilling your purpose the.

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But it is not that any time you pick up it can give you laser action. So, you need to have you know certain condition fulfilled as we know for any active medium that one can use for laser. Also this you know there is a general requirement that these dyes which we can use for laser action they should have an absorption band in the visible or near I R range preferably in the visible range and they have a you know fluorescence band which should be quite broad ,then we can you know exploit it quite well. Now here I have shown a figure which shows that what are the different regions of the spectrum that we can cover using dyes x active medium that is in dye lasers. So, we can see it goes all the way from near UV to near infrared. So, you can achieve any wavelength between this range three 50 to 11,000 nanometer using dye lasers. So, all you need to have is the right time and the right pumping source.

So, the most famous dye that is used in dye laser is probably rhodamine 6 G, this is a commercial name and the molecular formula for that is given here and this is the molecular structure of rhodamine.

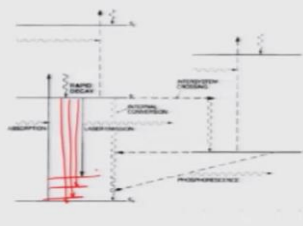
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In solution, the corresponding energy levels are broadened due to the strong molecular interactions of the liquid state, and they overlap to such an extent that an energy continuum is formed for each electronic state.

the absorption of visible light results in a transition from the ground singlet state S_0 to the energy continuum belonging to the first excited singlet state S_1

This is immediately followed by a rapid radiationless decay to the lowest energy level within the S_1 continuum



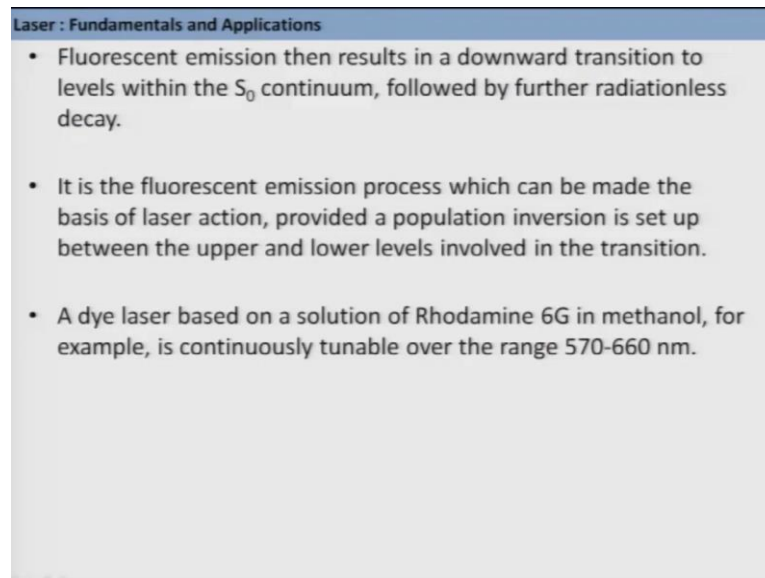
The diagram illustrates the energy levels and transitions for a dye laser in solution. It shows the ground singlet state S_0 and the first excited singlet state S_1 . The S_1 state is represented as a continuum of energy levels. The diagram illustrates the absorption of light from S_0 to the S_1 continuum, followed by rapid radiationless decay to the lowest energy level within the S_1 continuum. It also shows the emission of light from the S_1 continuum back to the S_0 state.

So, earlier we mentioned that like solid state lasers, this dye laser also gives much broader fluorescence spectrum and that is you know good in many senses and this broadening takes place due to the interaction of these molecules with the surrounding environment and because they are you know freely moving around.

Now, this broadening can be you know compared to a continuum state. So, what happens in case of you know the excitation of a dye solution? So, a visible light will take the dye molecule from ground state S_0 to the singlet excited state S_1 and from there from this S_1 , there will be rapid decay to the lowest vibrational level of this S_1 continuum and from there it will you know emit and this emission can be used as my laser.. Now just I think previous class of the one earlier to that we said that this emission can take place from the lowest vibrational level of the excited state to different vibrational levels of the ground state. So, you can see that it can come back here, it can come back here, it can come back here and here. So, all this corresponds to different vibrational levels.

So, you can get an overall broad spectrum and because it is a broad spectrum I can do something to select my you know output wavelength and I can have a tunability.

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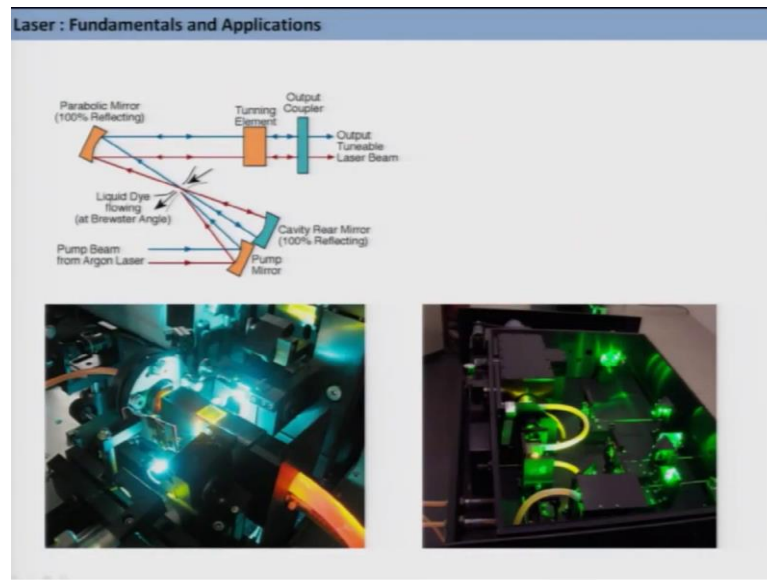
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- Fluorescent emission then results in a downward transition to levels within the S_0 continuum, followed by further radiationless decay.
- It is the fluorescent emission process which can be made the basis of laser action, provided a population inversion is set up between the upper and lower levels involved in the transition.
- A dye laser based on a solution of Rhodamine 6G in methanol, for example, is continuously tunable over the range 570-660 nm.

So, this is actually we write here explicitly that the fluorescence emission which is resulted to due to this downward transition from S_1 to S_0 is essentially a transition to a continuum because we have several vibration level at S_1 , S_0 . Now you utilize this particular fluorescent emission you know to act as the lay in as a laser output and of course, this is only possible when there is a population inversion creation is there.

So, if it is possible to create population inversion, it will act as new lasing system otherwise it will not. For an example, a dye laser based on rhodamine 6 G dissolved in methanol it continuously tunable over this range. So, what is this tunable? Whenever we say that this is the range of tunability for any particular blazer, what we mean is that the emission spectrum is having this particular range and I can select the particular wavelength and I can achieve a tunable laser. So, so here the spectral line width is really broad and I can select different wavelength within this range and get you know at overall tunable laser system.

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Now, let us have a look at the experimental aspect of this. So, how this is achieved? So, the dye laser is taken in a sealed you know in transparent container, so either you know glass or cores container and this is excited by either using a flash lamp or using another laser. So, most common excitation for dye laser is a pumping by a solid state laser like Indiac laser in the visible. So, India we said like you know it gives like 1064 nanometer as fundamental light once you frequency double that particular 10 64 nanometer using you know non linear optics, you get 532 nanometer. And that 532 nanometer laser light is used to pump that dye that we are talking about. Say for example, rhodium 6 G in methanol and the emission from this particular you know excitation is now taken and it is and I cover you know optical cavity is constituted by mirrors and we create population inversion and we get ultimately the laser output. So, this is what it is shown here.

So, you bring the you know pump beam from this argon ion laser here and you hit that dye cell which is kept right here, all right and the fluorescence is shown by this green light. So, that is you know that travels back and forth between this output coupler and this high reflecting curved mirror and you can get the output from this output coupler. On your left down there is an actual picture of an dye laser and a particular the region where the you know dye cell is kept is shown here. So, the dye cell is kept here in this square kind of qubit. Now one thing is very essential which is not shown explicitly here, but it is you know mentioned that the liquid dye is flowing. So, actually you can see that there are this tube which helps the dye to circulate. So, the dye solution does not stay

stagnant in that dye cell, but it you know continuously flows. Why this is necessary? Because the organic dyes are well known to undergo photo bleaching; if they are continuously pumped; so, in order to avoid the degradation of this time molecules you need to remove the excited you know dye you know very soon so that we can avoid the degradation photo degradation.

So, this dye solution is continuously flown and if you want to get much higher output then what you can do is you can you know further amplify this output that you get from this oscillator and you can use a grating to select the particular output that you want because this process spectrum is quite broad and you would like to have a narrow band light coming out of your laser and also you want to have it tunable. So, if you have a grading then you can select a particular wavelength out of that spectral window that your dye is going to give you and get a narrow band, but tunable laser.

So, so we have you know discussed in quite detail about several different lasers, solid state lasers, gas lasers atomic and molecular gas lasers ion laser chemical lasers and also this dye laser. So, with this we will end our discussion about different types of light you know laser system in you know next few classes. So, whenever it requires if we are dealing with some other type of lasers then, then and there we will discuss about that particularly lasers. So, we will come back again in the following class and I thank you for your attention.