Ultrafast Processes in Chemistry
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Lecture-01
Introduction

You are welcome to laser Spectroscopy for chemistry, the purpose of this course is to discuss certain aspects of use of lasers in chemistry .We mainly focus on ultrafast dynamics but we will talk about other applications of lasers in chemistry as well. So, to start with what you see here is going to be our main textbook.

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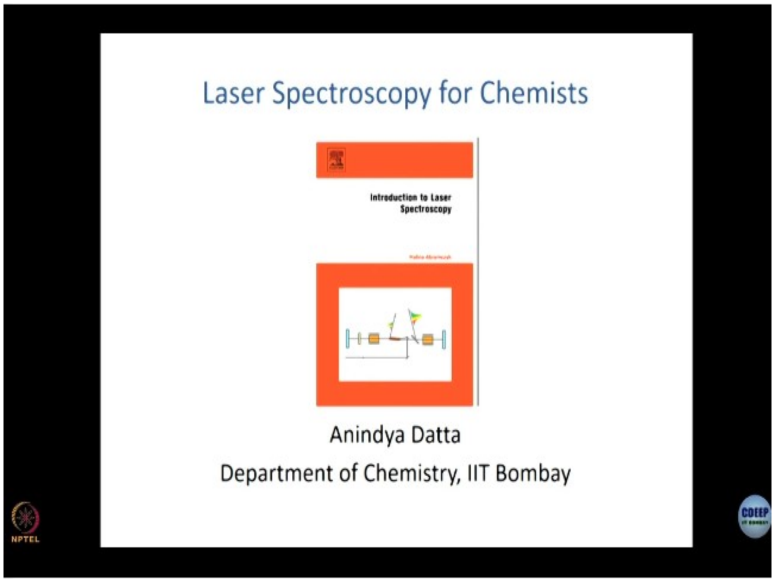

Laser Spectroscopy for Chemists

Introduction to Laser Spectroscopy

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It is available in the library you can show it and I have a copy as well right. So to start with we all I think know what the properties of laser are. when I was a child when I was in college lasers are novelty many of a us has not seen lasers the only lasers we saw are the laser guns in flash Gordon movie or Star Trek or some such thing but then the world has moved you have a lasers everywhere right here you have a lasers. So you very well know what the properties of laser are. You can see the laser light and you can tell me perhaps some of the properties.

So Vikas can you tell me some properties of this laser. Monochromatic it is coloured light. Unlike the light that comes out of tube light it looks colour. So lasers are monochromatic later on when we talk about ultra fast processes you are going to say that lasers may not always be as monochromatic as they think they are but still some element of colour will always be there. So monochromaticity is a property. Anything else; intense of course, see this light even though so many lights on in this room I can still see this colour green light that is there.

So its intense anything else; then let us leave that for the last anything else; no something other than coherent will come to coherent but before that something easier something even easier than polarized, yes we already said high intensity well say it is collimated is not it right, it is collimated light from the tube light dissipation all directions but the verifact that laser travel all the photons of travel in the same direction that is why you can use them is laser pointer okay.

And then comes what you are all saying its coherent of course as a little more sophisticated term what it means is that all the photons actually move in phase okay. You think of light as wave all the light waves that there are moving in step that is the meaning of coherence. And coherence also has a very important role to play in some of the applications we are going to discuss later on. But for now these are the properties.

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Properties of laser

- Intensity
- Monochromaticity
- Pulsed operation
- Coherence

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And one thing that we did not say is that the laser is capable of pulsed operation. I hope you all understand what the meaning of pulse is pulse means light goes on for a very small amount of time and then it remains off. And then after a while it goes on again so for those us who have watched in lab very well know what the meaning of pulse in his truest sense but for beginners all of us are actually seen pulse in everyday life. Can you tell us some examples of pulse that you have seen outside the lab.

It is monsoon season in this season lightning, lightning is perhaps the easiest example of a pulse of light it goes on for short time it is different from the pulses of light that we use in lasers because this lightning bolts are not correlated you can have lightning now then after few seconds there is no correlation between one lightning bolts and the other or you can think of but if you think of isolated flashes pulses then lightning bolt is definitely a pulse it is just that it does not repeat at regular interval unlike laser anything else.

Some manmade pulse of light that we have all encountered when you take photograph using flash that is also pulse right, now flash is there even in your mobile phone camera right you take a photograph light goes on momentarily and then it goes off that is an example of a flash of a pulse. So laser as we are have going discuss later on some lasers are actually capable of pulsed operation by themselves naturally there are like that. Some lasers can be made to operate in pulsed mode by using some extrinsic external device or may be even without using any external device.

You are going to come to rather interesting pulsed operated interesting kind of pulsed operation when you talk about titanium surface laser where it is almost it looks like it has a mind of its own and it is getting pulsed by itself. But actually not because titanium surface as you going discuss later that also actually gives continuous wave and non pulsed operation unless some certain stringent conditions are made. But these are the 4 properties and these 4 properties is make laser very useful in chemistry.

So to start with let me give you couple of examples, the first example is from well it is from some research paper but you can read it in something as ubiquitous McQuarrie and Simons physical chemistry book the spectrum of ICL. So first of all let me show you the spectrum of ICL. In a spectrometer that is so call not high resolution low resolution spectrum.

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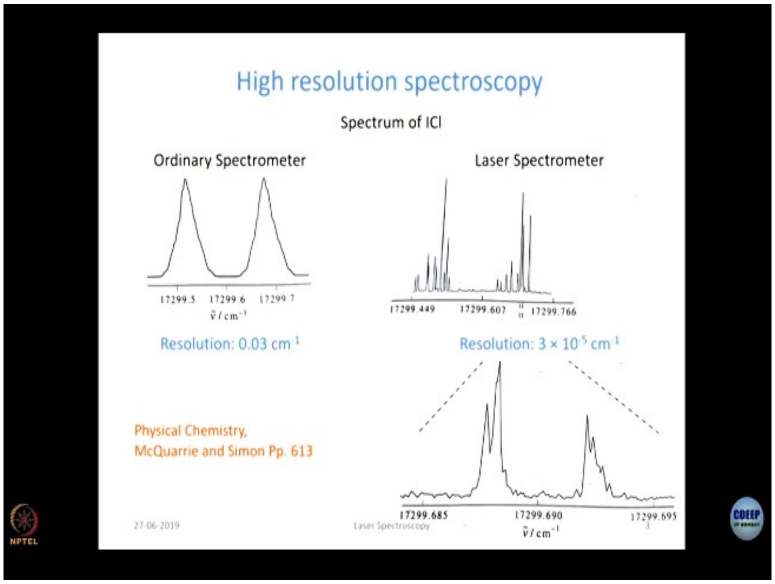

High resolution spectroscopy

Spectrum of ICl

Ordinary Spectrometer

Laser Spectrometer

Resolution: 0.03 cm^{-1}

Resolution: 3×10^{-5} cm^{-1}

Physical Chemistry,
McQuarrie and Simon Pp. 613

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In ordinary spectrometer of course when I said ordinary spectrometer is not so ordinary also because as you can see the resolution is 0.03 centimeter inverse. The resolution is much better than what we normally used for our absorption of recent studies but let us says that this ordinary spectrometer resolution is only 0.03 centimeter inverse. In this kind of spectrometer this is what a spectrum of ICL looks like use it 2 bands and the area depicted it this bands look quite broad actually not so broad if you read the x-axis is 17299.5, 17299.6, 17299.7 centimeter inverse.

So even this so called ordinary spectrometer is a high resolution spectrometer okay. Let us see what happens when use a laser spectrometer. When you record this spectrum of ICL in a laser spectrometer the resolution there is 3 into 10 to the power minus 5 centimeter inverse. So now is everything is relative right so 0.03 centimeter inverse is actually extraordinary compared to the measurement that we make resolution phase but when you are comparing it with a resolution of 3 into 10 to the power minus 5 centimeters inverse it looks quite ordinary right.

So this kind of laser spectrometer the same spectrum looks like this. You see that so much of structure so many features are there so at look like to broad bands turn out to be 2 bunches of really narrow lines. And in fact you can while before going there this read the x-axis once again. Now it reads 17299.449, 17299.607, 17299.766 which means instead going to the first place of decimal we have the accuracy up to third place of decimal.

In fact you perhaps sufficiently better if you zoom into a little more zoom into this small region denoted by the dashed lines and this is what you see. Now look at the x-axis 17299.685, 17299.690, 17299.695 that is the kind of resolution that you can get if you use is really monochromatic laser. Point to note not all lasers are monochromatic to this order and sometimes you might want lasers to be not so monochromatic.

But this is one application the first application that starts with for laser where monochromaticity is used to the maximum possible extent. It is difficult to imagine that it can get any better if you try to get resolution better than this perhaps you will be limited by what is called natural line width. So this is as good as it gets so using a laser which is efficiency monochromatic you can actually see spectra width the maximum possible resolution that you can think of that is one application.

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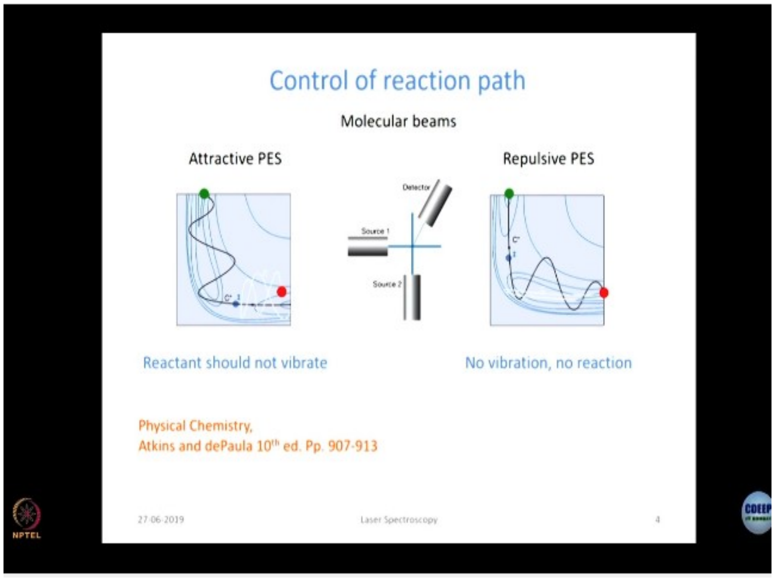

Control of reaction path

Molecular beams

Attractive PES

Repulsive PES

Reactant should not vibrate

No vibration, no reaction

Physical Chemistry,
Atkins and dePaula 10th ed. Pp. 907-913

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Second application is in an area which is considered to be one of the holy grails of chemistry. In chemistry as chemist is our job is to carry out reactions now our job is to carry out reactions in the way that you want them to proceed. Of course in synthetic chemistry it is done by using by playing around with reagent of substrate for conditions and so on and so forth but one of the holy grails that has remained almost elusive over the last few decades in chemistry is that can we make a reaction go in a particular direction at a molecular level very fine level.

And some success has been achieved in controlling the reaction path using lasers and I will give you an example here but I will just tell you the theory of it how it can happen to do that we need to invoke what is called potential energy surfaces. A potential energy surfaces basically tells us what kind of energy barrier is involved in the reaction depending on which path it takes and the way you are drown it here is contours.

So in this contour the reactant is here in the bottom right hand path the product is the top left hand path and these lines of contour denote increasing values of energy. So as you see the reactant is in a minimum the product is another minimum. So as you go from reactant product as you know usually you are going to encounter a reaction barrier. Which mean you think in terms of energy the energy of the system will keep on going up until you reach the maximum and then it goes down as you proceed towards the product.

So in this plot this is how it is drawn so it is like a mountain, see go up energy keeps increasing until this point after which energy gives decreasing and intentionally reactant for channels as show to be perpendicular to each other. So you can think of this diagram as a mountain right, in which this is the minimum this is the minimum and the path is you keep going up reach the maximum this is called the saddle point and then you go down this path to reach the product right. So this point here is called the saddle point look at this point if you go in any direction.

What happens if you go towards the reactant do you go up or down in an energy. You go down if you go towards the product if you go up or down if you have a perpendicular direction then you go up okay. So this is small energy this is small energy and this is the next contour which mean is even higher energy so you need to visualize this so it is like a path short of the pass in the mountain okay you go up turn right and then go down and if you go in perpendicular direction you have the walls of a mountain it is like a pass in a mountainous terrain alright.

Why it is called a saddle point because it is look like a saddle here if you have seen a saddle if you want to sit on a saddle your legs will be on 2 sides see go down and you do not want swipe on the horse saddles goes up in front of you and behind you. So that is what this place looks like. That is why it is called the saddle point okay. Now this is a potential energy surface the way of drawn it here it is an attractive potential energy surface. Which means the saddle point occurs quite early in the path of the reaction.

The other opposite example occurs be repulsive potential energy surface which means the saddle point occurs quite late in the reaction path. Now depending on what kind of potential energy surface it is here reactant has to behave differently in order to reach the product okay. Let us see how. Let us say this is the reactant now it is easiest if you think of the reactant to be a ball that is rolling up and then rolling down you are giving some energy it rolls up and then rolls down.

Suppose we will start in such a way that the reactant does not vibrate, does not vibrate means it go straight what will happen will it pass the barriers let us see what happens. Let us say first the reactant is vibrating then what happens is now try to visualize the picture you have this path going up and down. And the saddle point is quite early if the reactant vibrate then it will be go up and down the path and finally it will come back like this right, what happens if it does not vibrate then it go straight and then it has a chance of passing saddle point moreover.

Once it crosses the saddle point so it go straight hits a wall so goes up little bit and comes down so when it comes down in the direction of the product it is going to oscillate like this okay. So if you want if you if you happen to have an attractive potential energy surface and if you want the reaction to happen then you want the reactant to not vibrate at all. It should only have translation energy no vibration energy right, what happens if the potential energy surface is repulsive in nature where the saddle point is more towards the product.

Now see if the reactant goes straight it cannot reach the saddle point. In order to reach the saddle point it has to turn and the only way that can happen is the reactant goes up the path in a vibrating manner. Otherwise it will not turn anyway right, so it has to go like this and then it has to be in the right place when it goes down it should be on the other side of the wall okay something like this if it goes straight it hits the wall and comes back if it vibrates then this is what happens alright.

But now how are you going to tell the molecule that depending on the potential energy surface you go straight do not vibrate or you please vibrate yes and the amount of energy that is given is best given by using a laser. So what you do is use this kind of a set up this is called a cross peen arrangement, cross peen experiments are nothing new there are 5 classical and their first design so that you have 2 reactants coming into 2 directions yes this reactions they would collide and then the product formed. In this case what you do is.

If you have the reactant coming and in the other path you do not have another reactant your light going in. So in the first case very do not want the molecule to vibrate what you do is if you make it undergo what is called Supersonic expansion then there is no vibration energy only goes straight. If you wanted to vibrate you excite it with an IR laser of appropriate frequency so this way you can make them reaction go in a particular direction or block a particular direction. So using lasers you can think of controlling the reaction path and then you can determine the trajectory right.

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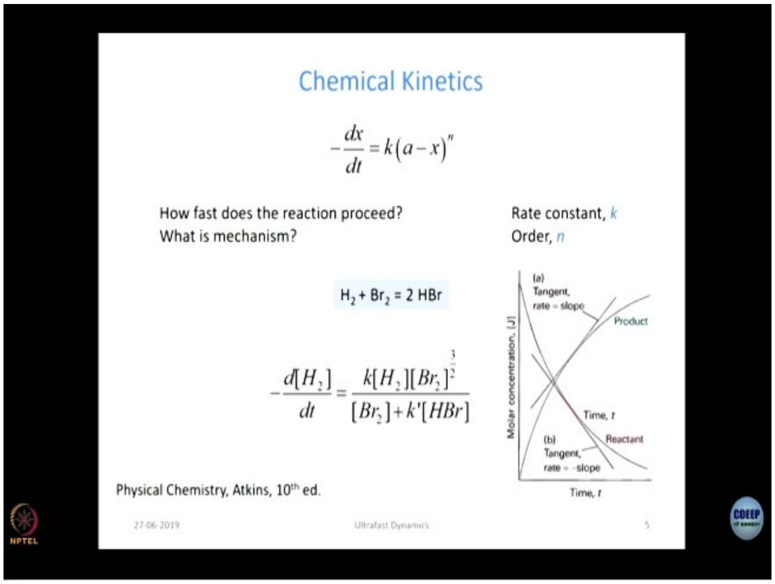

Chemical Kinetics

$$-\frac{dx}{dt} = k(a-x)^n$$

How fast does the reaction proceed?
What is mechanism?

Rate constant, k
Order, n

$H_2 + Br_2 = 2\,HBr$

$$-\frac{d[H_2]}{dt} = \frac{k[H_2][Br_2]^{\frac{3}{2}}}{[Br_2]+k'[HBr]}$$

Physical Chemistry, Atkins, 10th ed.

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Now let us come to the main theme of our discussion ultra fast dynamics before you start the discussion let us first understand what is the meaning of ultra fast what is the need of studying ultra fast reaction. To do that we go back to our class 11, class 12 level knowledge of chemical kinetics. We know that for many of the reactions we are able to write a rate law like this

It is very simple rate law what is the order of this reaction n, it necessary that a reaction must always have an order no because I can have a rate law where you cannot write it like this. It might be quit complicated okay it is not necessary that reaction must have well defined order okay. If you can write the rate law like this then n the exponent is order of the reaction alright okay. And what is k rate constant, so for a faster reaction is k larger or is k smaller. k larger right.

Suppose I give myself this challenge that I want to know what the k will be for the fastest possible chemical process let us see that we can get there. But before that why do we need to know to n, k you have already told me. Rate constant k tells us how fast the reaction proceeds what does n tell us i will tell n is the order but why do you want to know n. How many molecules are reacting widely little dangerous it is not always correct remember the definition of order is the exponent n to which you have to this concentration if it can be written that way that is your order of the reaction okay.

So what does it tell us why do even study chemical kinetics the answer is mechanism right, we talk about so many kinds of mechanisms SN1 SN2 E1 E2 how do you know which mechanism is been followed. Because if you propose a mechanism then will invariably be able to work out a rate equation for it okay. And then your job becomes to find out whether the experimentally observed rate equation matches the expectation from your mechanism. If the match then it is possible but not always guaranteed that your mechanism is correct okay.

Let us come back to this well this is what it is H 2 + Br 2 2HB r it is very straight forward you might think that the rate constant is H 2 concentration multiplied by Br 2 concentration multiplied by k. But actually is not it is found out that the rate law is quit complicated right, rate law is quite completed. So that is because the reaction is not just H 2 and Br 2 coming together colliding and giving you 2 HB r that is more to it. So free radical reaction so when you propose a mechanism you actually come to this kind of rate law right. Now let us come back to our main issue that we want to discuss.

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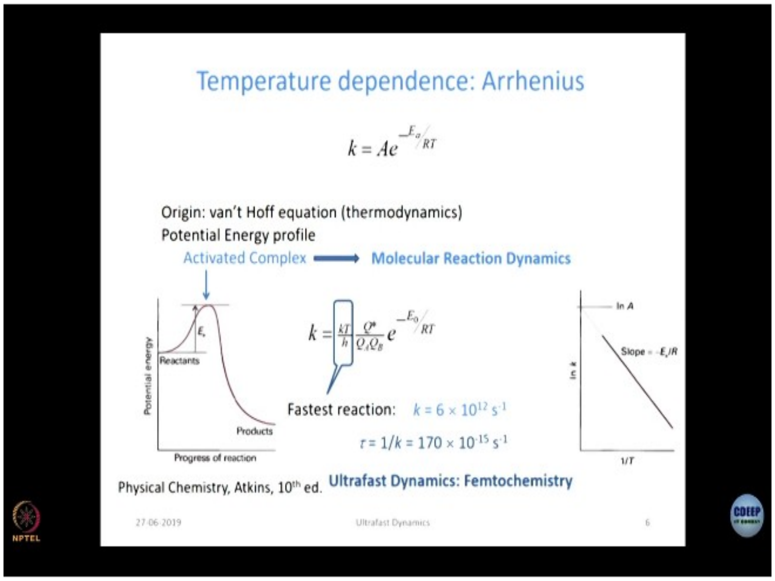

Temperature dependence: Arrhenius

$$k = Ae^{-E_a/RT}$$

Origin: van't Hoff equation (thermodynamics)
Potential Energy profile
Activated Complex ⟶ Molecular Reaction Dynamics

$$k = \boxed{\frac{kT}{h}} \frac{Q^*}{Q_A Q_B} e^{-E_0/RT}$$

Fastest reaction: $k = 6 \times 10^{12}\ s^{-1}$

$\tau = 1/k = 170 \times 10^{-15}\ s^{-1}$

Physical Chemistry, Atkins, 10th ed. **Ultrafast Dynamics: Femtochemistry**

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What is the fastest possible reaction to do that let us again remind also something temperature dependence. I think we know the temperature dependence of rate constant is given by this kind of an Arrhenius equation k equal to Ae to the power minus E by RT where Ae is activation energy okay. So and we are all familiar with this potential energy profile so and so forth. Now perform a little more detailed discussion on the activated complex then we arrived at the subject which is called molecular reaction dynamics.

And to understand that properly what you need to know is statistical mechanics right. And using statistical mechanics thermo dynamics there you get an expression like this just believe me on this one. k is equal to will k T by h where 2 k is here do not get confused that big k is the rate constant and the little k is bozeman constant. kT by h Q star by QA QB where Q are the partition coefficients e to the power minus E 0 by RT. Now let us ask van't hoff theory thus is equation our name hiding equation.

So for hiding equation let us ask when are we going to get the maximum possible value of k first point what about e 0 if e 0 is large does k go up or to go down, down. So what is the smallest possible value small value of e 0 is going to be a large value of rate constant what is the smallest possible value of e 0, 0. So when it is 0 then e to the power minus E 0 by RT becomes 1 do not worry about that.

And let me once again just believe me when I say that the best possible scenario is that this ratio of partition coefficient is also equal to1 okay. So what are you left with them you left with k T by h. k T by h is the maximum the largest value of rate constant that you could get okay. And at room temperature this Trans out the value of 6 into 10 to the power 12 per second okay. Theoretically this is the limit.

You cannot have a rate constant that is larger than this for chemical process and this is something that we would better remember when we do experiments like versus quenching because our many reports in which bimolecular quenching constants of 10 to the power 13 and 10 to the power 14 per second and reported they are all un physical they are wrong those values come because something is wrong with the model that is being used but we come to that later.

So this is the largest value of k you can get so what is a smallest time that would be associated with the chemical process inverse of this okay. Inverse of this Trans out to be 170 femtosecond right. So this is short of the limit that is why you want to study what is called Femtochemistry because if you have an instrument that allows us to study a process that is as fast as 170 femtosecond then will be able to study all chemical kinetics that is there.

You do not need anything faster than this in chemistry of course now a day it will do ultra second spectroscopy but that is not chemistry that is beyond chemistry okay. So this is what we learn that what is the limit of time constant or rate constant in chemistry. The fastest chemical process takes place in about 170 frames per second that is the expectation.

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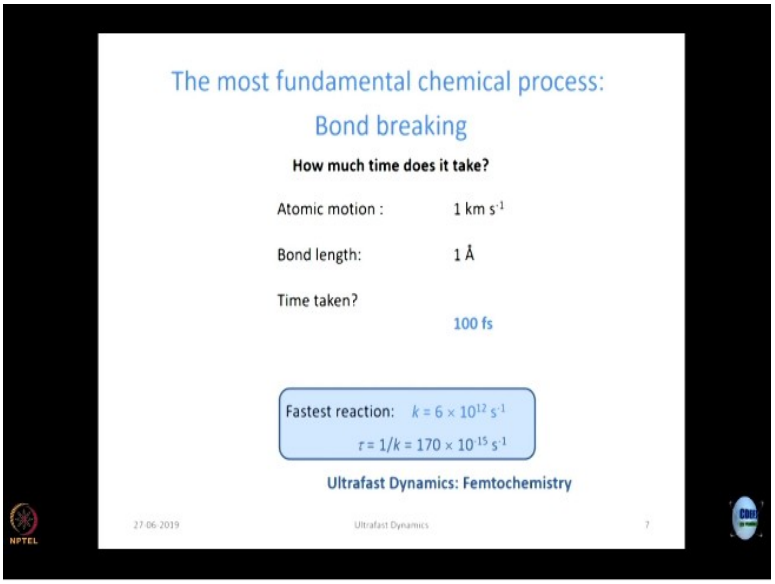

The most fundamental chemical process:
Bond breaking

How much time does it take?

Atomic motion : 1 km s^{-1}

Bond length: 1 Å

Time taken?

100 fs

Fastest reaction: $k = 6 \times 10^{12}\ s^{-1}$

$\tau = 1/k = 170 \times 10^{-15}\ s^{-1}$

Ultrafast Dynamics: Femtochemistry

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And this another way of arriving again it what is the what is the fastest possible chemical process you can think of in generic very generic terms. Bond breaking right breaking of a bond now very too simply stick way of calculating this as well if you want to know how much time it takes to break a bond will atomic motion is typically associated with speed say 1 kilometer per second and a bond is typically 1 Armstrong right. So if you can move the atom by 1 Armstrong than the bond is broken. The ratio is very simply stick way of thinking of it.

Value of 1 was better so what is the time taken if speed is 1 kilometer per second what is the time taken to travel 1 Armstrong. The time transfer to about 100 frames per second okay. So even though this is the very course way of thinking of it. The number we get is not different from the number we get from the hiding equation. So say 100 frame per second 150 frame per second that is the kind of capability that we need if you want to actually see a bond break okay.

So that is what tell us to the ultrafast dynamics. That is why you want to study ultrafast dynamics. So that there is nothing in chemistry that you cannot study okay.

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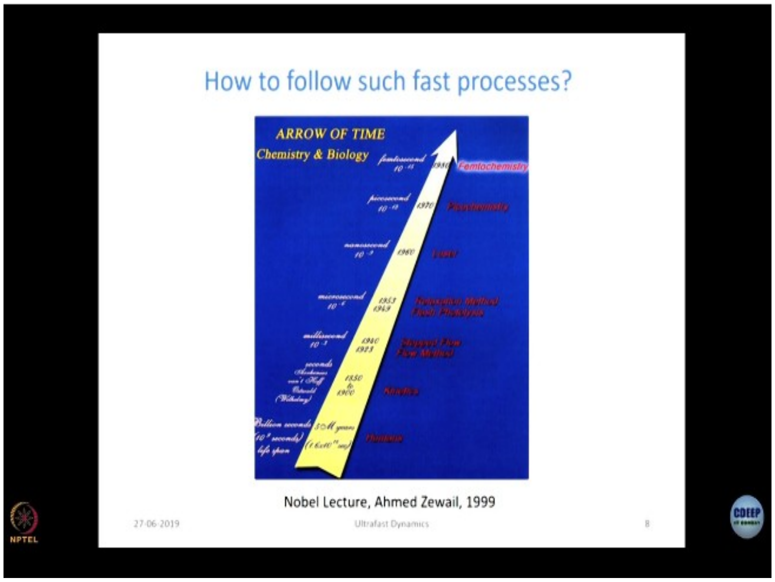

How to follow such fast processes?

Nobel Lecture, Ahmed Zewail, 1999

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How do you follow such a fast pulses the problem is you cannot use a stop clock you cannot use electronic sizing because every electronics every electronic component has its own response time and that response time is much larger than frame per second. So even before I go to frame per second the easiest way of doing it is to create let us say the disturb an equilibrium you have a system in equilibrium. You disturb it, how to disturb it you already discussed in pulses of light.

And remember laser can have pulsed operation to use a suitable pulse to disturb the equilibrium. If you putting in a very simple way use a laser pulse to create an excited state population okay. And then what will happen the population is going to decay right. If you can someone follow this decay of population in time then you can find out the rate constant or time constant associated with it okay. And capability of following faster and faster reaction has also increased exponentially as you see you are in 1940 we could measure about milliseconds.

But between 1940 and 1980 capability will drop from milliseconds by using different experimental techniques. This slide is quit famous this pictures quit famous it is called the arrow of time and it is taken from the Nobel lecture of Ahmed Zewail who got Nobel Prize in 1999 for well we see for what.

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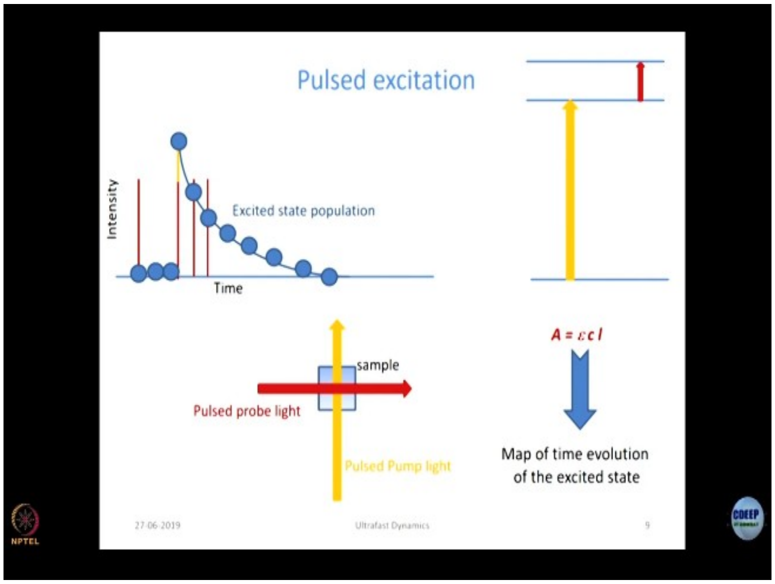

Pulsed excitation

Map of time evolution of the excited state

So this is the idea you need for pulsed excitation you need to produce an excited state population or a disturb population are something and then you measure the relaxation time. How you do that will come to it 1 by 1.

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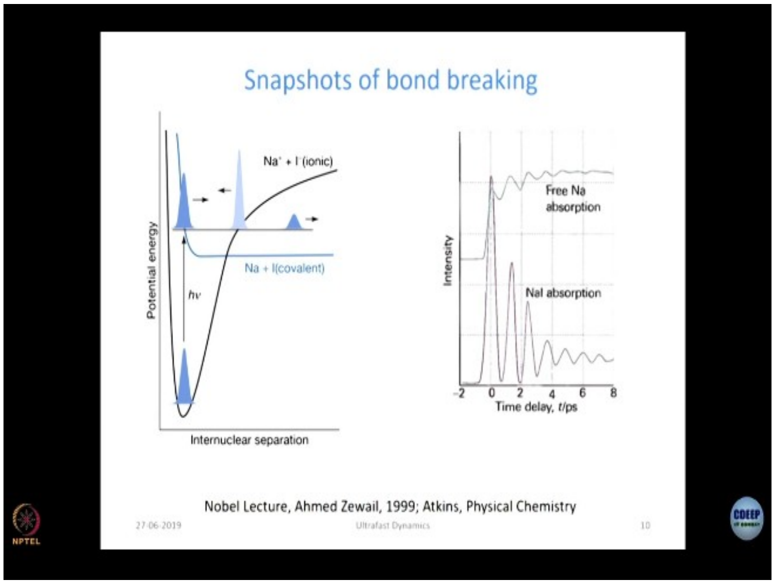

Snapshots of bond breaking

Nobel Lecture, Ahmed Zewail, 1999; Atkins, Physical Chemistry

But let us end today but show by showing one of the pieces of data that 1 0 is noble prize. You only to understand what this means right now but what it says is that it could short off take photograph snap shots of the bond actually breaking. And the way could do it was by using very intense Ultra short pulses of light okay and here you see you can see this oscillation right, this oscillations come because of something called wave packet dynamics that is where this thing you are saying coherent that is where coherence of laser becomes very important okay. So this is what will study over the course slowly step by step.