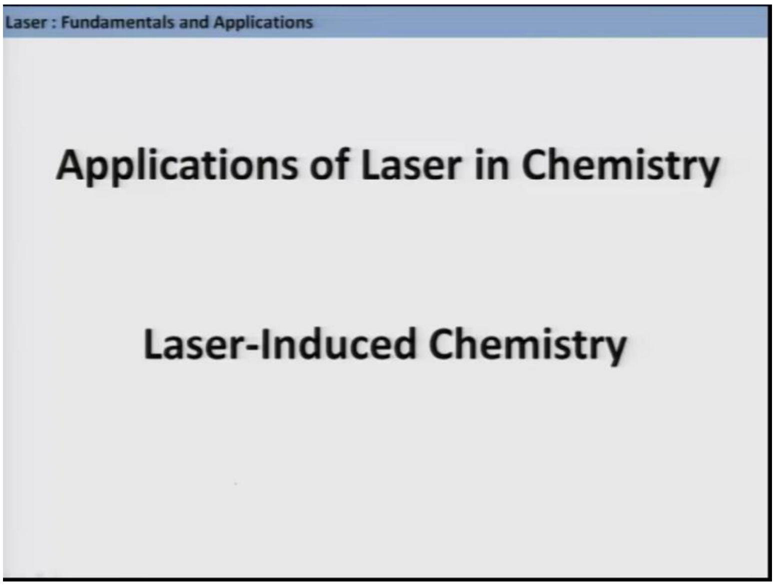
Laser: Fundamentals and Applications
Prof. Manabendra Chandra
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture – 36
Laser Induced Chemistry

Hello and welcome this is the last and final week of this course and I will tell you at the beginning what are we going to look at in this week. So, we look at various applications of lasers.

(Refer Slide Time: 00:30)



Laser : Fundamentals and Applications

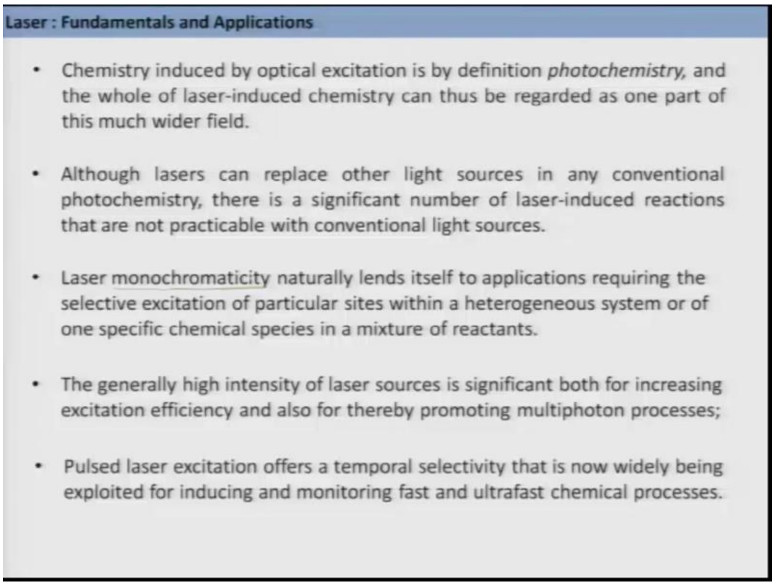
Applications of Laser in Chemistry

Laser-Induced Chemistry

For example, application of lasers in chemistry which is a big and wide field, laser induced chemistry, you know the application of laser in medical sciences in treating you know different types of diseases. We will also learn the applications of laser in material science and metallurgy, and also we will learn about the role of lasers in optical communications and you know one last thing that we look at which is extremely important to learn is about laser safety and with that we will conclude this course. So, let us start today's lesson with applications of lasers in chemistry.

So, the first thing that we will look at under this topic is the laser induced chemistry.

(Refer Slide Time: 01:39)



Laser : Fundamentals and Applications

- Chemistry induced by optical excitation is by definition *photochemistry*, and the whole of laser-induced chemistry can thus be regarded as one part of this much wider field.
- Although lasers can replace other light sources in any conventional photochemistry, there is a significant number of laser-induced reactions that are not practicable with conventional light sources.
- Laser monochromaticity naturally lends itself to applications requiring the selective excitation of particular sites within a heterogeneous system or of one specific chemical species in a mixture of reactants.
- The generally high intensity of laser sources is significant both for increasing excitation efficiency and also for thereby promoting multiphoton processes;
- Pulsed laser excitation offers a temporal selectivity that is now widely being exploited for inducing and monitoring fast and ultrafast chemical processes.

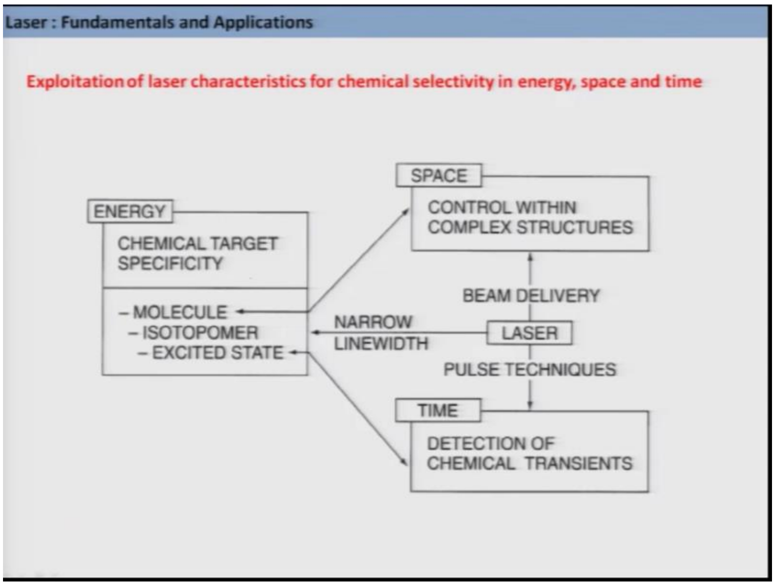
So now, the chemistry that is induced by the optical excitation is by definition called photo chemistry. And the laser induced chemistry also then fall in under of this you know topic photo chemistry and this is controlled by all the principle of photo chemistry. Now although lasers can replace any other conventional light source in any conventional photo chemistry, there are certain you know number of photochemical processes which are not possible get induced by conventional light sources and without the application of laser is not possible to get those you know photochemical processes and those applications.

Now, what are the main characteristics of laser that you know is utilized in laser induced chemistry. One of course, is the monochromatic city of laser. So, why this particular property of laser is so important? Because using the monochromatic light from laser, one can selectively excite any particular site of interest within any heterogeneous system or any you know specific chemical species when you have a mixture of reactants and thereby you can initiate any photochemical reaction.

Second thing is that, the laser is a provider of very high intensity light. So, this high intensity of laser light is significant both for increasing excitation efficiency and also for thereby promoting multi photon process. We will as we progress today we will see how this multi photon process is important in the field of you know chemistry. Now you know the laser excitation source can be anything, but particularly pulse laser excitation offers a temporal selectivity. That is nowadays being widely used or they are you know exploited for inducing and monitoring fast and ultra fast reactions or ultra fast reaction dynamics. And this is extremely important in the field of chemistry where you know bond making and bond breaking needs to be understood very very clearly.

So, this you know monitoring ultra fast reactions or dynamics of chemical bonding is a totally new domain in the field of scientific research and this is known as ultra fast sciences and this has been revolutionized by the invention of ultra short pulse lasers. So, we will look into this particular part in a bit detail towards the end of this class or maybe early in the next class. So now whatever we say it so far if we can sum up like you know what are the characteristics of laser lights? And what are the you know applications? Then we can have a chart like this as shown on your screen.

(Refer Slide Time: 05:23)



Laser : Fundamentals and Applications

Exploitation of laser characteristics for chemical selectivity in energy, space and time

ENERGY

CHEMICAL TARGET SPECIFICITY

- MOLECULE
- ISOTOPOMER
- EXCITED STATE

NARROW LINEWIDTH

SPACE

CONTROL WITHIN COMPLEX STRUCTURES

BEAM DELIVERY

LASER

PULSE TECHNIQUES

TIME

DETECTION OF CHEMICAL TRANSIENTS

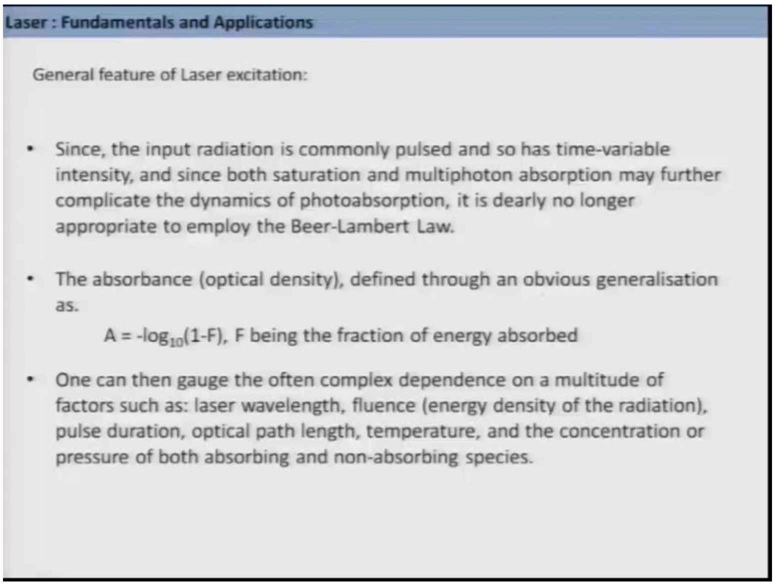
So, because the laser has a very narrow bandwidth or narrow line width, it can you know really be applied to do high resolution spectroscopy meaning that you can really selectively use, selectively excite one particular you know state and thereby you can you know use this property to develop tools to you know or develop analytical tools to be precise to separate different molecular entities, different isotopes and also you can access various different excited state.

So, you can really achieve so called the specificity because the laser light has high you know monochromaticity. Now you can also you know utilize the you know different laser pulse widths from continuous to in a short pulse to ultra short pulse and then you can really study various different you know chemical processes going on in a short to ultra short timescale. And you know you can also be very selective about specific excitation in a complex molecular structure or even a complex environment.

So, you can see that you know properties of laser can really be useful. So, you know another important thing is that, it can you know same the light to a specific point even you have like a complex environment say like you know within you know tissue. You can use the you know property of the laser light that is it has a you know larger skin depth. So, the beam can be delivered to a remote to a you know within a you know tissue in our body which is you know beneath our skin by quite you know a millimeter or centimeter distance.

So, you can even then you know go and excite certain targets within the tissue.

(Refer Slide Time: 07:49)



Laser : Fundamentals and Applications

General feature of Laser excitation:

- Since, the input radiation is commonly pulsed and so has time-variable intensity, and since both saturation and multiphoton absorption may further complicate the dynamics of photoabsorption, it is dearly no longer appropriate to employ the Beer-Lambert Law.
- The absorbance (optical density), defined through an obvious generalisation as.

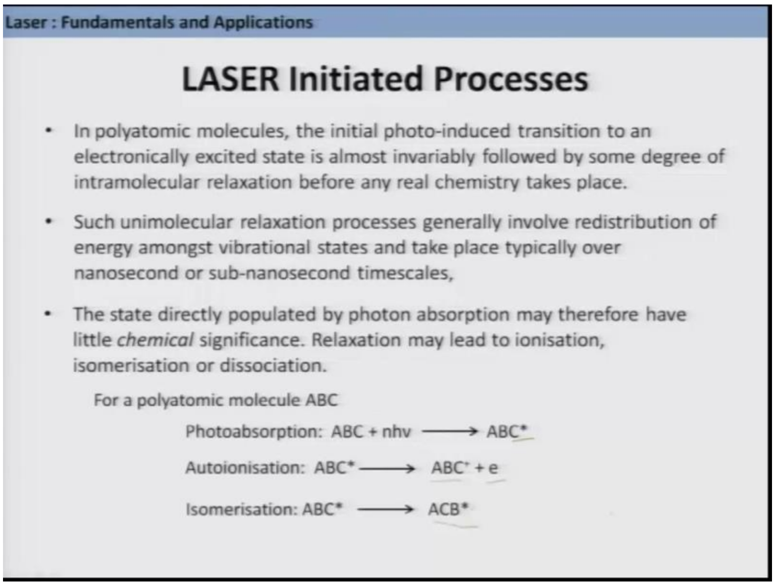
  $A = -\log_{10}(1-F)$, F being the fraction of energy absorbed
- One can then gauge the often complex dependence on a multitude of factors such as: laser wavelength, fluence (energy density of the radiation), pulse duration, optical path length, temperature, and the concentration or pressure of both absorbing and non-absorbing species.

Now these are the general features that you know the laser excitation generally has now. Apart from these, I will mention a couple of points here which is of tremendous importance that is normally in chemistry we use pulsed laser for achieving any particular purpose and since this input radiation is commonly pulsed and it has a time variable intensity. This is true for any pulsed light and since both saturation as well as multi photon absorption may further complicate the dynamics of photo absorption, it is no longer you know appropriate to use Lambert Beers Law.

So, normal absorption processes we deal with we use Lambert Beers Law to understand that, but here we may have a complicated situation like multi photon absorption called saturation which no longer you know falls within the limit of Lambert Beers Law. So, we should be very very careful in applying Lambert Beers Law when we are applying lasers to achieve any chemical reaction or to probe any chemical process by laser. Now specifically you have mentioned here the you know absorbance or the optical density which is defined through obvious generalization as A equals to minus log base 10, 1 minus F, where F is the fraction of energy absorbed.

So, one can then you know gauge the often complex dependence on a multitude of factors such as laser frequency, laser fluence or the energy density of the radiation, the pulse duration, optical bulk link, temperature and the concentration or the pressure of both absorbing and non absorbing species. So, these are the few things that we should keep in mind.

(Refer Slide Time: 10:07)



Laser : Fundamentals and Applications

LASER Initiated Processes

- In polyatomic molecules, the initial photo-induced transition to an electronically excited state is almost invariably followed by some degree of intramolecular relaxation before any real chemistry takes place.
- Such unimolecular relaxation processes generally involve redistribution of energy amongst vibrational states and take place typically over nanosecond or sub-nanosecond timescales,
- The state directly populated by photon absorption may therefore have little *chemical* significance. Relaxation may lead to ionisation, isomerisation or dissociation.

For a polyatomic molecule ABC

Photoabsorption: $ABC + nh\nu \longrightarrow ABC^*$

Autoionisation: $ABC^* \longrightarrow ABC^+ + e$

Isomerisation: $ABC^* \longrightarrow ACB^*$

Now, let us look into the detail of certain laser initiated processes. So, to start with if we look into a polyatomic molecule, the initial photo in this transition to an electronic excited state is almost inevitably followed by some degree of intermolecular relaxation before any chemistry can takes place; which is easily understandable a molecule will a polyatomic molecule have several you know bands. Now if I excite it then there are several vibrational degrees of freedoms and this energy that the excited molecule has now it can redistribute that energy into different vibrational degrees of freedom that is generalized into different different you know bonds.

Now, this what we were talking about is about you know uni molecular process, that I take a molecule and excite with the photon. I am not considering a molecule another separate molecule and colliding which is the prerequisite in most of the reactions that we you know encounter most of the time which are like by molecular reactions and they are preceded by collision. Here we are just thinking about one molecule and bringing in my laser light, exciting it and then you know look for that you know chemistry to take place.

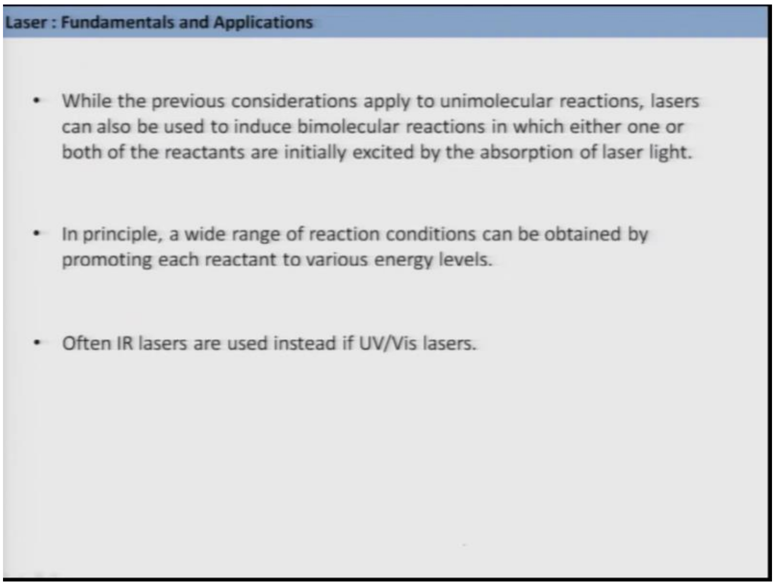
Now, as I said that before that chemistry can take place there may be relaxation. So, this relaxation is you know essentially it consists of redistribution of energy, in different vibrational degrees of freedom or vibrational states in other words. And this happens typically in the order of Pico seconds. The electronic state that we directly populate by laser, they may not be of tremendous significance or you know quote, unquote chemical significance because they may undergo relaxation.

So, the initial absorption may not really do something and this relaxation they may also lead to dissociation or ionization or even isomerization. They of course, lead to chemical reactions. Now if we take an example of a polyatomic molecule given as ABC, then one can have a photo absorption that is you give photon from the laser to this molecule ABC and ABC goes to the electronical excited state which is given by ABC star. And then you can also have another process which is known as auto ionization.

So, that will create a positively charged ABC and expulsion of an electron. The next process that we can have is an isomerization. So, if you have say you know the molecule as ABC star, that is after excitation you have the excited ABC that is ABC star it can undergo isomerization to form like ACB. So, you we know that isomer did not differ in terms of their overall composition right they remain intact, but there are some changes. So, there may be several different types of isomerization. So, this is one of such example where after the initial haute excitation one can have isomerization. And lastly one can have a photo dissociation where the excited states molecule will break into two fragments, so A, B and C.

So, you know all this you know processes all this consideration that we just showed, they essentially apply to unimolecular reactions and laser can, but laser can be also used to induced bi molecular reaction in which either one or both of the reactants are initially excited.

(Refer Slide Time: 14:03)



Laser : Fundamentals and Applications

- While the previous considerations apply to unimolecular reactions, lasers can also be used to induce bimolecular reactions in which either one or both of the reactants are initially excited by the absorption of laser light.
- In principle, a wide range of reaction conditions can be obtained by promoting each reactant to various energy levels.
- Often IR lasers are used instead if UV/Vis lasers.

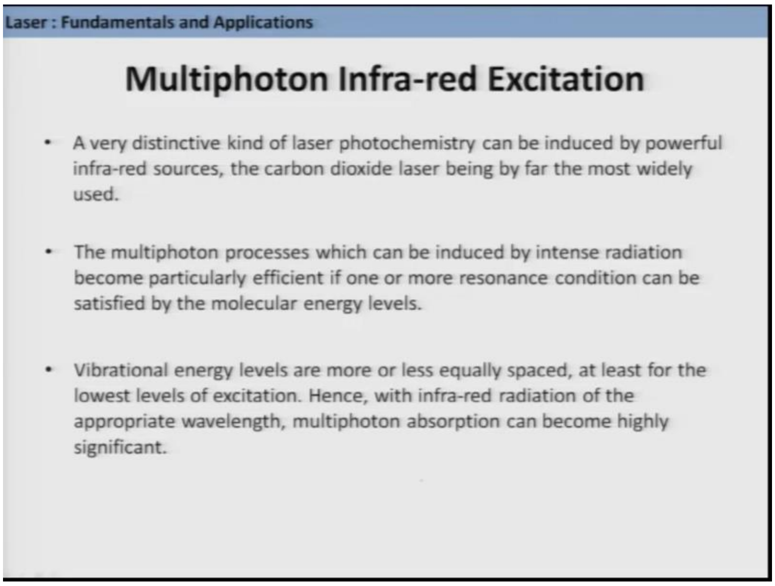
So, as I was saying just few minutes back that you can have you know a couple of molecules, they collide each other and then that in you know results to a reaction. So, here you know so far we have been talking about taking one molecule excited and then you know that will lead to certain reaction; bond breaking or you know isomerization, ionization like that.

But I can also have like instead of one molecule I have two molecules and I excite one of them to excited state or both of them and in the excited state they can you know react and produce a desired product. So, in principle a wide range of reaction condition can be obtained by promoting each reactant to various energy levels, which is quite understandable if you remember the you know last class where we talked about isotopic separation we use something similar. So, we excite to a selective level and from there we ionoize. So, bi molecular reaction also which essentially takes place in a you know mixture of molecules there we can you know use monochromatic radiations from laser and selectively excite the electronic states or vibrational states of you know each. And every molecule and then allow a specific reaction to proceed.

One important point here that you know many of these photochemical applications of laser involved the usage of infrared lasers over ultraviolet and visible laser; why? Because most of the cases what you know may achieve when you use UV or visible laser, is that they will lead to electronic excitation. And this electronic excitation depending on the frequency of the laser and depending on the molecular state distribution you can actually end up getting a dissociation or a photo ionization, which may not give you the desired product as you would otherwise expect to happen if you are looking at a by molecular reaction induced by laser.

So, instead of using electronic excitation you do a vibrational excitation by using infrared pulses. And this you know selective excitation to different vibrational level can give you the desired selectivity toward the end product And moreover there is something very important about this infrared laser is that using infrared laser you can achieve multi photon absorption which we will be talking about in the next slide.

(Refer Slide Time: 16:57)



Laser : Fundamentals and Applications

Multiphoton Infra-red Excitation

- A very distinctive kind of laser photochemistry can be induced by powerful infra-red sources, the carbon dioxide laser being by far the most widely used.
- The multiphoton processes which can be induced by intense radiation become particularly efficient if one or more resonance condition can be satisfied by the molecular energy levels.
- Vibrational energy levels are more or less equally spaced, at least for the lowest levels of excitation. Hence, with infra-red radiation of the appropriate wavelength, multiphoton absorption can become highly significant.

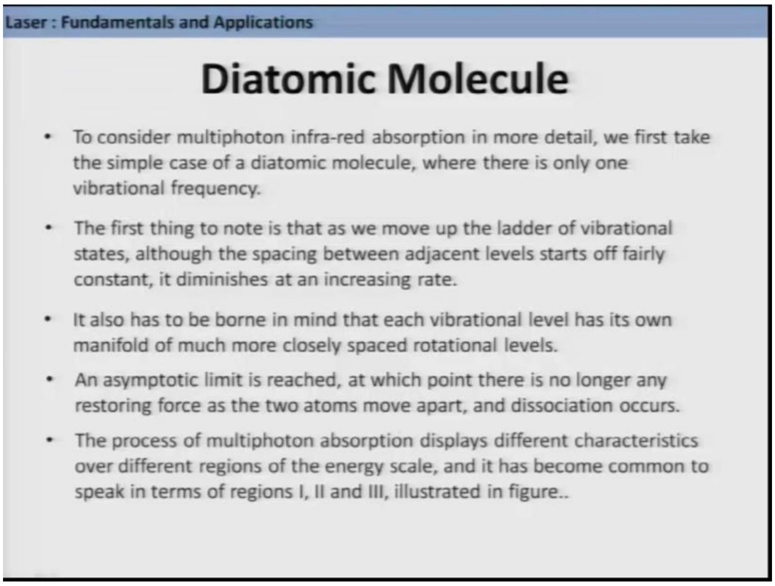
So as we have written here, that a very distinctive kind of laser photochemistry can be induced by powerful infrared sources; the carbon dioxide laser being the most widely used laser for this purpose. And this multi photon process which can be induced by this strong laser light and become particularly efficient if one or more resonance conditions can be satisfied by the molecular energy levels. This is again you will be you know able to relate to the previous class where we used you know instead of single frequency sources, we took two frequency sources and then achieved an absorption between the ground state and the first excited state and then using the second frequency we achieved the desired organization.

So, this proceeding you know resonant transition helps in achieving that desired chemical reaction. Now this vibrational energy levels which can be populated by infrared laser excitation, these vibrational energy levels are more or less equally spaced at least at the beginning of the well. So, if you look at the potential well diagram or any particular bond you will see the vibrational energy levels. So, when you are considering anharmonicity, that is the real condition then of course, the vibrational levels they will be close spaced as you move upward in energy. They are not equi spaced, but at the lower part of this you know potential energy well, the vibrational states can be safely assumed to be more or less equi spaced.

So, you know gap between two successive vibrational energy levels are more or less equal, though actually they are shorter as you move upward. So, as long as this gap is pretty much like you know equal, you can have a situation where the infrared radiation of a particular appropriate wavelength you can achieve multiphoton absorption. And this can be very very efficient how? Because if you have a pretty similar energy gap between successive vibrational energy levels you definitely have some width of the laser pulse. So, this you know they have a central frequency and then they have certain width. So, you know there is a frequency spread.

Now, this energy gaps you know say like you know between V equals to 0 to V is equal to 1, V is equal to 1 to V is equal to 2, V is equal to 2 to V is equal to 3 and so on. If this energy gaps are not differing by too much then that you know slight difference falls within the bandwidth of the laser. Therefore, you can actually keep on exciting molecule from 0 to 1, 1 to 2, 2 to 3. So, you can have essentially multiphoton excitation.

(Refer Slide Time: 20:26)



Laser : Fundamentals and Applications

Diatomic Molecule

- To consider multiphoton infra-red absorption in more detail, we first take the simple case of a diatomic molecule, where there is only one vibrational frequency.
- The first thing to note is that as we move up the ladder of vibrational states, although the spacing between adjacent levels starts off fairly constant, it diminishes at an increasing rate.
- It also has to be borne in mind that each vibrational level has its own manifold of much more closely spaced rotational levels.
- An asymptotic limit is reached, at which point there is no longer any restoring force as the two atoms move apart, and dissociation occurs.
- The process of multiphoton absorption displays different characteristics over different regions of the energy scale, and it has become common to speak in terms of regions I, II and III, illustrated in figure..

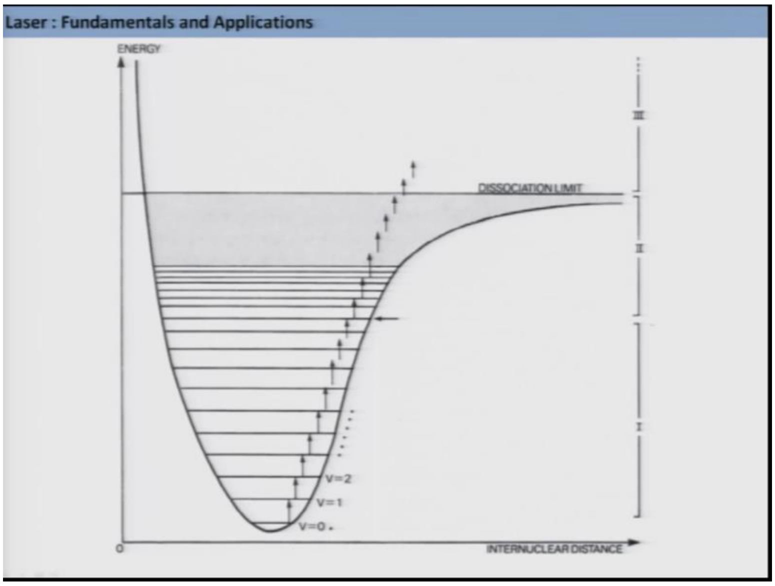
In order to consider this multiphoton infrared absorption in more detail let us first take the simple case of a diatomic molecule where, there is only one vibrational frequency right.

So, if you know about vibrational degrees of freedom and other degrees of freedom like you know rotational and translational, then you can easily calculate a diatomic molecule there is only one vibrational degrees of freedom. So, you have only one vibrational frequency that is a stretching frequency.

So, in that case you know explaining things will be lot more easier and for you also it will be easier to understand. So, the first thing that we should note here that, as we move up the ladder the vibrational energies states, although the spacing between the adjacent level starts off fairly constant that is at the lower part of the level. But as you go further this you know gap becomes shorter and shorter and shorter and then it reaches a continuum. And this happens at quite faster rate as you increase in the energy within the potential well. It also has to be you know borne in mind that each vibrational state has its own manifold of much more closely spaced rotational levels. We have talked about that in you know last few classes whenever it you know came into the picture. So, the vibrational levels have also the rotational levels within.

Now, you know in a real potential scenario you have a and anharmonic oscillator model and you have a dissociative level at some point of time and this is the asymptotic limit and this as you approach this asymptotic limit, there is no restoring force and the molecule essentially get dissociated. So, that is the dissociation limit. Now the process of multi photon absorption displays different characteristics at different region of this you know potential well. So, they are also you know described by different different you know regions. So, like you know first region, second region, third region as shown in this picture on your screen.

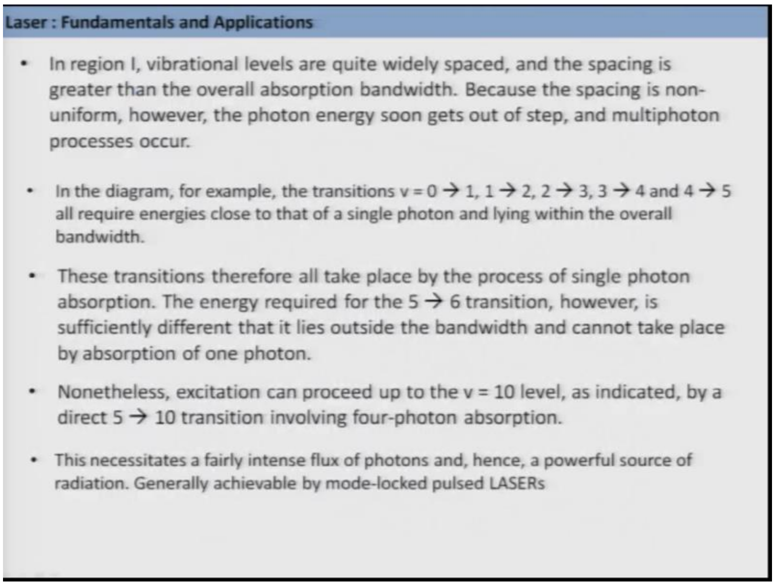
(Refer Slide Time: 22:48)



Laser : Fundamentals and Applications

So you know up to this point, this is region 1, then you have this part region two and above dissociation level is region three and each of these regions you know we should discuss a little bit more in detail.

(Refer Slide Time: 22:59)



Laser : Fundamentals and Applications

- In region I, vibrational levels are quite widely spaced, and the spacing is greater than the overall absorption bandwidth. Because the spacing is non-uniform, however, the photon energy soon gets out of step, and multiphoton processes occur.
- In the diagram, for example, the transitions v = 0 → 1, 1 → 2, 2 → 3, 3 → 4 and 4 → 5 all require energies close to that of a single photon and lying within the overall bandwidth.
- These transitions therefore all take place by the process of single photon absorption. The energy required for the 5 → 6 transition, however, is sufficiently different that it lies outside the bandwidth and cannot take place by absorption of one photon.
- Nonetheless, excitation can proceed up to the v = 10 level, as indicated, by a direct 5 → 10 transition involving four-photon absorption.
- This necessitates a fairly intense flux of photons and, hence, a powerful source of radiation. Generally achievable by mode-locked pulsed LASERs

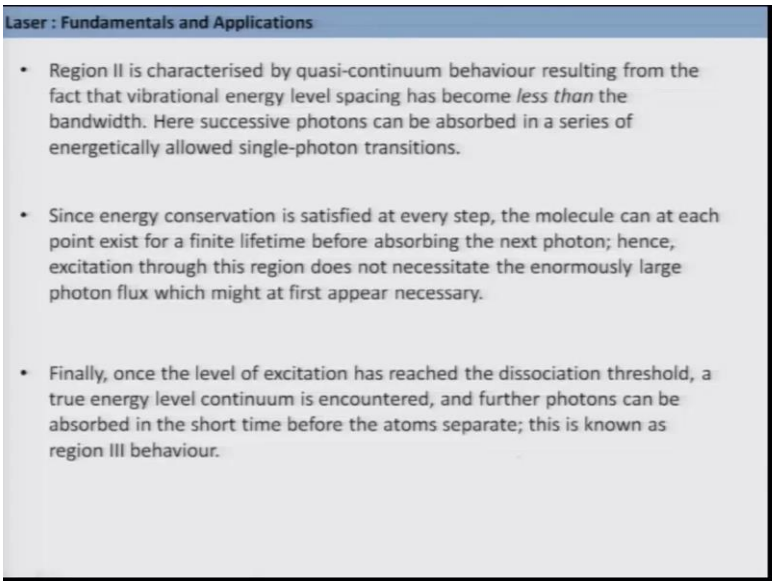
So, in the region 1, the vibrational levels are quite widely spaced, as I discussed already and the spacing is greater than the overall absorption bandwidth. So, you know you have sufficient gap between two levels and your laser frequency bandwidth is much much narrower than this gap. But the bandwidth can be such that the gap between this and the gap between the next two levels, those two values if you subtract one from other then that difference may be comparable to your laser bandwidth and that is why you can have multi photon absorption.

Now, the this spacing between the vibrational levels is non uniform, but the photon energy soon gets out of step and you can have multi photon absorption, which we just explained. And you know looking at the diagram here you have different different level V is equal to 0 to 1, 2, 3 and so on. So, you know the transition from V is equal to 0 to 1 or 1 to 2, 2 to 3, 3 to 4 all required energies close to that of a single photon, that is what exactly I said and it lies within the overall bandwidth we have already stated that.

Now therefore, this transitions all of them take place by the process of single photon absorption and you can keep on populating one after another. So, V is equal to 0 to 1, 1 to 2, 2 to 3 and so on. So, that is exactly the multi photon absorption. Now it cannot keep on going further. So, the excitation can proceed up to V equals to 10. Now if you have to have actually multi photon process going on that is 0 to 1, 1 to 2, 2 to 3 and so on simultaneously, you need a lot more flux of photon; that means, you need to really intense laser light which generally comes from the pulsed laser light.

So, this multi photon processes in order to you know happen you need a pulsed light source and most often this is you know taken from mode lock you know laser pulses which are highly intensed.

(Refer Slide Time: 25:54)



Laser : Fundamentals and Applications

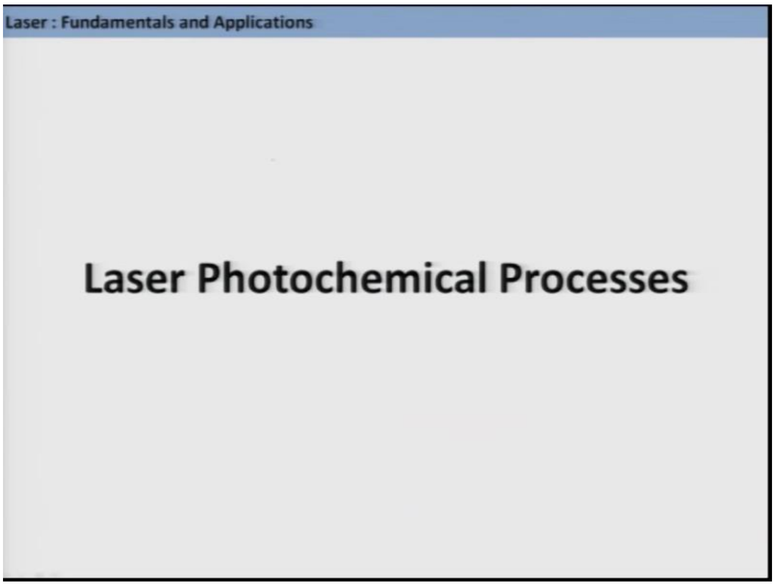
- Region II is characterised by quasi-continuum behaviour resulting from the fact that vibrational energy level spacing has become *less than* the bandwidth. Here successive photons can be absorbed in a series of energetically allowed single-photon transitions.
- Since energy conservation is satisfied at every step, the molecule can at each point exist for a finite lifetime before absorbing the next photon; hence, excitation through this region does not necessitate the enormously large photon flux which might at first appear necessary.
- Finally, once the level of excitation has reached the dissociation threshold, a true energy level continuum is encountered, and further photons can be absorbed in the short time before the atoms separate; this is known as region III behaviour.

In the reason 2, this is characterized by quasi quantum behavior which results from the fact that vibrational energy level spacing has become less than the laser bandwidth. So, here successive photons can be absorbed in a series of energetically allowed single photon transition, but that does not mean much because that energy spacing is almost like a continuum.

Now, since the energy conservation is satisfied at every step molecule can at each point exist for a finite lifetime. True for any transition before absorbing the next photon, hence the excitation through this region does not necessitate the enormously large photon flux which might, at first may seem necessary. So, this is you know quite different from the excitation at region 1, which is clear. And finally, once the level of excitation has reached the dissociation threshold a true energy level continuum is encountered. So, far we were talking about the quasi continuum because the energy space between the two successive levels at a very high energy level of the potential energy diagram was very very small and you know that this you know difference was within the laser bandwidth. So, it is like almost like a continuum, but not yet completely continuum.

But the true continuum we you know be there once you reach the you know dissociation threshold at that region. And here the photons can be absorbed in the short time before the atoms separate and this is known as region three behavior. So, there it is when it reached the dissociative level that is right here, if the photon is here it has reached here. So, if it goes in this direction it will be dissociated because this axis is my inter nuclear distance. So, if it goes far apart when there is no interaction between those two they are broken. So, once it reaches here, then I can actually bring in my short pulses and we can you know take snapshot at different different positions and then I can actually find out the overall dynamics. I can take the snapshots at different different places and overall I can prepare a movie how the molecule is being dissociated? We will discuss about that.

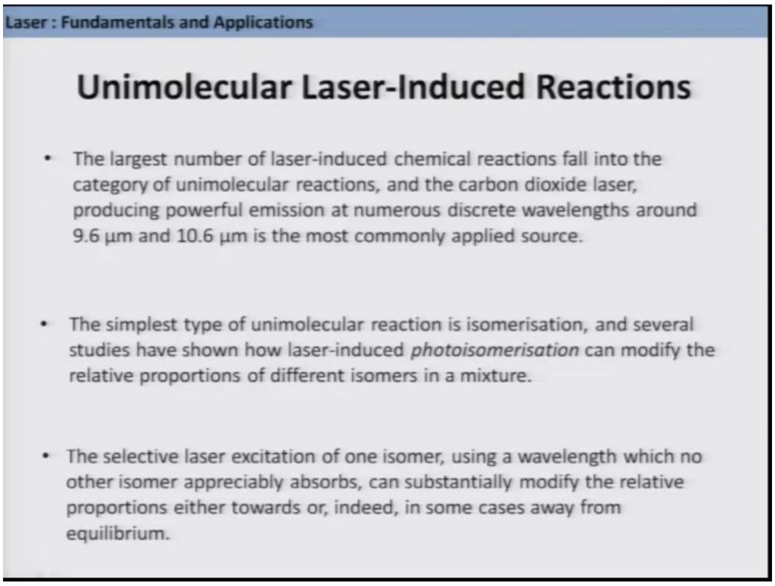
(Refer Slide Time: 28:40)


Laser : Fundamentals and Applications

Laser Photochemical Processes

Now, let us move on to the laser photochemical processes where we will first talk about the unimolecular laser induced reactions.

(Refer Slide Time: 28:48)



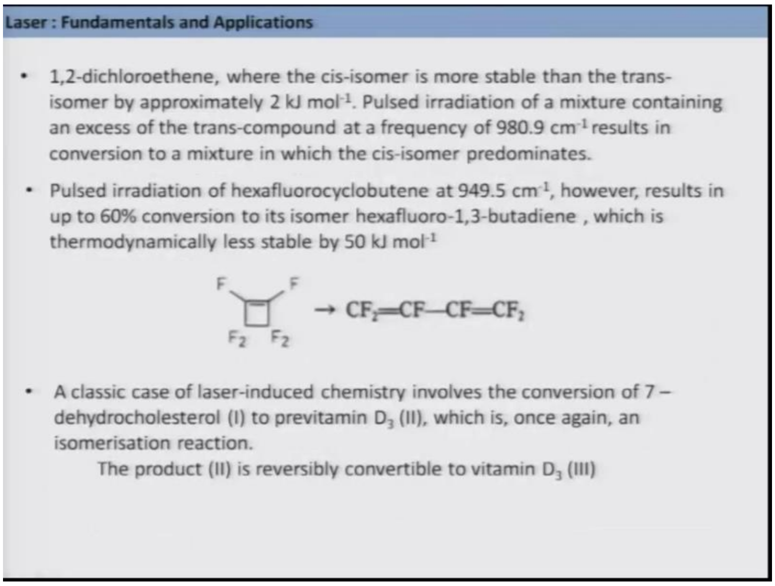
Laser : Fundamentals and Applications

Unimolecular Laser-Induced Reactions

- The largest number of laser-induced chemical reactions fall into the category of unimolecular reactions, and the carbon dioxide laser, producing powerful emission at numerous discrete wavelengths around 9.6 μm and 10.6 μm is the most commonly applied source.
- The simplest type of unimolecular reaction is isomerisation, and several studies have shown how laser-induced *photoisomerisation* can modify the relative proportions of different isomers in a mixture.
- The selective laser excitation of one isomer, using a wavelength which no other isomer appreciably absorbs, can substantially modify the relative proportions either towards or, indeed, in some cases away from equilibrium.

So, the largest number of laser induced chemical reactions fall into this category. And the carbon dioxide laser is mostly used laser here particularly in the range of like 10.6 micron or 9.6 micron wavelengths. The simplest type of unimolecular reaction is isomerization and a lot of studies on this photo isomerization has already been done. And it has shown that you know how laser induced photo isomerization can modify the relative proportion of different isomers in a mixture. One example you have seen in you know the last class, and a selective laser excitation of one isomer using a wavelength which no other isomer appreciably absorbs can substantially modify the relative proportion either toward or truly in some cases away from equilibrium.

(Refer Slide Time: 29:57)



Laser : Fundamentals and Applications

- 1,2-dichloroethene, where the cis-isomer is more stable than the trans-isomer by approximately 2 kJ mol^{-1}. Pulsed irradiation of a mixture containing an excess of the trans-compound at a frequency of 980.9 cm^{-1} results in conversion to a mixture in which the cis-isomer predominates.
- Pulsed irradiation of hexafluorocyclobutene at 949.5 cm^{-1}, however, results in up to 60% conversion to its isomer hexafluoro-1,3-butadiene , which is thermodynamically less stable by 50 kJ mol^{-1}

$\rightarrow CF_2{=}CF{-}CF{=}CF_2$

- A classic case of laser-induced chemistry involves the conversion of 7 – dehydrocholesterol (I) to previtamin D_3 (II), which is, once again, an isomerisation reaction.
  The product (II) is reversibly convertible to vitamin D_3 (III)

Now, let us look at you know some examples. So, say 1, 2 dichloroethene where the cis isomer is more testable then the trans isomer by approximately 2 kilo joule per mole. Now if you irradiate it by a pulsed lasers, when you have a mixture of the cis and trans dichloroethene if you come with 980.9 centimeter inverse laser light which actually falls in the infrared region. And you hit the mixture which contains more trans compound, that results in the conversion of you know predominantly cis isomer.

The pulsed irradiation of hexaflurocyclobutane at 949.5 centimeter inverse; however, results up to sixty percent conversion to its isomer hexafluoro 1, 3 butadiene which is thermodynamically less stable by 50 kilo joule per mole. And that is given here and we will you know stop today by stating one classic case of laser induced chemistry, that involves the conversion of 7 dehydrocholesterol to pre vitamin D 3, which is one again an isomerization reaction. And once this isomerization takes place to pre vitamin D 3 that can very easily gets converted into vitamin D 3 which is very useful for our body. So, we will stop here today and we will come with more in the following class.

Thank you very much.