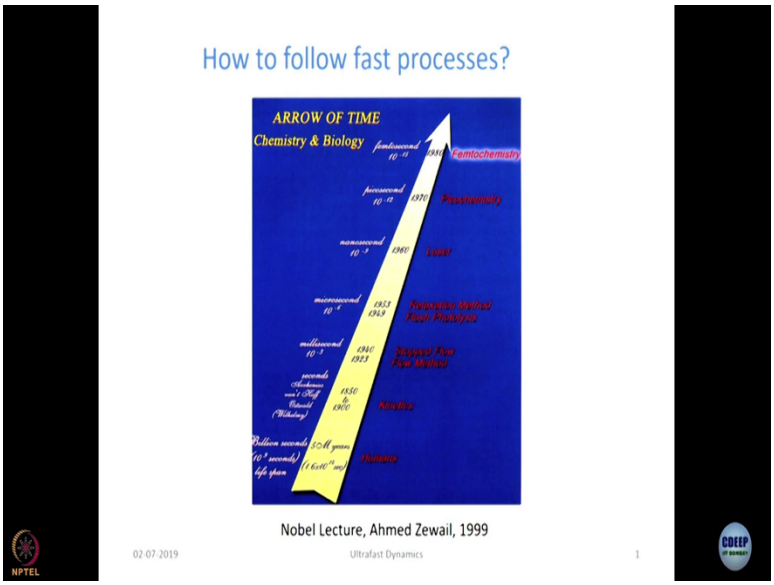
Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture No. 05
Excited State Process

The last couple of modules will learn how to record steady state absorption and emission spectra. But then let us not forget that the purpose of this course is to learn how to make time resolve measurements, how to measure the rate constant of ultra-fast processes. So, that is the direction in which we will proceed after this. But to do that, it is important that we record steady state spectra first. Without that, it makes no sense. Starting to do the time reserved experiment right away because you did not really know them what kind of sample you are handling what the energetics are and so on and so forth.

Just to recollect what we have done so far the correct sequence of doing experiments is that you must record an absorption spectrum first followed by emission spectrum, and then you must record an excitation spectrum. And you are happy if the excitation spectrum exactly matches a normalized absorption spectrum. If it does not, then either you have something interesting going on there is ground state heterogeneity or you have some impurity in the sample most of the time, unfortunately, the second case is correct. So, one needs to be careful even when we do seemingly mundane steady state experiments, that being said, let us come back to the question we had asked in one of the earlier modules.

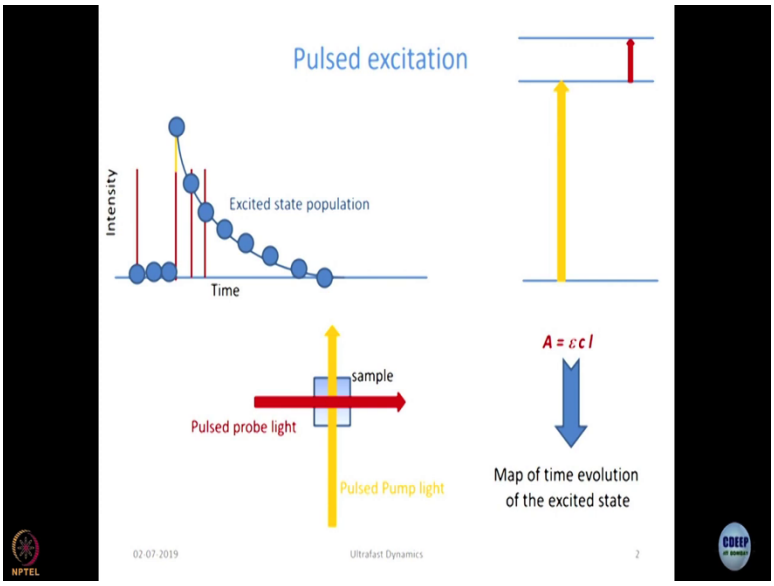
(Refer Slide Time: 01:48)



We want to follow fast processes. And we know what how fast, processes are in chemistry. The fastest process we have learned is expected to take about 170 femtosecond and we have shown you some data from Ahmed Zewails work where they have actually taken snapshots of a bond breaking. But now suppose we want to do an experiment like that suppose we want to follow a really fast process, how do we do it?

That is what we are going to discuss today, how to follow fast processes. And what we do now is we will restrict our discussion mainly to electronic levels. But it is not very difficult to incorporate vibrational levels into this or to go over to completely vibrational levels altogether.
That is what we discussed, how to follow fast processes. And this is something that we had shown earlier, from Nobel lecture of 1999.

At one time, we have said that the capability of following ultra-fast processes or fast processes has increased tremendously. Over the last few decades, as you see in 1960s, one could actually measure nano second in 1953 and 1950s. One could measure microsecond, but 1960s onwards, the journey towards picosecond and femtosecond and subsequently to attosecond has been quite rapid. So it is not very difficult anymore to measure processes that are in femtosecond time regime.
(Refer Slide Time: 03:27)



So we will start with that kind of an example. So the first thing you need is you want to initiate a process by a pulsed excitation. We have discussed briefly what the pulses are pulses light that goes on for a short duration and then goes off again. And here we typically work with femtosecond to picosecond maximum nanosecond pulses, and so femtosecond pulses, I mean full width half maximum is of the order of femtosecond.

So let us say it a source of pulsed radiation and we excite whatever molecules we have using pulse excitation, how does a pulse what does the pulse look like? Like this? If x axis is time, then the ideal pulse would be a delta function. What is a delta function? so it means that it has some delta function has a finite value only at one value of time or one value of x and for all other values it is equal to 0 and of course, I know we are performing an idealized discussion, it is actually not possible to get a pulse that has absolutely 0 wi dth all that is related.

But for now, let us say that we have a capability of having a pulse which is a delta function and you excited sample with it. Now, let us think of what happens to excited state population before the pulse comes, is it possible to have any excited state population, no right, what happens when the past comes all of a sudden this is the pulse? Let us say these are the 3 energy levels in the system, the pulse has come and we are going to call it a pump pulse, because what the pulse does is that it takes the system from this energy level to that energy level.

So, as a pump pulse now, what happens at the instant the pulse is on at that instant, some molecules depending on how strong the pulse is, some finite number of molecules would get promoted to the excited state. Or in other words, at that instant, excited state population is created. And then the light goes off. What happens when the light goes off? We will all the molecules in the excited state come back to the ground state at that instant.

Do you think that would happen? That would not happen. So what happens rather, is that the excited state population decays over time. This is sort of like nuclear decay, you know, that radioactive nuclear decay to more stable nuclear as, and it is the first process. Now they are left to discover themselves is the first startup process by which the decay here. So, what we have done essentially is that we have created an excited state population.

And we have let the molecules there to decay by themselves. So this decay in the simplest case scenario is going to be a first order or exponential decay. The question is, how do I follow it? And how do I follow it with femtosecond time resolution? Did not forget our purpose is to study things in femtosecond timescale. To do this, what we do is, let us consider this is your sample. This square right here. Let us consider this is the past conflict we need a second pulse before the time evolution of the excited state that pulse is called a probe pulse.

And the pulse let us say for now is such that its energy exactly matches and absorption of the excited state that is created by the pump pulse and what we do is we detect the intensity not of the pump light but rather the probe light, let us have a detector here not here, then I will be following the intensity of the light that passes through the light that passes through the sample. And what we have learned in steady state absorption spectroscopy is that when we look at instant intensity like this, it makes sense to talk in terms of absorbance epsilon CL.

And the advantage working with absorbance is that of course it is proportional to concentration. So, now see this red light the probe light is absorbed by the excited state and not by the ground state. So, if I work out absorbance of the probe light then I get to know the concentration of the excited state is not it. So, whatever absorbance value I get a time 0 that should be able to give me a measure of the concentration of the excited state produced as a result of instantaneous excitation.

Now let us say, I delay the quality the pulse probe light with respect to the pulse pump light and that can be done very easily. Let us say we have a pump source and we have approved source of light we have to reflect light using optics and mostly in femtosecond time region. We does not want to use lenses we, as far as possible, we want to use mirrors. Let us say and we will go to the lab and see for ourselves, let us say that we have given some kind of path difference to the pump or to the probe.

And let us say that path differences are exactly the same to start with the pump and the probe lights appear at the sample exactly at the same time. Then what will happen? The probe light is going to interrogate this situation, that kind that time at which the path difference between pump and probe is 0 is called time 0. So, that is what the probe light is going to interrogate it is going to tell us what is the population of the excited state at the instant of excitation what happens if I change the path length a little bit? Suppose the path length to start with is such that the probe has reached the sample before the pulse.

Then of course there is the receptive state population and observance for the probe light is 0 that is the situation at this point in time, then when times it is achieved, then all of a sudden, we see a strong absorbance because that instant the excited state population has been created. Now, if I keep on changing the path length of the probe light. Now, suppose the probe light this is the sample after the pump light said this instead what will happen by the time the excited state population would have decreased from here to here.

So, in this expression, see what have gone down and correspondingly absorbance would have also gone down. So, what I get here is that I get a decreased value of absorbance of probe light like remember, we get a decrease in the absorbance of probe light like that is proportional to the decrease in the excited state population in that time. So, if I keep on changing the delay of the probe light. Then it is going to come later and later compared to the pump light and it is going to interrogate lesser and lesser population of the excited state correspondingly absorbance will go down.

And now the plot that you get what is shown as these big circles in this diagram, the plot that you get is exactly of the same shape as the plot of decay of excited state population with time after excitation by pulse light. So, this is how one can follow the dynamics in time by giving a path length. Now, let us do a quick little bit of math what kind of path length do I have to give in order to get, say 1 femtosecond time resolution. So, it is useful to remember something that is very easy.

Light travels 1 foot in 1 nanosecond. And when I said why foot I mean 30 centimeters that comes quite easily if you know the speed of light and you agree with me that 1 foot is approximately 32nd and 30 centimeter. So, how much time does it take for light to travel 1 micron and you work that out or maybe 3 micron how much time does it take for light to travel 3 micron. Light requires 1 nanosecond 10 to the power minus 9 seconds to travel 30 centimeter.

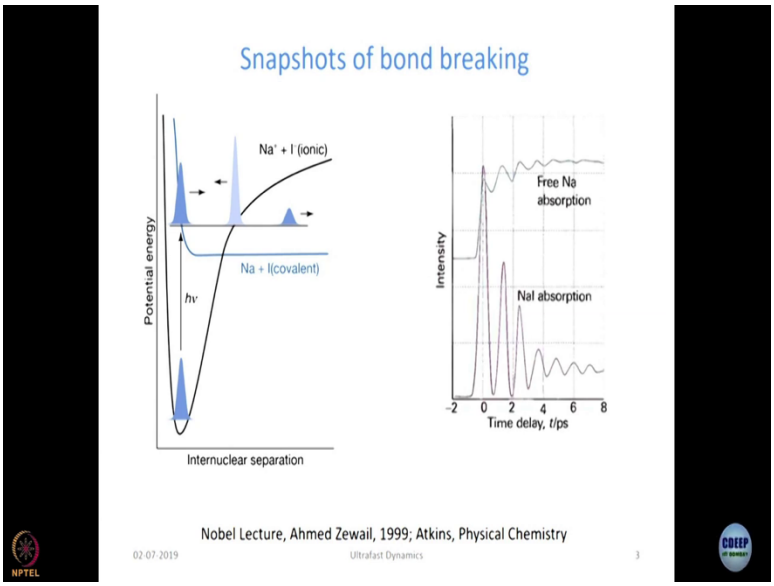
So, to travel 3 micron, how much time is required 1 femtosecond is that right or 10 femtosecond we have 2 answers, remember 1 centimeter is 10 to the power minus to 10 femtosecond not 1 femtosecond. So, if I can give a difference of 1 micron then that is equivalent 10 femtosecond is it easier is it difficult to mechanically produce a path length of 1 micron. So, when I say giving a mechanically giving a path difference of 1 micron, what I mean is that the light will come and strike a mirror.

Let us say, then I will move the mirror forward by half a micron, then the path difference that will come of the light that is being retero reflected, that is 2 mirrors actually, 1 meter like this 1 we are like this light comes it is this mirror comes here goes back, I moved this assembly of mirrors by half a micron. That is equivalent to 10 nano 10 femtosecond time delay. And then, the way we always give time delay is that we were going to sit in the lab, we mount this whole thing on a screw.

So, we have could just turn the screw very minutely. So that the linear displacement is less than micron that is very easily done. So it is not very difficult to achieve femtosecond time resolution by giving path differences of a micron or less. They are going to come back to this when we discussed when we femtosecond optical gating, but the technique that we have discussed in a very

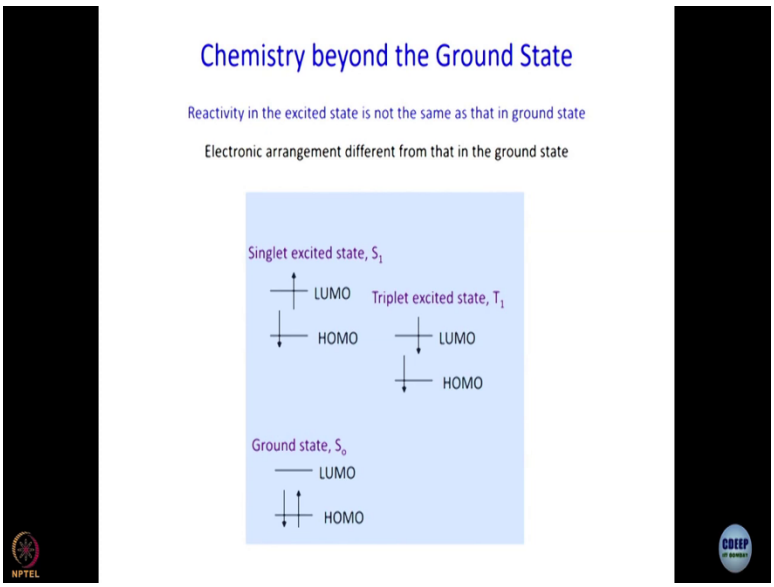
preliminary manner here is called femtosecond pump probe technique. And most of the ultra-fast studies are based on some variant of this technique or the other like.

(Refer Slide Time: 14:39)



If you come back to this, these are delta that I showed you earlier snapshots have been breaking here. So what we have had done was that they use the pump and they use the probe, but then they did something more. They used very short pulses so they could do what is called the excited a wave packet and they could look at wave packet dynamics that is why they could see oscillations like this. We will come back with wave packet dynamics when we are a little further into the course.

(Refer Slide Time: 15:06)



But before that, let us ask a simpler question. We are saying that we are going to create an excited state population fine, but we create an excited state population, and then the molecule comes back to the ground state. That is not much of a fun. At most we measure the excited state population, but then what will we do with that number? The question that we want to ask is, can we initiate some chemistry some chemical reaction by using this pulses of light? And the answer is yes. How would you do it?

Suppose I have some photochemical reaction by which I excite a molecule and the molecule you so protons, this phenomena is called photo acidity. That is what we are going to discuss now. Now, suppose we take that molecule a photo acid, which gives us protons when excited by light at this time we excited with pulse light what will happen will get a burst of photons coming out of the molecule when the light pulse hits it.

So within the past week, let us say we are 100 femtosecond pulse within this hundred femtosecond per second, we would have created a certain concentration of proton in the vicinity of the laser, the light spot that is incident on the sample. So we can create burst of photons this way. And then suppose you have some acid catalyzed reaction. We can initiate that acid catalyzed reaction with the with femtosecond time accuracy.

If we release the protons were using a femtosecond pulse. The question is, why is it that protons will be released in the first place as a result of irradiation with light, we understand that let us go back to some fundamental photochemistry. And let us recall that reactivity and excited state is actually not the same as that in the ground state. Why is that? So? Before we go to that, let me ask a very simple question. In chemistry, what is it that determines the reactivity? What is it that determines how a molecule will react and easy? Well wants to yes but something more fundamental electron configuration molecules were 2 atoms.

What is it that determines that sodium is going to give up an electron and become sodium plus, what is it that determines that chlorine likes to take up an electron and become chloride? It is electron configuration? In chemistry we know that electron configuration determines the reactivity

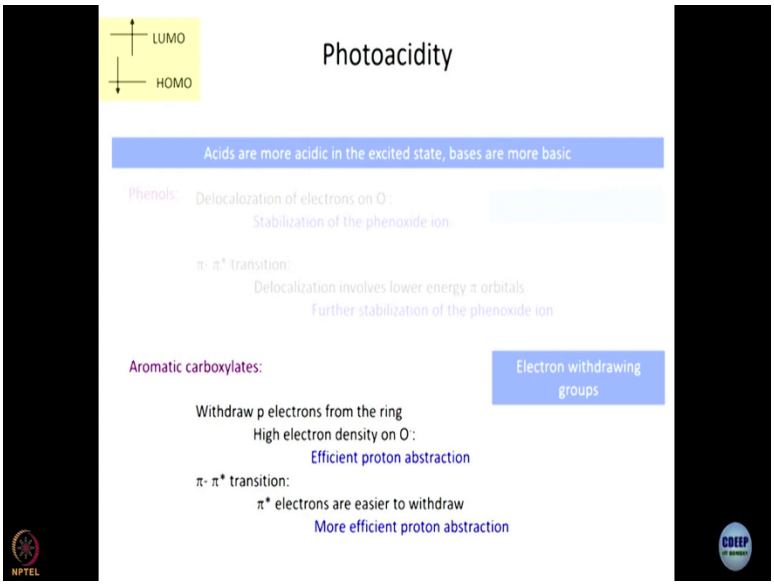
and what we now need to appreciate is that electronic configuration is different between the ground state and excited state that is actually obvious, but sometimes even the obvious has to be restated.

So let us look at this simple diagram here electronic arrangement is different in the excited state than the ground state. So let us see what is electronic arrangement the ground state in a very simple organic molecule no unpaired electron no nothing we can write like this simply there is a more complicated picture but for now we can live with this we have a doubly occupied homo I stuck by molecular orbital and of course an empty lowest unoccupied molecular orbital.

Now let us say we perform a homo to lumo excitation. So in this case, the excitation in the ground state is called singlet ground state it is S0. What is the electron configuration if I denote homo by h and lumo by l? h to l0. Now, let us see perform a homo to lumo excitation. Now, what is the configuration h1 l1 so configuration is different, the activity can be different. I am not saying that it has to be different or it can be different, thats first point to take home.

Second point is that this is not the only way in which you are excited state can be formed. It is not necessarily that you are excited state is going to be a singlet it can be a triplet also. And once again, triplet excited state actually has a little more profound meaning but for now, we can live with this. and triplet state as I think we know has T1 has a lower energy than S1. We will not discuss why we have discussed is in a little more detail in our molecular spectroscopy course. So the point is that electronic arrangement is different in the excited state. In the ground state, so the activity might be different, there was a general discussion.

(Refer Slide Time: 20:08)



Now, let us go to a little more specific discussion. Let us talk about the problem that we introduced a little while ago for to acidity. It is a general rule that organic acids I have written acids here so I did not mean sulfuric acid, nitric acid, perchloro acid, I mean organic acids, organic acids are more acidic in excited state, organic bases a more basic. To explain this let me once again ask a question the answer to which is known to everyone. Let us take an example of an organic acid.

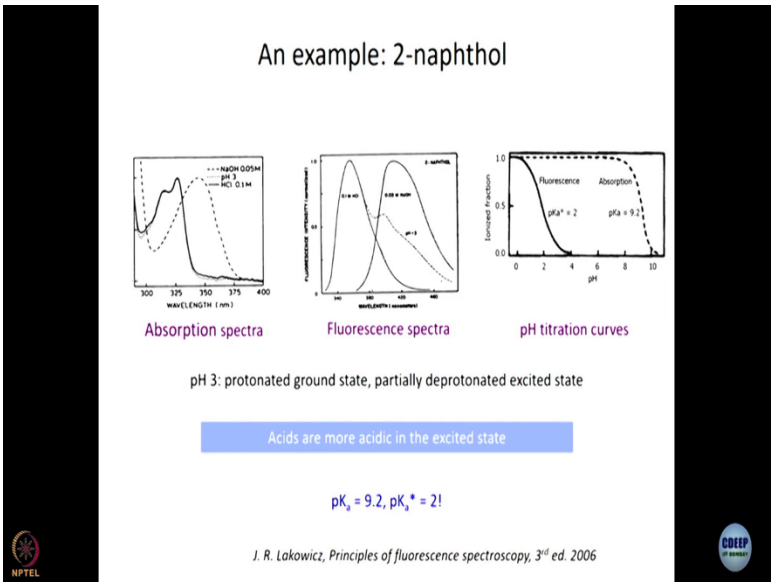
The first example that comes to my mind of course, first example that comes to your mind could be carboxylic acid. But let us talk about phenol, phenol acidic, strongly acidic or weekly acidic is a weak acid will shortly discuss what the PKAa is for at least one phenol. Why is phenol acidic? Release of H+. phenoxide ion that is formed by release of a H+ is stabilized, how you stabilized? I did not want to use resonance because resonance is a valence bond, I mean the tool by which valence bond theory to move that beyond two center two electron system and the problem is yes.

And the problem is that it does not allow you to access excited state. So, let us talk about molecular orbitals. The localization is something we can live with. Now let us think a little bit, we have phenol, we have proton has gone out. So have phenoxide ion. So, let us not think in terms of those electron pairs or anything let us think in terms of an electron cloud on oxygen, is not a happy situation, if it can get the delocalize it gets better. So now if it has to be a delocalized in the same molecule it has to be accommodated in some molecular orbital .what is the molecule orbital that is available the unoccupied antibonding orbitals.

If you go back to the simplest example of will phenol a benzene ring and OH, then I think we remember the energy level diagram for benzene 3 bonding MOs a most 3 antibonding MOs So, one of those 2 degenerate antibonding MOs is the lowest energy molecular orbital available to accommodate the incoming electron cloud from oxygen. And that is what happens and that is why phenol is acidic now the think we are performed a pi-pi* excitation homo to lumo excitation now what will happen? Now you create a vacancy in the lower energy bonding orbital.

Now the incoming electron cloud from oxygen can happily reside in the lower energy bonding molecular orbital, it does not have to go to the higher energy antibonding orbital that is very happy a situation and that is why phenol is more acidic in the excited state than in the ground state. And you can build a similar argument for things like automatic carboxylate which are bases they also become stronger bases for similar reason. This is discussed in any standard photochemistry textbook, now I have proposed something, but there is no reason for you to believe what I am saying unless I show you some experimental proof.

(Refer Slide Time: 23:46)



And here we are showing you an experimental proof. This discussion is available in lakowicz's principles of fluorescence spectroscopy showing you here is absorption spectra of beta naphthol at different acidities. So, first one is this black line denotes absorption spectrum of beta naphthol

in 0.1 molar HCl very strongly acidic. So, we can safely say that this absorption spectrum at high acid concentration is that of undissociated beta naphthol?
Now, look at the spectrum that is in dashed lines. That is for beta naphthol in presence of 0.05M sodium hydroxide. And it is distinctly different from the absorption spectrum that we have for your high, highly acidic solution. Why is that so what is the species of beta naphthol that is going to be there in an alkaline medium like .05M sodium hydroxide. Beta naphthalte proton is not there. So now we know our alphabet. This is the absorption spectrum of naphthol this year the redshifted one is the absorption spectrum of naphthalate.

Now look at the situation at pH 3. Can you even see the absorption spectrum of beta naphtholate at pH 3 in this diagram, if you look very carefully in this region, you see some dots? You did not see it because it is so nicely overlapped with the absorption spectrum of beta naphthol in highly acidic solutions. What does that mean? That means at pH 3, there is no naphtholate it is beta naphthol all the way. Now let us look at the fluorescence spectrum.

This here is the emission spectrum of beta naphthol at pH highly acidic concentration. So, we can safely say that this spectrum is for undissociated beta naphthol . this spectrum here is for naphtholate because it is not highly alkaline solution. Now, at pH 3 you see, the spectrum that we get the emission spectrum is not exactly what we get into the high acidic solution. Rather, you get a shoulder that more or less matches what the emission spectrum would have been in highly alkaline condition.

What does that mean? The absorption spectra tell us that at pH 3, beta naphthol is completely undissociated emission spectra tell us that in emission, we get signature of some naphtholate at pH3 but in ground state there is no naphtholate. Where did this naphtholate come from that is emitting, it must have come as a result of excited state dissociation or photo dissociation of beta naphthol. So, it seems that photo acidity is real. at pH 3, even though there is no beta naphthol at ground state everything is all molecules are in naphthol form.

Some of them actually lose proton in the excited state to be beta naphthol signature of which is a obtain in the emission spectrum. So, photoacidities qualitatively demonstrated, now, let us see it a

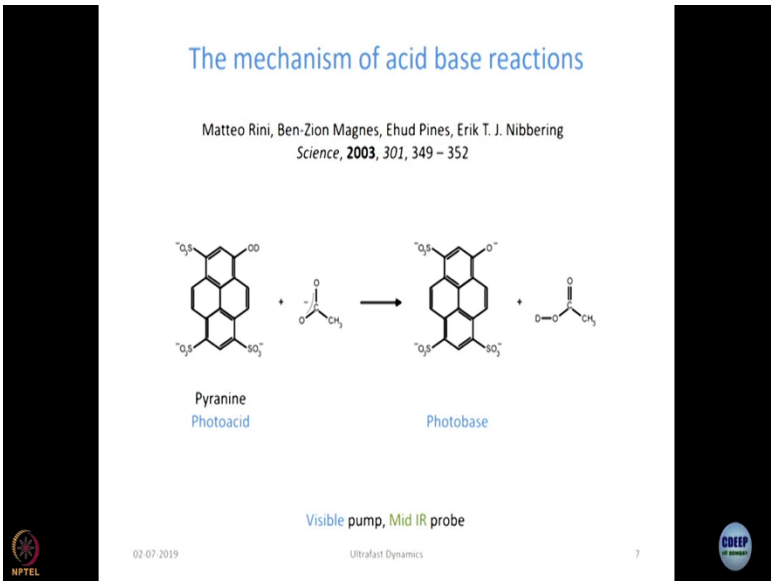
little more quantitative manner. So, using absorption spectrum you can construct a titration curve, inflection point of that graph is going to give you the pKaa in the ground state. If I do a similar exercises and emission spectrum, again I am get a PKA will that PKA of the ground state? No, it will be of the excited state.

Let us see what this titration curves look like. These are the 2 titration curves for the ground state, you see, PKA turns out to be 9.2. As you said correctly, it is a very weak acid in the excited state PKA turns out to be 2 and remember, pKa is log of hydrogen ion concentration hydrogen and activity, so, when we go from 9.2 to 9 or 9.2 to 2, we are saying the change in concentration of protons is from 10 to the minus nine to 10 to the power minus 2, seven orders of magnitude change.

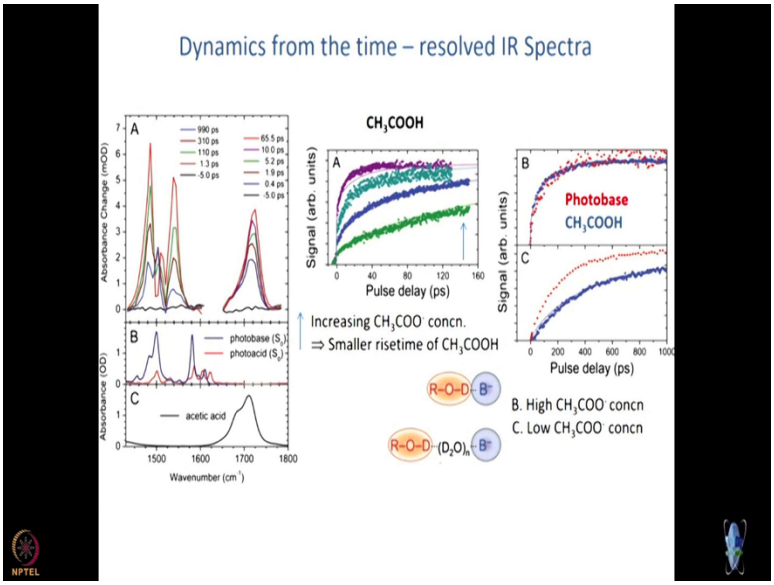
So, photo acidity is actually A is not something that is very trivial it is a strong effect. So, now, if I take the same beta naphthol and I excite it using pulsed light what will happen, the moment the pulsed light is incident on the beta naphthol solution will get a burst of protons coming out. Now, if there is, if I want to follow the kinetics of any proton mediated process, proton catalyzed process acid catalyst process, then I can do that. First of all, I can even work out the time it takes if I can for the beta naphthol to form, naphtholate to form from beta naphtholate post excitation.

All I have to do is I have to do a pump probe experiment using probe in this region, we will talk a little more later on about pump probe spectroscopy about the different kinds of signal today is only an introduction. So, we could actually follow the dissociation of this. But more interestingly, we can also follow the kinetics of processes that are triggered by this burst of protons that were released.

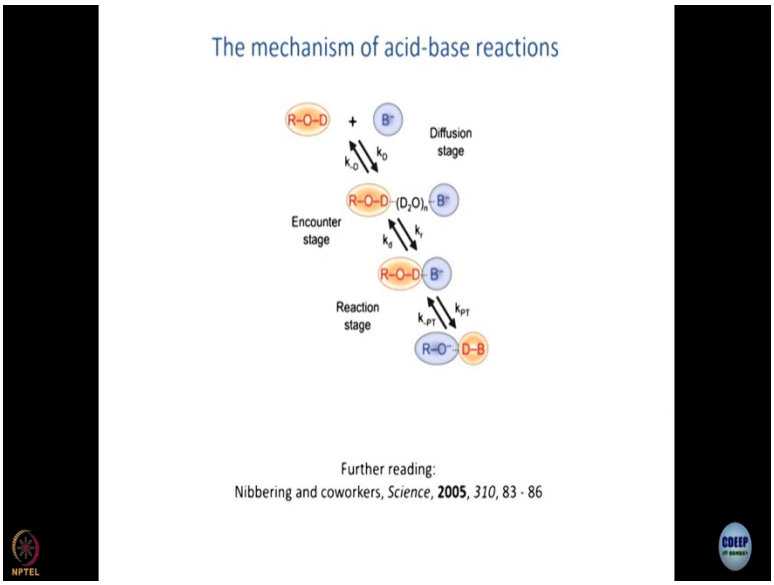
(Refer Slide Time: 29:51)



In fact, this kind of an experiment has been done. In 2003, the first paper was published inside what you see here by the name pyranine this is a very strong photo acid and when excited it proton comes out and a base that was used is acetate using UV pump, proton was liberated from pyranine. **(Refer Slide Time: 30:16)**



And using an IR probe I think we all know what IR spectroscopy is used for. IR spectroscopy is used to identify functional groups in a molecule. So, in this example, when proton goes out what will happen this stage is going to go down with time and then here this acetate way this will come up with time. So, that is the experiment that is done. And once again we will come back and discuss this experiment in more detail later on. But in a nutshell, this is what the kind of delta you get. You see a rise in absorbance, which is which signifies protonation of acetate. **(Refer Slide Time: 31:08)**



And the little closer analysis of the data, what was done by the group of nibbering and co-workers is that they could work out the mechanism of reaction between an acid and a base all of us are studied in school that acid base reaction is very fast and you cannot define the mechanism that is not true any longer and it has not been true for 13 years now, 14 years because the mechanism of acid base reaction has been worked out using ultra-fast UV pump or visible pump IR probe experiments. So, that is the kind of information you can get from ultra-fast pump probe experiments, so, this is our introduction to how to follow ultra-fast processes. Next we are going to move on to see how you follow dynamics of fluorescence in hundreds of picosecond to hundreds of nanoseconds using a technique called time correlated single photon counting.