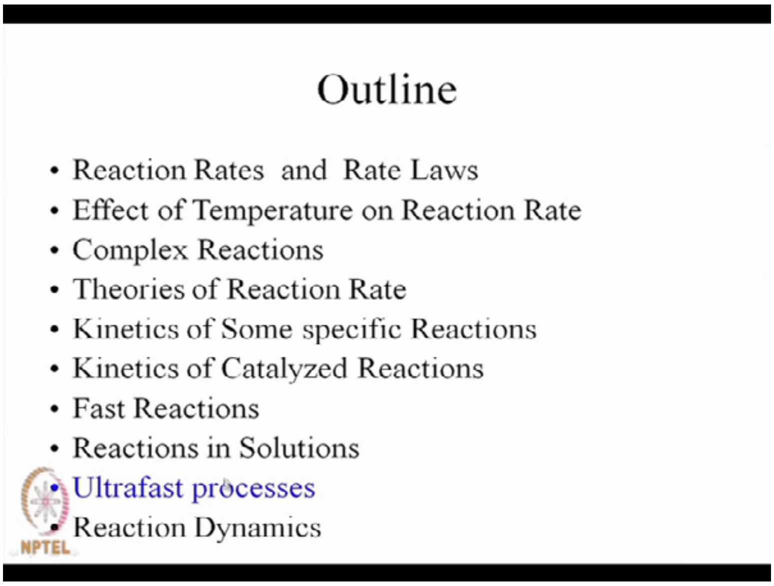
Rate Processes

Prof. M. Halder
Department of Chemistry
Indian Institute of Science, Kharagpur

Lecture No # 28

Ultrafast Process

(Refer Slide Time: 00:35)



Outline

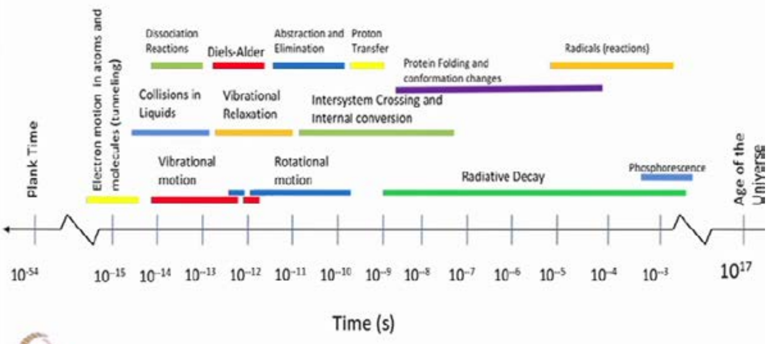
- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

Good morning everybody. Welcome to the class of I mean the series of lectures on rate processes, today I am going to talk on ultrafast processes. I will just give you brief introduction of this topic. Now that is ultrafast processes in chemistry, now in our last two lectures we have talked about this electrode reactions that is redox reaction, which is going on at the electrode surface. That is when a metal piece is dipped into a solution containing electrolytes then various things happen and if you pass electricity then you knows various reactions may take place depending on the voltage then current density etc etc.

So, under that heading one aspect which we have not talked about if time permits later on maybe we can take up that is corrosion maybe we will have a very brief introduction on that also. Now, we have talked about fast reactions none now various methodologies maybe adopted to detect you know the rate for those fast reactions like stopped flow then plugged flow then relaxation methods. So, these are used to prove fast kinetics, now yet another you know time domain is there which is faster than these fast reactions, which occurs maybe in less than a nanoseconds that is maybe in the picoseconds times that is 10 to the power minus 12 seconds or maybe in the femtosecond time scale that is 10 to the power minus 15.

Imagine 10 to the power minus 15 second and our persistence of vision is one tenth of a second. So, how fast imagine how fast those processes are taking place in molecular systems. So, that we are just going to talk about you know not in great detail, but we will just give you brief introduction, because of the limitation of the scope. We may not be able to go deeper into the subject.

(Refer Slide Time: 03:30)

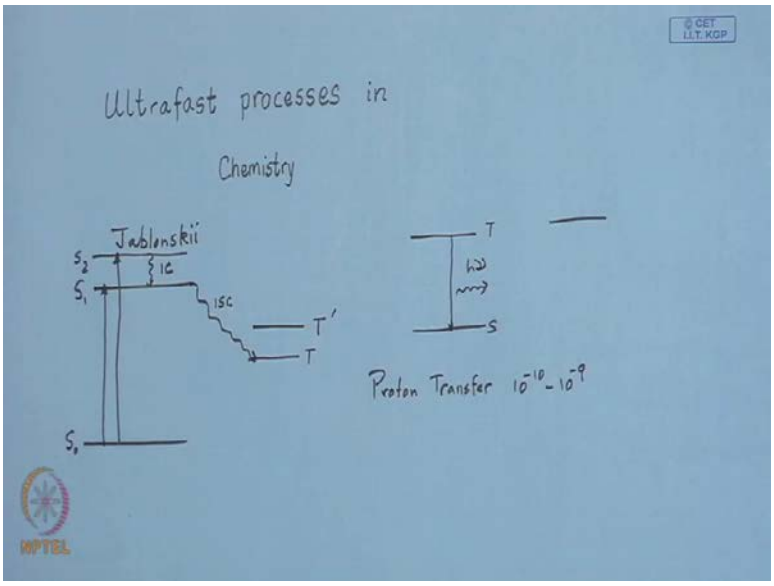


Timescale of various processes and reactions related to chemistry

Let us look at the time scale of various processes and reactions related to chemistry, you see it starts from you know 10 to the power minus 54 to 10 to the power 17. That is the age of the universe and 10 to the power minus 54 that is the plank time you see in between. It is you know starts from 10 to the power minus 15 minus 14, 13, 12, 11 and up to 10 to the power minus 3 or maybe when longer that is second 10 to the power 0. So, just look at the various processes there are various processes and depending on the time scale of observation. You know we can classify first let us have a look at you know let us start from the slowest one in under this classification that is phosphorescence.

What is phosphorescence? It is also a radiative process and radiative process which occurs and you know between the states of different multiplicity that is suppose you know if there is a radiative transition that is occurring between say triplet to a single or maybe singlet to triplet maybe some singlet to another that is there is a change in spin multiplicity, while the transition is taking place along with emission of radiation h nu.

(Refer Slide Time: 05:16)



Ultrafast processes in Chemistry

So, this is called phosphorescence and it is a very slow process that is time. If you think of the time required for the process to be completed, it takes you know maybe even seconds it starts from millisecond less than millisecond to maybe up to seconds in certain cases. When you use rigid matrix, solid matrix or maybe if you go to a very low temperature maybe 77 Kelvin, that is liquid nitrogen temperature. You can see observe phosphorescence maybe visible phosphorescence or maybe may be any other infrared phosphorescence. So, this is a very slow process then comes the radical reactions, now radical reaction that occurs you know in the time scale of 10 to the power of minus 3 to 10 to the power minus 5 seconds.

It is more than microseconds it takes time when I talked about this radical pair recombination that is spin chemistry in that case your time scale of observation process mostly comes in the range of microsecond, but sometime it is a little faster maybe several nanoseconds as well. So, radical reactions it spans from minus 5 to minus 3. So, this is also a slow process although, if you think of observation by eyes it is because 10 to the power minus 5 to minus 3. Only thing that you can observe phosphorescence if it is you know life time is of the order of seconds, otherwise it is not possible. Because of the limitation of our eyes because of the persistence of vision. If you think of there is a huge range that starts from maybe more than a millisecond down to a nanosecond which is encompassed by a radioactive decay a huge range minus 9 to minus 3 even more.

Then in violet color you see it is protein folding and conformational changes with time it is again a red process protein folding means biomolecules. They biopolymers you know specific sequence of a amino acid residues and when these amino acid I mean this biopolymer is present in the in solution phase. So, it is folded in a definitive pattern it has got a folded three dimensional structure. So, what happens is that if you change the fields of the solution maybe you add some additive from outside maybe urea or guanidinium chloride or maybe and then this folded structure gets unfolded or maybe even if you increase the temperature then this unfolding may take place. So, this folding unfolding it takes time.

So, this protein folding and also the corresponding conformational changes that falls in the time scale of the order of nanosecond. A little more than a nanosecond to know the several hundreds of microseconds. So, this timescale is encompassed by protein a folding and conformational change, that is time required to undergo conformational modifications. Beside because of binding of the second substance with the protein what is happening that you know this protein may get folded or maybe get unfolded. Next look at this intersystem crossing and internal conversion, it is also encompassing a huge range maybe minus 11 to a little more than minus 8 or maybe a little less than minus 7.

So, in between minus 11 and minus 7. So, intersystem crossing is basically, if you think of the jablonski diagram which is well known in photo chemistry jablonski diagram. Which you know represents which is a composite form where all the processes probably process can be integrated in a single photograph or a single description. So, this is s 0, s 1. Then maybe this is t 1 or maybe higher states say s 2 maybe there is another t this t prime this is t. So, this is you know absorption this is another absorption this is internal conversion that is from s 2 to s 1 without change in the multiplicity or maybe from here to here non radiative de excitation from singlet to triplet. There is a change in multiplicity.

So, this is called the intersystem crossing. So, this is inter system crossing and internal conversion these are all non radiative that is de excitation to another state giving rise to heat not giving rise to photon. So, it is called the non radiative de excitation. So, non radiative de excitation of these two kinds that has got time scale of observation of the order of 10 to the power minus 11 to 10 to the power minus 7 in between that. Again if you think of proton transfer process it is in the range of minus 10 to minus 9 in the range of minus 10 to minus 9. So, proton transfer process 10 to the power minus 10 to 10 to the power minus 9. So, it is also fast and maybe if you recall the diffusion control limit parallel to that maybe. So, I mean reverse of this you know time is constant.

So, time constant is of the order of diffusion control may be a little different, but in that range now there is a proton transfer falls in that range. Then you know abstraction and elimination reaction these abstraction elimination reactions are quite fast it is minus 12 to minus 10 in this range minus 12 to minus 10 in between this. So, maybe hydrogen abstraction process or maybe elimination e 1 or e 2 like elimination reaction or maybe elimination of some group maybe you have read in organic chemistry.

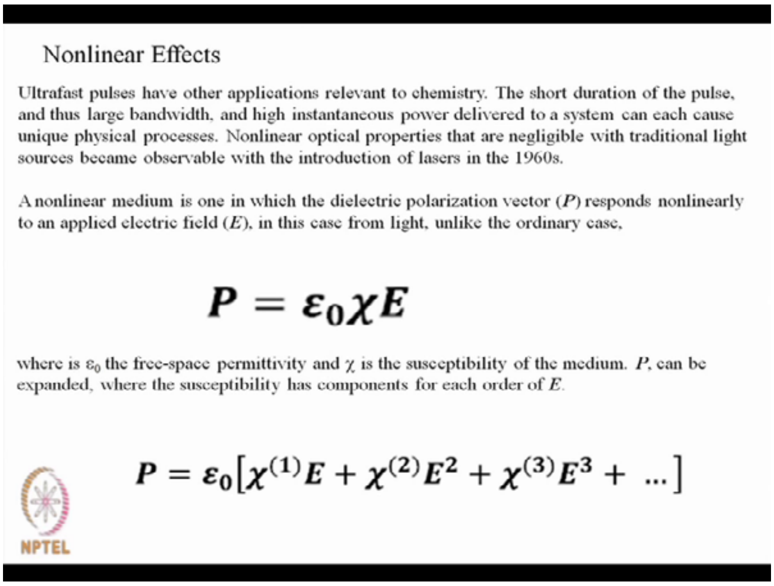
So, that is also very fast in the range of picoseconds to maybe sub nanosecond then there is another thing, which is rotational motion. Rotational motion means if you think of a molecule, this molecule can have various motions and quantized motion. If you think of quantized motion then it has got electronic motion then vibrational motion and then rotational motion translational motion. You know is in spectroscopic trivial, because it is does not represent any quantized motion. So, these are the three degrees of freedom that is electronic, vibrational and rotational degrees freedom is there.

So, rotation is basically like this maybe about the inter nuclear axis or maybe like this or maybe like this depending on whether the molecule is a linear or is a non-linear. So, this rotational motion it is quite fast it is in the range of 10 to the power minus 12 to 10 to the minus 10 a little less or more. So, this rotational motion it takes time compared to other motions like still faster motion that is the vibrational motion. So, vibrational motion is like this supposes you have got water. So, it is doing like this motion or maybe like say this is triatomic system or maybe diatomic system like a diatomic system it is doing like this. So, it is a vibration.

So, vibration is faster you see for rotation to occur this molecule I mean atoms. This atom or that atom has to change it is position while doing that, because it does not recur rotation means this atom maybe transferred to here I mean by this motion so; that means, there is a huge change of position from here to here, but for vibration it is not that much therefore, vibration takes less time compared to rotation. So, vibrational motion it is of the order of you know little more than 10 to the power 14 to 10 to the minus 12 in picoseconds range vibrational relaxation is in between vibration and rotation vibrational relaxation means why vibrational relaxation it loses. It is energy and when gets excited to high vibrational level then it does like this.

So, energy is dissipated and thereby it goes to the lower energy level. So, that is called the vibrational relaxation. So, system is relaxed to a lower state. So, vibrational relaxation takes in between vibrational motion and rotational motion. There is another reaction which is called diels-alder reaction. So, diels-alder reaction it is another kind of reaction maintaining the vital symmetry, this reaction is also like say the typical example is a diene and dienophile.

(Refer Slide Time: 17:33)



Nonlinear Effects

Ultrafast pulses have other applications relevant to chemistry. The short duration of the pulse, and thus large bandwidth, and high instantaneous power delivered to a system can each cause unique physical processes. Nonlinear optical properties that are negligible with traditional light sources became observable with the introduction of lasers in the 1960s.

A nonlinear medium is one in which the dielectric polarization vector (*P*) responds nonlinearly to an applied electric field (*E*), in this case from light, unlike the ordinary case,

$$P = \varepsilon_0 \chi E$$

where is ε_0 the free-space permittivity and χ is the susceptibility of the medium. *P*, can be expanded, where the susceptibility has components for each order of *E*.

$$P = \varepsilon_0 [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ ...]$$

So, you have got a diene and a dienophile. So, this will give rise to typical mechanism as if this is, but it is not like a maybe it is better represented by a six membered transition state. So, it is a typical diels-alder reaction. So, diels-alder is in between you know is close to vibrational relaxation time wise and it is also falling in between vibrational and rotational it is of the order of 10 to the power minus 13 to maybe 10 to the power little less than 10 to the power a 11 minus 11. Collisions in liquid it is average number is 10 to the power minus 14 seconds disassociation reaction is even faster compared to your abstraction and elimination reaction it is in the range of course, in the 10 to the minus 14 to minus 13.

Now, electron motion it is around 10 to the power minus 15 in femtosecond time scale this is picoseconds, this is nanosecond, this is microsecond, this is millisecond. So, femtosecond and where electron motion in atoms and molecules and also tunneling. So, I told you that if you think of a molecule then it can have electronic motion it can have rotational motion, it can have vibrational motion. So, these three motions of these three motions electronic motion is fastest compared to vibrational and rotational motion. So, I guess I just given you rough estimate of the time scales of observation of various processes and that is journey from say millisecond to femtosecond. That is means how you can reach I mean not in terms of you know in between what you encounter in between like phosphorescence and electron motion.

What are the other possible motions that fall in between this is in the intermediate time scale between minus 15 to minus 3. So, there are quite a number of processes that one maybe thinking of. So, when it is the question of here what we are going to focus on is the electronic motion maybe vibrational motion as well or various faster motion? So, primarily this ultrafast region maybe somewhere over here. So, maybe minus 12 around minus 12 to minus 15 it is the ultrafast region it is the very fast process. And therefore, if this is a very fast process then you need to of course, to observe this faster events you need to have a very fast detecting system I mean detector or maybe a system which is capable of detecting this faster changing I mean fastest changing processes.

So, that is also a big challenge for these ultrafast processes. So, here to prove this ultrafast processes we have take the help of this light of course, light because it is speed is huge and maybe in one nanosecond it travels about one foot . So, by you know in that case you can generate the time lag between two successive photons or maybe two pluses by changing the optical path. There is a path which is traveled by the light beam between maybe one mirror and that another mirror. So, that is the optical path in between that. So, from this mirror reflected to this mirror if and then it is reflected to.

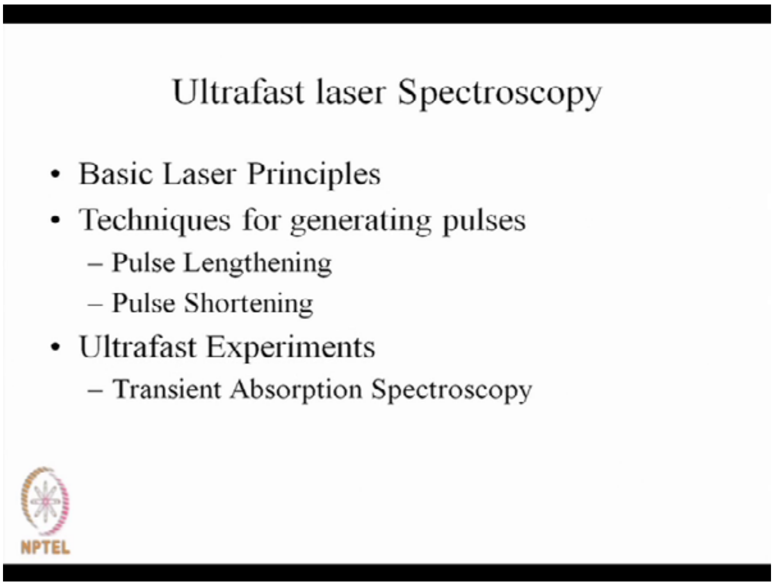
So, this is the optical path between these two points. So, we have to take the help of lasers, now it is in that case you know this faster process here. There is a predominance of non-linear effects and ultrafast pulses have their applications relevant to chemistry, now when it is you know duration is very short. So, you know if you think of this energy time uncertainty Del e Del t is of the order of each cross. Then if this time uncertainty is small that is if is femtosecond this then energy uncertainty is more so; that means, short duration of the pulses and it has got a lager bandwidth that is energy uncertainty is more and a high instantaneous power. Which is delivered to the system can cause unique physical and some cases chemical processes as well.

Because peak power is high for ordinary lights or maybe say xenon lamp. Xenon lamp is generally used for doing many spectroscopic experiments although this is intense, but ordinary light or may these lights they are not that intense because it is not a directed beam. So, it is you know this way divergent. So, that is why intensity y it is small, but with the advent of lasers. Now traditional light sources are replaced with laser light. Laser light means intensity that is peak power is high; if it is a pulse laser or even if it is a continuous laser. Since the light beam is I mean all the photons are directed therefore, you know intensity is high. Now a non-linear medium is one in which the dielectric polarization vector P responds nonlinearly to applied electric field in this case from light unlike the ordinary case that is P is basically a polarization vector.

Dielectric polarization is directly proportional to E with E zero if silencer there is the free space permittivity chi is the susceptibility of the medium and for intensity. When intensity is high then it can be expanded to higher power. So, therefore, polarization you know dielectric polarization is very much dependent on the intensity of the electric field. So, if the intensity of the electric field is low then these terms are not that important. But when the moment it is increasing means suppose in case of high power laser that is short pulse lasers. You know (( )) it is pulse see if the duration of pulse is very small say several hundreds of femtosecond or maybe may be picoseconds.

So, pulse height is high and peak intensity is high therefore, electric filed intensity increases therefore, E square and E cube terms these are progressively increasing. So, these terms are contributing therefore, non-linear I mean this dielectric polarization vector has got some non-linear contribution. So, nonlinearity non-linear effects come into action. So, that is why we take the help of ultrafast pulses then the non-linear effects are quite obvious.

(Refer Slide Time: 26:43)



Ultrafast laser Spectroscopy

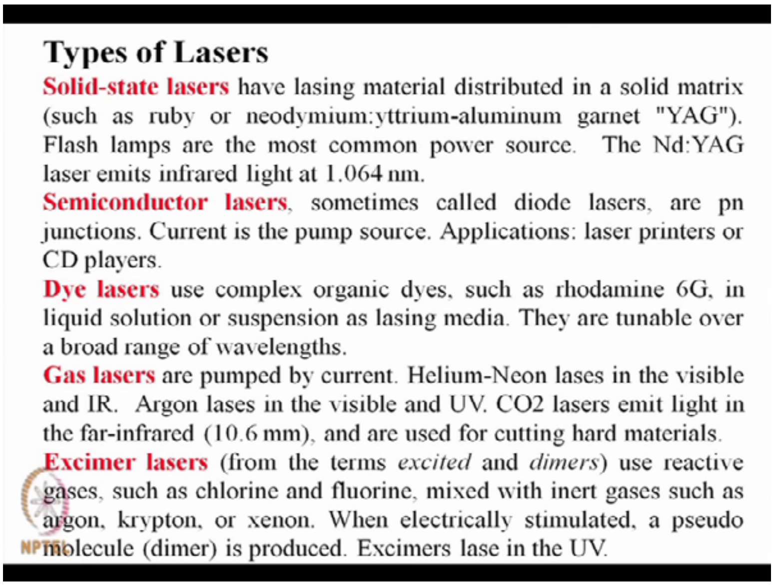
- Basic Laser Principles
- Techniques for generating pulses
  - Pulse Lengthening
  - Pulse Shortening
- Ultrafast Experiments
  - Transient Absorption Spectroscopy

Now ultrafast laser spectroscopy you know basic laser principles I already have explained to you in another instance that is when I talked about this laser flash photolysis. That is a modification of the conventional flash photolysis, that is a modification of the convention and there we would have talked I mean ruby laser helium neon laser and there are many other kind of lasers. So, this and there are many variations of this like, when it is a pulse laser you may shape the pulse or maybe you can lengthen the pulse you can shorten the pulse. So, that part is not you know we are not going to discuss on that because that involves a separate topic that is you know spectroscopy. So, which is beyond the scope of this current course?

So, we will skip this portions we will just consider that here, laser source is needed and maybe depending on our requirement we need a short pulse, we need a long pulse an ultrafast experiment among ultrafast experiment transient absorption spectroscopy is one of the important experiments like flash photolysis that is also transient absorption, but in that case your laser pulse width is longer maybe several nanoseconds, maybe 5 nanoseconds or 6 nanoseconds or 7 nanoseconds like that. So, of the order of 10 and you are close to 10 nano seconds. That means, it is a time window is quite long. Therefore, if any process is occurring like even less than 1 nanosecond. We cannot detect that is ordinary conventional laser flash photolysis, you cannot detect much faster process.

That is you cannot go down to like less than 1 nanosecond, because your laser pulse is wider. So, that is a difficulty that is why another variation of transient absorption spectroscopy where you use ultra short lasers is needed. So, that is called another name of this is called the and it has got another name which is called the pump probe spectroscopy that is your pump a system to high level and then in the x steady state. What is going on you can probe with the help of a second weak light source that is basically what you do try to find out you probe the absorption due to excitation is there, any change in absorbance due to excitation that we want to probe and that we probe as a function of time.

(Refer Slide Time: 30:01)



Types of Lasers

Solid-state lasers have lasing material distributed in a solid matrix (such as ruby or neodymium:yttrium-aluminum garnet "YAG"). Flash lamps are the most common power source. The Nd:YAG laser emits infrared light at 1.064 nm.

Semiconductor lasers, sometimes called diode lasers, are pn junctions. Current is the pump source. Applications: laser printers or CD players.

Dye lasers use complex organic dyes, such as rhodamine 6G, in liquid solution or suspension as lasing media. They are tunable over a broad range of wavelengths.

Gas lasers are pumped by current. Helium-Neon lases in the visible and IR. Argon lases in the visible and UV. CO2 lasers emit light in the far-infrared (10.6 mm), and are used for cutting hard materials.

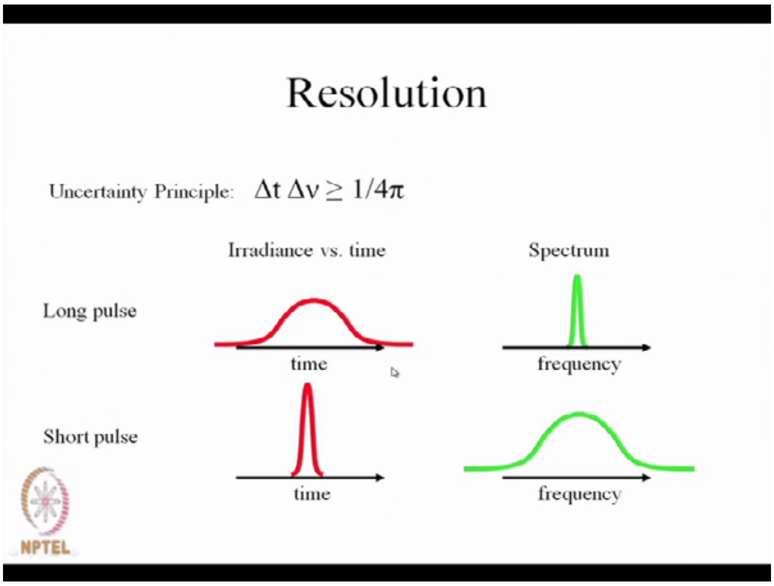
Excimer lasers (from the terms *excited* and *dimers*) use reactive gases, such as chlorine and fluorine, mixed with inert gases such as argon, krypton, or xenon. When electrically stimulated, a pseudo molecule (dimer) is produced. Excimers lase in the UV.

Now there are many types of lasers I mean I talked about solid state like solid state lasers lasing material distributed in a solid matrix. Such as ruby or neodymium laser that is neodymium: yttrium-aluminum garnet and flash lamps are in most of the cases they pump source. And this Nd: YAG laser emits in the infrared region 1064 nanometer not one point it is a typo. So, 11064 nanometer semiconductor lasers sometime called the diode lasers these are the p n junctions or p n junction. These are p n junction and current is the pump source and maybe the has got the application in laser printers or CD players these are the basic application, these are semiconductor laser dye laser.

So, complex organic dyes are used such as rhodamine 6G, many coumarin dyes are used and it is the lasing medium what you do and it a tunable over a broad range of wavelengths and depending on it is sense spectra and this lasing is achieved by another laser. So, that is your pump laser maybe that laser I know excites your pumps your dye to the excited state and then other processes occurring or occurring. So, in that case dye lasers are also tunable. Gas lasers like helium, neon, laser, argon laser which has which has hot visible and UV carbon dioxide laser. It is in the infrared region and is used for cutting hard materials. So, these are uses excimer laser UV.

So, it is excited state dimer laser use I mean use reactive gases such as chlorine fluorine etc mixed with inert gases such as argon, krypton, xenon and fluoride is a typical to excimer laser. When electrically stimulated a pseudo molecule dimer is produced and excimers leave in the UV region. So, there are there are many different kinds of (( )) now it is the semiconductor laser these are also used for pumping your ultra short lasers. So, solid state laser are very useful and they are having quite a long life time I mean they can they can run for they can be used for many years these are the types of lasers.

(Refer Slide Time: 33:04)

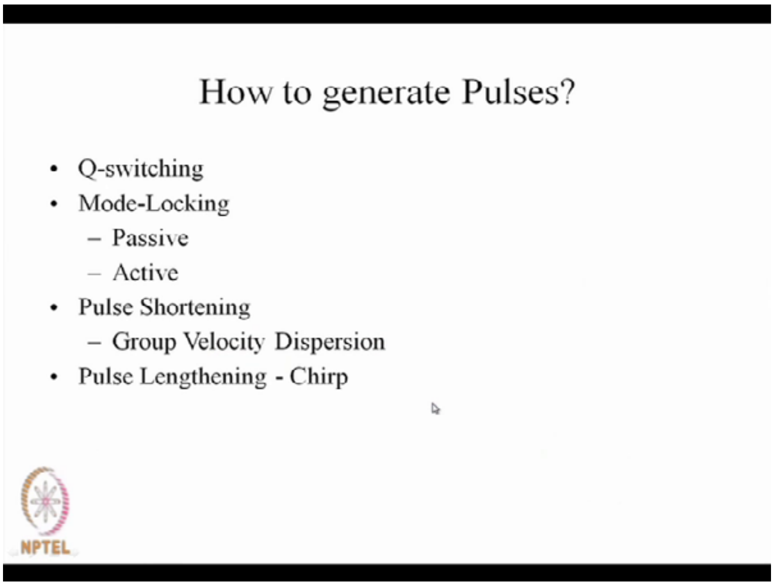

Resolution

Uncertainty Principle: $\Delta t \, \Delta \nu \geq 1/4\pi$

Now, what is a resolution as I told you that resolution is now delta t delta nu that is frequency uncertainty and time uncertainty? So, frequency uncertainty is less mean time uncertainty is more and vice versa. So, for irradiance verses time plot and this is the spectrum this one is the spectrum and this is the irradiance. So, for long pulse that is the pulse stays for longer time that is full with hop maximum, that is with at hop maxima. So, your maxima. So, I am hop maxima this with hop maxima field f w h m is more compared to this one and you see its spectrum is very narrow where as for the short pulse f w h m full with that hop maxima this is smaller, but it is dispersed more its frequency uncertainty is more. So, f w h m frequency f w h m is more compared this one; this comes from the uncertainty principle.

So, depending on whether we want a long pulse or we want a short pulse or we want a know spectrum which a narrower one or a broader one that is decided. You know by your requirement whether you want to prove a very fast process or a very slow process or a slower process. So, a faster process you should have this choice and this one. So, this is typical a nanoseconds laser flash photolysis thing and say this picoseconds, pump-probe experiment.

(Refer Slide Time: 35:03)



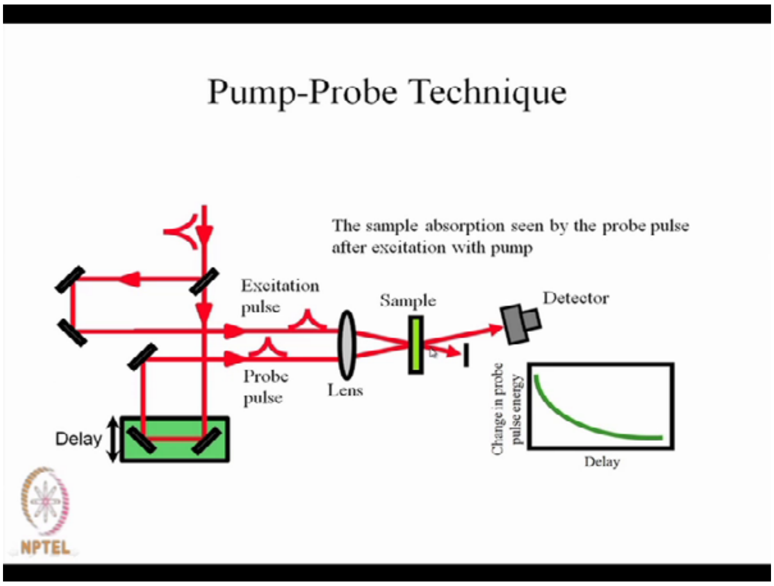
How to generate Pulses?

- Q-switching
- Mode-Locking
  - Passive
  - Active
- Pulse Shortening
  - Group Velocity Dispersion
- Pulse Lengthening - Chirp

So, how to generate these pulses there are many ways t generate these pulses Q-switching again I am telling you it is not I will just name because of the scope. So, Q-switching is one method I told you probably you remember that laser cavity requires two parallel mirrors. If you rotate one mirror like this way then the moment it is exactly parallel to that then standing way pattern I mean the cavity is filled with radiation and then again, if it is rotating no radiation again parallel radiation. So, it is some kind of you knows switching the cavity on and off. So, Q-switching is another way of generating the pulses.

Mode locking is another it can be passive or active mode locking pulse shortening can be done by GVD - Group Velocity Dispersion and pulse link thinning can be done by chirping pulse chirping.

(Refer Slide Time: 36:20)



Pump-Probe Technique

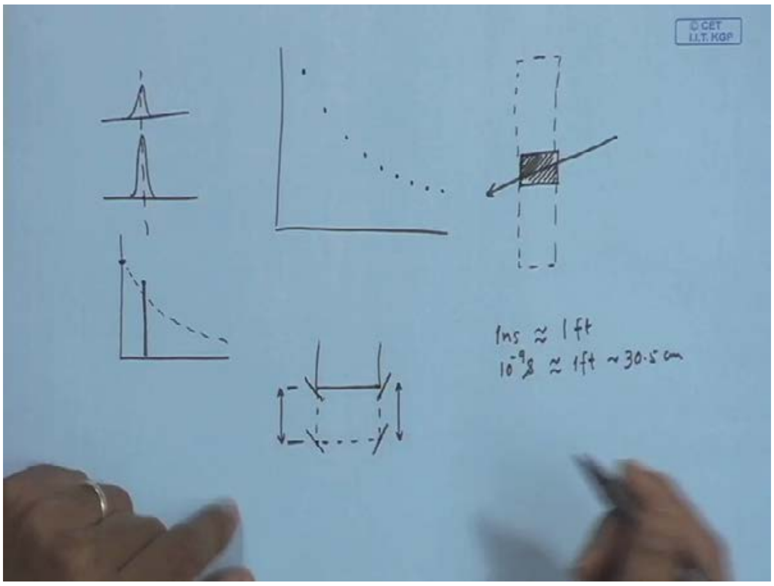
The sample absorption seen by the probe pulse after excitation with pump

So, these are the various ways to generate pulses, what is a pump probe technique? Now pump probe technique apart from this laser flash photolysis. Since it do you know in nanosecond time region? So, to generate your time axis you know this you just use the time axis of your (( )) you now you just pump your sample with radiation and the moment the pump pulse on your sample a second detector which detects fast incoming photon on to the sample that is a photo diode. So, that triggers your cathode ray oscilloscope and then it keeps on collecting the signal for some period. So, that generates your time axis.

Here since it is much faster that is for your cathode ray oscilloscope. So, electronically you generate the time axis. That is you measure the time you start measuring the time from the moment the light falls on to your sample, but if it still faster if it is faster than nanoseconds then electronics cannot do it has got some basic limitation . So, therefore, you have the help of you have to take the help of light to generate your time axis. So, you see that this is your excitation pulse it is divided into two, may it is 50 percent beam split then this is directed this way. So, this is your excitation pulse and another portion another portion maybe or maybe less than 50 percent that is maybe most of the pulse maybe say 90 percent not 50 percent. 90 percent is directed this way only 10 percent is directed this way.

So, the optical path length is from here. So, this length plus that length then this length and then this one up to sample this length. So, total length and this length when these two match then we say that these two pulses are in 0 time that is they are exactly matched. So, that is your matching and then what you do that you keep on changing this length by changing the position of this retro reflector I mean this reflect there is a pair of reflector. So, if you increase the length then probe pulse will reach the sample at some later time. So, what you do you start your experiment when this pump and probe excitation pulse and probe pulse they are exactly matched in temporarily in time. So, that is your 0 that is your 0 time. So, when they are temporarily matched.

(Refer Slide Time: 39:38)



So, this is your probe pulse and says this is your pump pulse and says they are exactly matched in time. So, this pump pulse initiates some reaction maybe some physical process, maybe some chemical process. So, it initiates some reaction and then what you do the moment it initiates that time this pulse is present I mean this the probe pulse you collect the signal. That is how this probe pulse means how much of this probe pulse is transmitted through the sample and to the detector, that is basically you are measuring the transmittance. So, maybe initial intensity you measure the intensity of the probe pulse as a function of this delay. Therefore, say intensity is this much maybe you change the delay and you increase the delay. So, that this probe pulse is reaching at some later point so; that means, not exactly at the very presence of the your I mean the moment this your pump pulse is present or entering to the sample.

So, after this pump pulse is entering. So, it your situation is here then say your system is decaying like this; that means, your active spaces which is absorbing maybe because it is a pump probe absorption technique. So, your active spaces are maximum at this time. So, therefore, you say your signal is here. So, if your probe pulse reaches somewhere over here then actives spaces is somewhat less therefore, your amount of absorption will be less that is amount of transmitted light will be more. So, absorption will be less I the same ways you keep on recording your detector number I mean how much the detector is detecting you detector signal.

So, what you do you send excitation pulse and probes pulse at the same time? So, that is your zero time and then you keep on keep on changing this delay increase the delay. So, that this probe pulse is reaching at some later point. Here this lens is used because they have to be you know directed at one point here, they should be specially and temporarily matched they may be temporarily matched, but if they are not specially matched, means suppose this volume of solution has got the excitation I mean say because of your pump pulse this much of solution out of say this huge volume of your solution is excitation, I mean say because of your pump pulse this much of solution out of say this huge volume of your solution is excited.

Therefore, you have to make sure that your probe pulse should and must pass through this region, where the active species is generated that is why this pumping and your probe pulse they are to be temporarily and specially overlapped. Temporarily means their pulse should be matched at 0 times that is called your temporal time wise, they are matched and also especially they should be matched and here is the detector which detects the signal as a function of this delay.

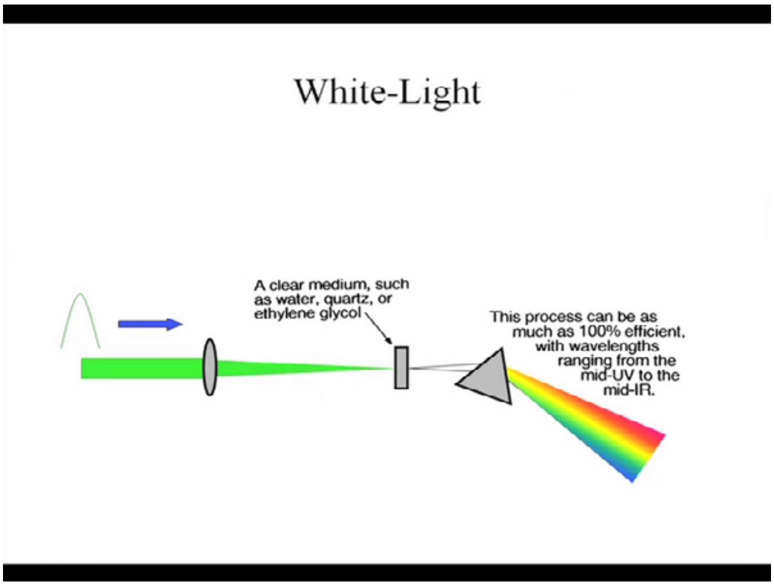
So, if there is any true absorption I mean if there is a true absorption then there will be change in intensity of the probe beam, intensity of the probe pulse will be changed. If there is any absorption or maybe there is any reemission stimulated emission then also probe energy probe pulse energy will be altered. So, this alteration is plotted as a function of this delay, now this delay means how much of lengthy this delay has been made, I mean how much of length is delay has been travelled by. So, I mean initially that said your delay is here I mean this retro reflector later on suppose it is shifted to here. So, this much of additional distance has been traveled due to has been traveled distance is traveled by the light.

So, that this addition length corresponds to some delay, why some delay? because this probe will reach at some later time, because time I mean the light source takes time light pulse takes time to reach one point to another although it is very fast, but maybe if you think in this way that one nanosecond corresponds to one foot so; that means, one nanoseconds 10 to the power minus 9 second corresponds to one foot that is 30.5 centimeter. That means, this much of this plus extra length corresponds to how much of time (( )). So, this way you plot I mean you generate your x axis and you generate the kinetics of the process and then you feet with appropriate function.

So, that you can generate various number that is the time required for a process to take place, that is the process which we are trying to probe the thing is that the sample has to absorb your excitation pulse and maybe it will generate some species and that species will be probed by your probe pulse. Sometime it is a white light or sometime it is close to some single color, because if it is a nano I mean picoseconds or maybe it is a femtosecond pulse then this wavelength separation that is a broadband pulse, it can be regarded as a broadband pulse like this. It is a broadband pulse.

So, broadband pulse you can scan for a range of frequencies. So, it is a pump probe technique by which you can also follow the kinetics of the decay or maybe kinetics of the generation of some species may suppose, because of this excitation pulse. A new species are generated suppose because of some reaction. That means, because of the generation of this new species maybe there is a change in probe pulse energy. So, that you have to monitor.

(Refer Slide Time: 46:29)



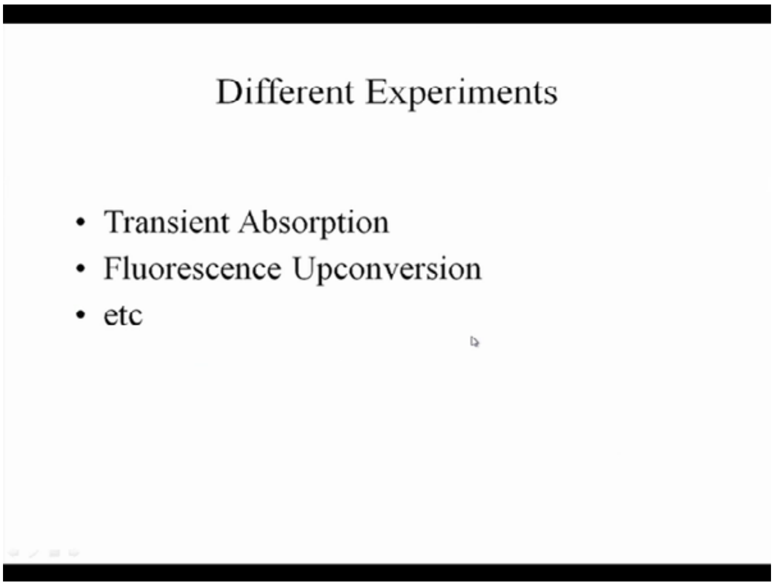
White-Light

A clear medium, such as water, quartz, or ethylene glycol

This process can be as much as 100% efficient, with wavelengths ranging from the mid-UV to the mid-IR.

So, as I told you white light maybe useful for this. So, for generating the white light maybe quartz or maybe ethylene glycol or maybe a sapphire plate is useful. If you shine this sapphire plate or maybe quartz plate or water pure water and if you shine I mean if you focus this ultra short laser on to this water then white light will be generated and with the help of a dispersing medium you can generate all the frequencies. So, it is ranging from mid-UV to mid-IR region. So, therefore, you know using ultra short light sources you can generate a white probe light, which is essential for following the I know doing the absorbance spectroscopy of the excited species.

(Refer Slide Time: 47:37)



Different Experiments

- Transient Absorption
- Fluorescence Upconversion
- etc

So, this pump probe is a transient absorption experiment. Transient absorption experiment means you generate this species this transient species and with the help of another second probe means another probe you prove I mean you look into the concentration of that species and that species is not present under ordinary circumstances only. Because of your laser incidence when laser falls on that because of your laser incidence this transient species is generated. So, transient absorption gives you a lot of information about the processes that are going on that may go that may proceed immediately after laser excitation that laser maybe your femtosecond laser maybe picoseconds laser.

So, it is basically a pump-probe technique like your laser flash photolysis only difference is that here to generate your times axis. You have to use the delay because otherwise if it is a picoseconds process then by the help of electronics, you cannot generate the time axis that is you shine with light and if you want to follow this change of intensity with time by means of a photo detector and your oscilloscope. It is not possible because of the time limitation of the electronics. So, for nanosecond flash photolysis or even microsecond oscilloscope is useful because there is no problem with it is limitation and also the time scale.

But here it is the problem that is why use your this device means for generating your time axis, that is we are taking the help that the requires a time from here to here. That is a time difference that may very small, but that we will be using to generate your time axis there is another technique, which is called fluorescence up conversion technique. That is amalgamation of two photons to generate one photon. So, that we will take up maybe in the next piece of lectures.

So, what we have learnt from this discussion. So, remaining part that is other different experimental thing we will take up one after another, but up till now what you have learnt. Let us try to go back that we have talked about this various time scales of observation of various processes maybe it is from your millisecond to femtosecond and these processes are very important in chemical sense. In chemistry maybe sometime in chemical biology as well like we see our vision that is also a light driven process, sometime live light driven activity of some anti fungal or some agent maybe photodynamic therapy there also light is very important.

So, you talked about this tried to understand the various time scales, then we gave a brief introduction of non-linear effect. To see this non-linear effect we need ultrafast lasers and then types of lasers. We just talked about little then resolution is an important factor we are compromising time resolution then we are compromising on to frequency and vice versa. Now various pulses may now shapes can be I mean whether it is long pulse or short pulse that can be generated and depending on our need, depending on the time scale of observation we can generate short pulse or long pulse.

We discussed out of various ultrafast techniques pump-probe is one of the popular techniques. So, white light is also useful for that and how this is done that also we just try to give you the idea. So, ultrafast processes are very interesting and very important in many cases. So, we will take up one after another and actually this using this ultrafast spectroscopy people, scientists have been able to probe the transition step. So, observation of quantum bits and that we are going to take up maybe in next piece of lectures. So, in the next lecture we will talk about other examples I mean different experiments. So, that we will take up, till then thank you.