(Foreign language) Knowledge is supreme.

The second part we can call, this is the name of module we are going to discuss now. Snap shots of bond breaking. Now this is not a name that I thought up, this is the name that Ahmed Zewail had given to his experiments and I think it was motivated by this, you must have seen, right. somebody many-many years ago had, a couple of peopled had argued about, how does a horse run. When a horse runs, is it ever that all the four hooves are of the ground, that was the bet, and to understand that… at that time there was no movie camera or anything, to understand that, the experiment that was done is that many cameras were set up, one after the other, and the shutters of the cameras were attached to some string and the horse was made to run so that in every step it would break a string and a photograph would be taken, so that was a high resolution spectroscopy in the day… sorry high resolution photography in… well many-many years ago when all this electronics was not there and I am sure all of you have seen those photographs of that horse running in different phases, and that tells you whether… I will not tell you whether all the four hooves come off the ground at the same time or not, you need to search and see, but those snapshots have actually been the motivation of many things starting from your movies to trying to understand how a very fast process takes place. So Ahmed Zewail called his experiment snap shots of bond breaking.
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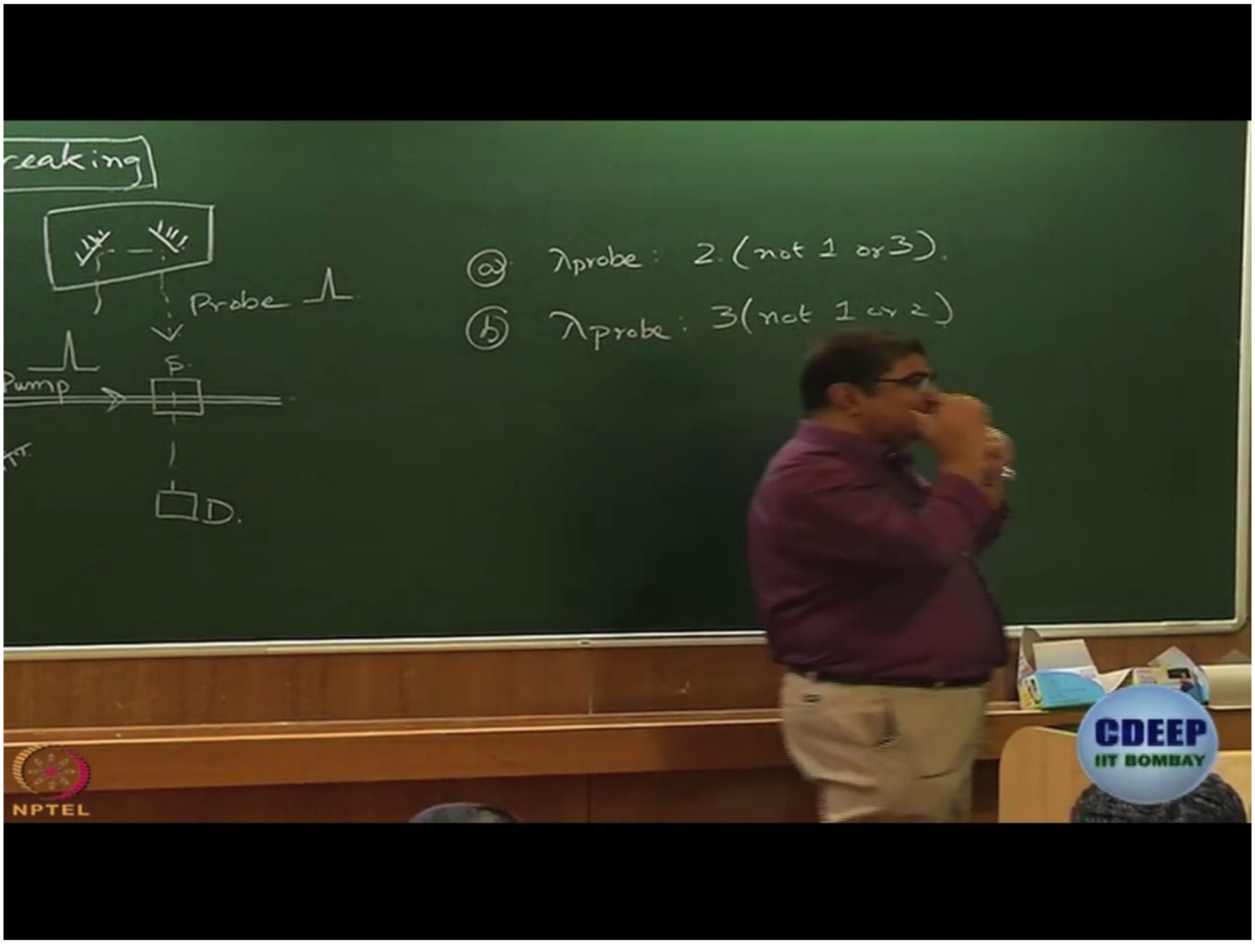

And the first experiment we will discuss is photodissociation of ICN, okay. That is a simple pump probe measurement. By the way this photodissociation of ICN, I don't know why I have not written it here, is discussed in McQuarrie and Simon's book. It is enough if you read this part from McQuarrie and Simon's book. Now in this experiment, there is a small modification from what we had discussed here.

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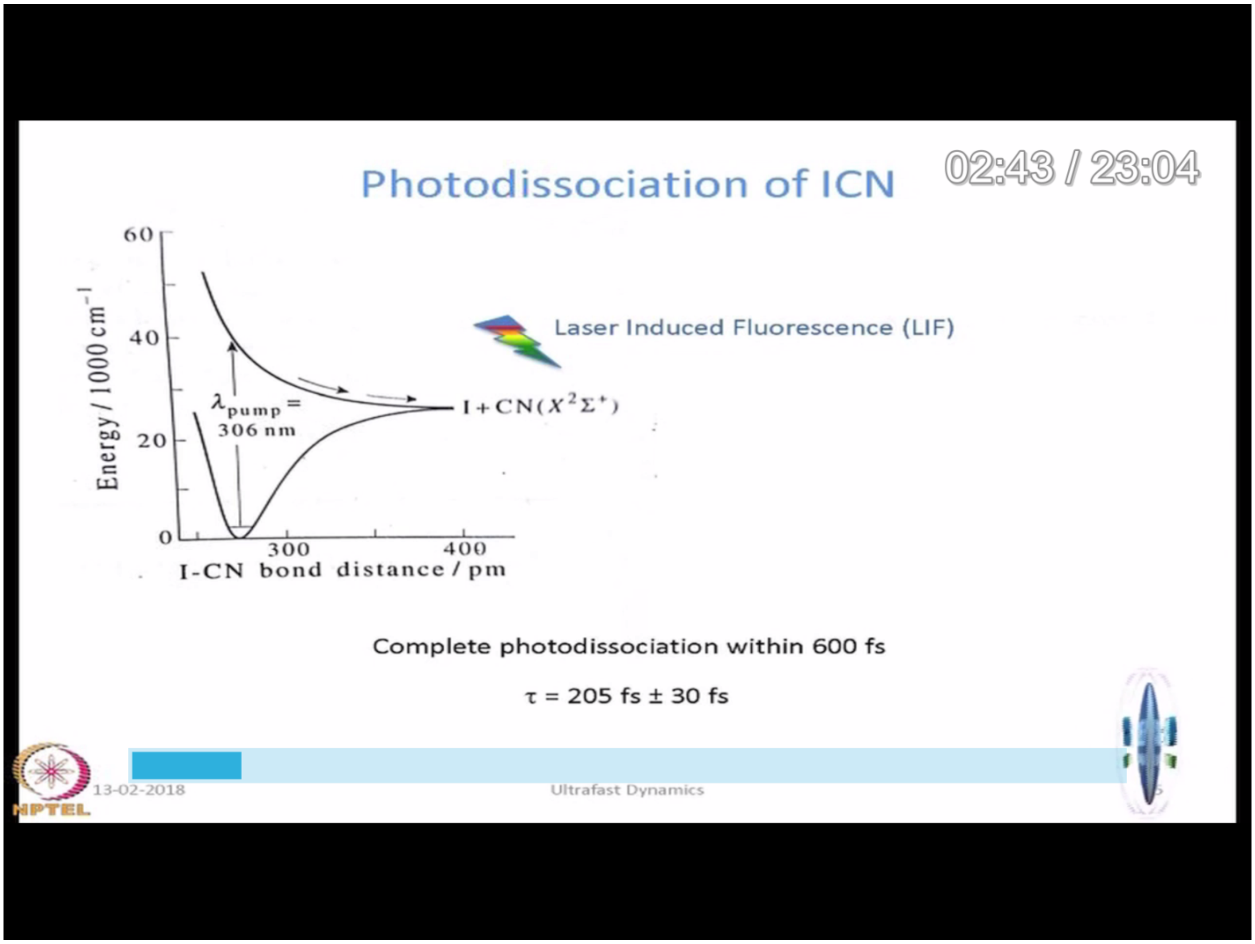

Photodissociation of ICN

Laser Induced Fluorescence (LIF)

Complete photodissociation within 600 fs

τ = 205 fs ± 30 fs

13-02-2018

Ultrafast Dynamics

Here we had talked about absorbents, right. In Ahmed Zewail's experiment of ICN, he did not monitor absorbents, rather he had monitored florescence, this is how the experiment was.

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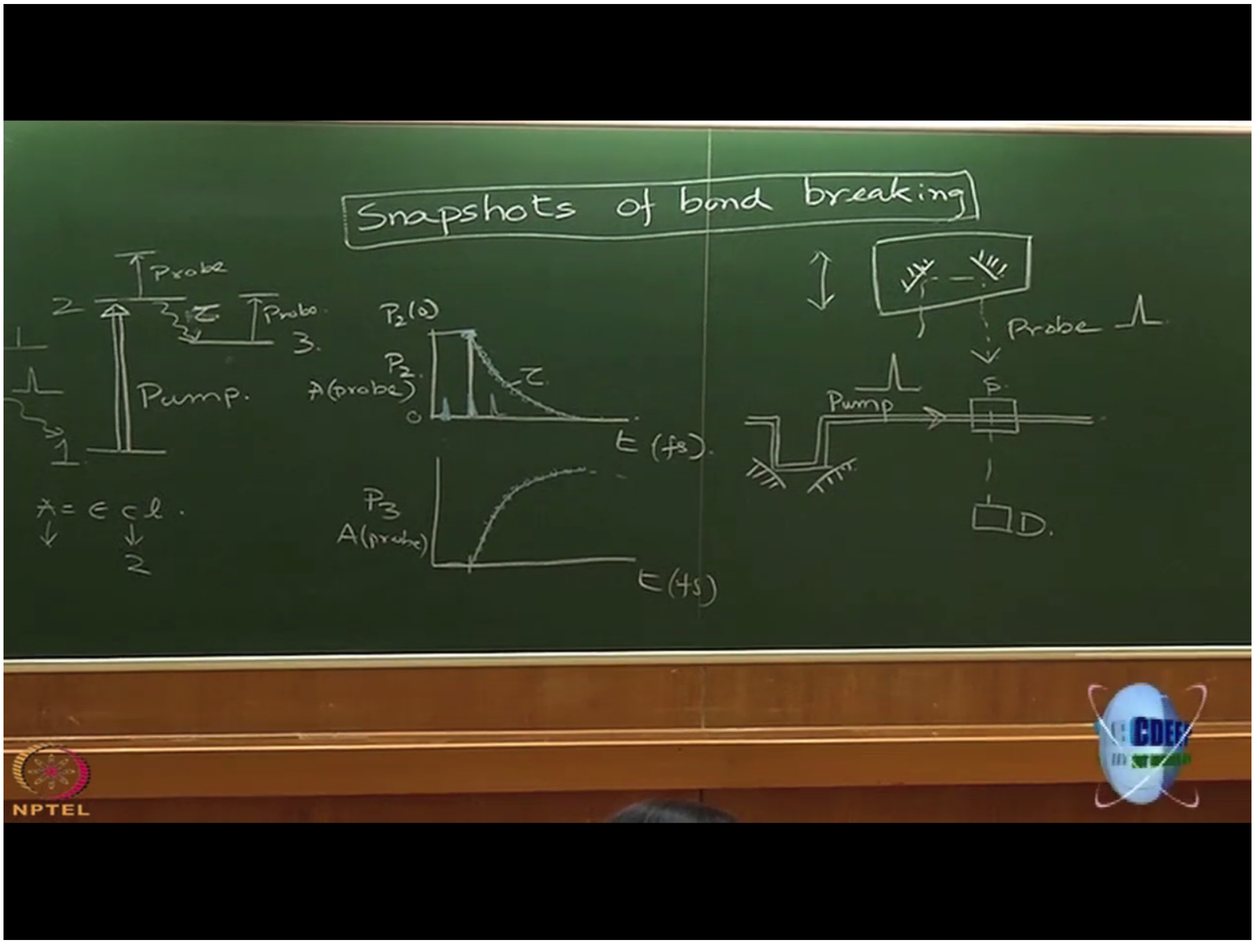

These are the two potential energy surfaces of ICN, okay. We have studied a course on chemical bonding, you would know very well, what these potential energy surfaces mean. So they are… they look very much like a bonding and anti-bonding, but let us just say for now that this is a potential energy surface where yes of course it is bonding, and this is a dissociative surface, right, there is no minimum in the upper surface. So these are the two lowest energy and potential energy surfaces of ICN that was known already from calculation. Now until yesterday we were talking about 1917, right Einstein's paper was in 1917, 101 years ago, now we have moved forward to 1980s, that's a huge jumping time, so by that time all these quantum chemical calculations and all were done and Ahmed Zewail knew that this is what the potential energy surface is supposed to look like. So what he did is, used a pump, which was UV, 306 nanometer, that took the system from the one with a minimum to the dissociative surface, okay. The moment it goes to dissociative surface what happens is you get the product I + CONSIDER, we need not worry about what is this Kai doublet Sigma places for the moment, but by the time we are done with the course, we will not what it means, okay. Let us just understand that when it goes here then the molecule goes to… so this IC bond dissociates, okay. So this is an efficient way of breaking a bond and remember what we are trying to do, we are trying to find out how much time it takes to dissociate a bond, that is the fastest possible chemical process. The way it was done is this. you go here then you get I + CN, right CN is the product and it was also known that if you use 388 nanometer, then CN goes to an excited state, which is emissive. So this emission was actually monitored as a function of time. Same pump-probe experiment, pump on one side, intense pump, feeble process. So what is the wavelength of pump 306 nanometer, what does it do, it takes the molecule to dissociative potential energy surfaces as a result of which IC bond breaks. Where is the probe, probe wavelength was 388 nanometer, right and that was not monitored, that was… that is the only additional thing, what was monitored was the emission, okay. So emission was monitored. This emission is called laser induced fluorescence that we had talked about very-very briefly yesterday, okay. Now when I look at this plot of laser induced fluorescence intensity against time, what kind of a plot do I expect to see.

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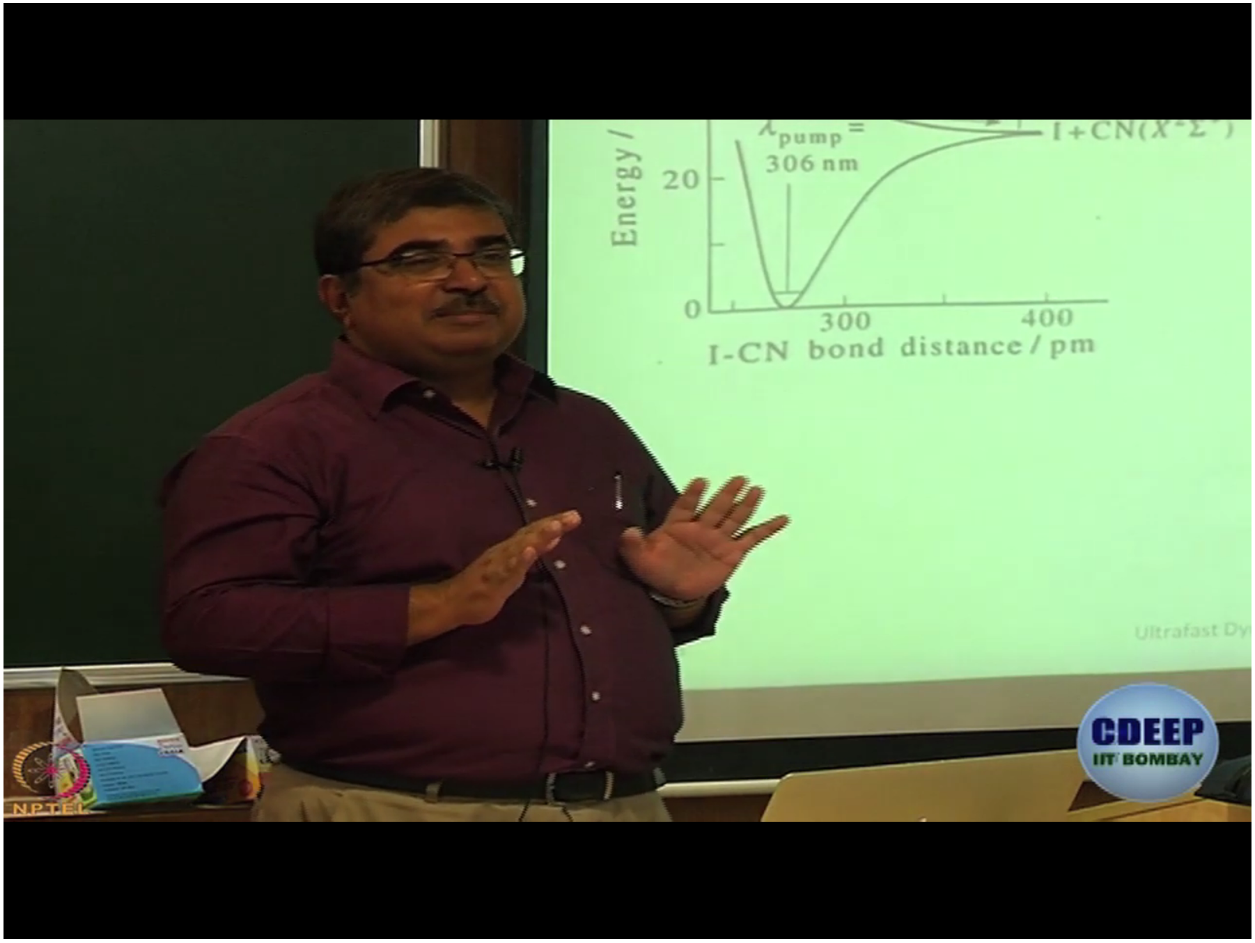

So this is exactly like this, state 3, right. ICN ground state promote to this locally excited state of ICN, immediately it crosses over 2 I+CN, I should not say immediately, because we will talk about some time there, so it crosses over to I+CN. Now we are monitoring the population of CONSIDER. How will the population of CONSIDER evolve with time, like this or like this, yeah like this or like this. When you do the pumping, does CN get populated, no right, what gets populated is the excited state of ICN. Where does CN come from, as a result of breakage of IC bond, okay. So CN is like this. So what is the time evolution of the state 3, this isn't it. So you should see a rise in the initial time, eventually it will decay.

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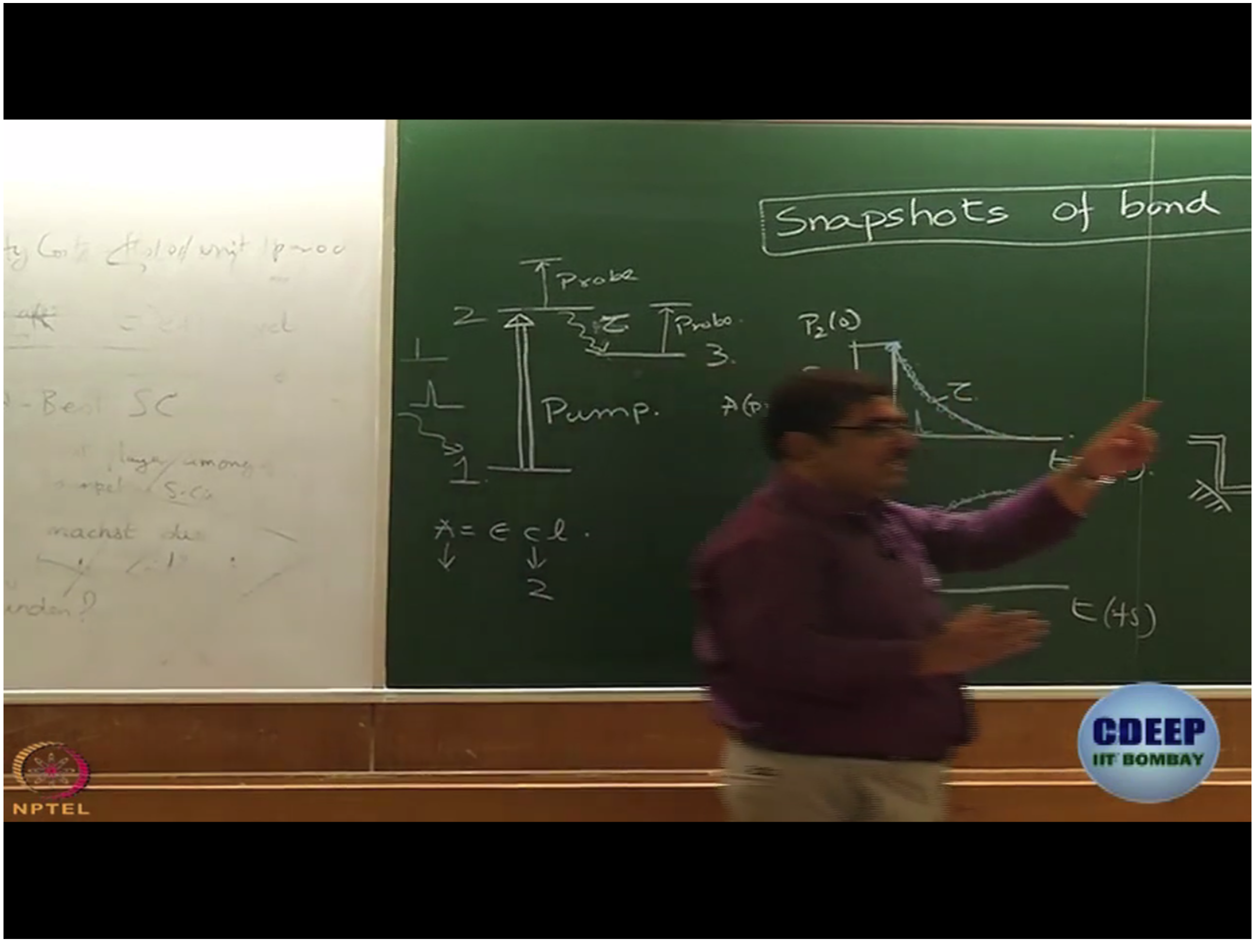

and this is the experimental result. See a rise, what does this plot mean, well -400 means what, the pump has arrived… sorry the probe has arrived before pump. As I told you time 0 means the time of arrival of the pump was, right. Initially what you have is ICN, IC bond is intact. Now at time 0 also more or less it is intact, then as time passes, the concentration of CN increases and finally it looks like it has reached saturation, actually it is not saturation. You go to watch longer times, it is going to decay also, but that is not of our interest, our interest is how much time does it take to go from the dissociated state to… sorry the un-dissociated state to the dissociated state, that is what we get by curveting to an exponential growth and the time that you get is 205 femtosecond, the error is plus/minus 30. If you remember what we had said yesterday and in the beginning of the previous module, we had said that from Eyring equation, the fastest chemical process, that is breakage of a bond should take about 170 femtosecond, that is the expectation from theory and this in front of you is the experiment that actually showed that the time involved is more or less what you get from Eyring equation, alright. So this was the first report of measurement of time of bond breaking and the only way you could do it was by using the speed of light that is spectroscopy, okay. And since that was so fundamental, it is no surprise that this what got professor Zewail his nobel prize in 1999. Are we… any question, any question on this experiment, or have we understood completely? Manthan says the intensity that we are measuring is proportional to the population of which state, right. It is proportional to the population of this state, because if you remember… remember the discussion we had towards the beginning of the course, we will keep coming back to those basics time and gain. Intensity of emission is determined by which parameter, quantum yield, what is quantum yield, well IM by Ifs, I0 x 1 minus 10 to the power minus absorbents, right and at low absorbents that actually just becomes A. Okay so measuring fluorescence or more the absorbents, more the fluorescence, right. So when I major fluorescence of this stage, indirectly I measure the absorbents of this state, okay. If more light is absorbed by this state then only I will get more fluorescence from here that's all. And the reason why fluorescence was used instead of absorption is that, there is a problem whatever, I have told you here I have only told you the positive side of the story. I have not revealed the problematic side of this experiment. The good thing about this experiment is that it can let you see everything, anything that absorbs. The bad thing about this experiment is that it lets you see everything, anything that absorbs. The strength is actually a short coming as well, because the signals that you get from here, if you look at absorbents are so very complex.

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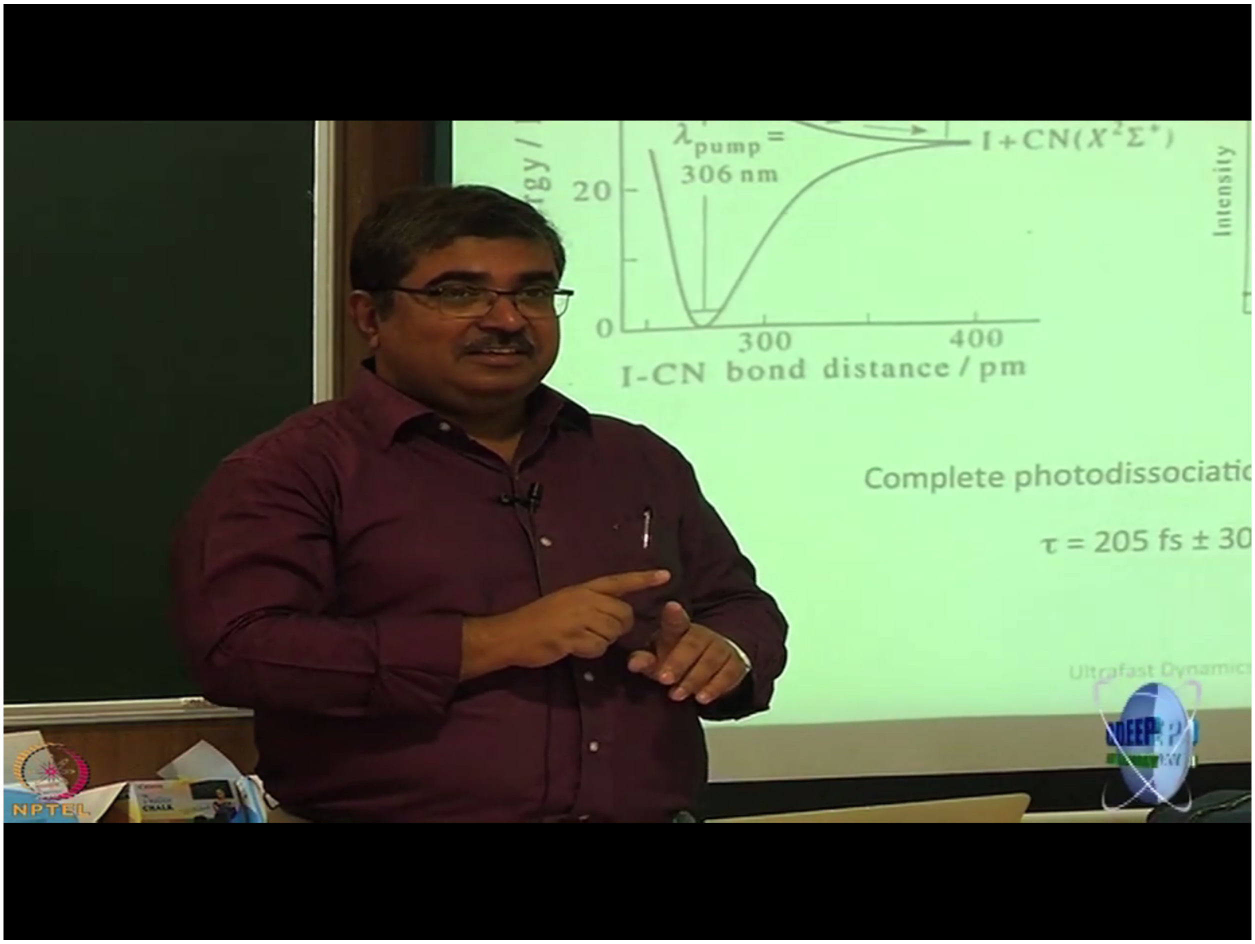

Because see what I have done here, the way I have presented this problem to you, I have kind of tricked you into thinking that this state absorbs energies that are absolutely not absorbed by this state, that is not necessarily correct, that is not usually correct. Invariably there are regions of overlap of absorption of 1 2 3 and whatever, other states that are there. So this experiment is called transient absorption, right. This transient absorption data are usually very complicated and not easy to understand, alright. And here since such a fundamental question was being addressed and since there was a way of bypassing the problem, because this emission, if you look at emission, only this state is emissive, nothing else is. So if you look at emission, then you end up probing only this CN and nothing else, that is why emission was used rather than absorption in this case. Manthan are you answered, okay. Any other question, yes. How do I get from the second time resolution, okay. Let us do simple calculation. Suppose I want to, so if you remember what I am doing essentially is, I am changing this path length, I am playing with the path difference of pump and probe, how I am doing this, by moving these mirrors. So by what distance do I need to move this mirror, if I want resolution of 1 femtosecond. I have the position of the mirrors, this is it, okay, well actually it's like this two mirrors, it's called a retroreflector. I move it to some distance S to get a time resolution of 1 femtosecond. How do I get it, simple, you know what is C, right. S/T = C, S = CxT, this is 3x10 to the power, I will write it in centimeter, no I will write in meter, 3x10 to the power 8 meters multiplied by time is 10 to the power minus 15, this is meter before I forget, so this turns to be Cx10 to the power 7 meter minus 7 meter, actually this is not right, isn't it. There is a factor of 2 as well. Because if the mirror moves by S path length that you have produced is actually 2S so factor of 2 will also come in, okay, but we are not bothered about that, let us just look at this. 10 to the power -17 m, means what 0.1 microne, right. So I have to be able to move it by 0.1 microne. What is the easiest way of getting translational motion, of course I am not going to go and push it, I have to use gears, I have to use… essentially what is done is the spectro reflector is mounted on a long screw, okay, to turn the screw a little bit, this thing moves a little bit, okay. So what determines time resolution essentially is the pitch of the screw. I hope we have not forgotten what the pitch of the screw means, right. What is the pitch of the screw? A screw has grooves, right, separation between two grooves essential, right. And what is the least count. The least count is actually smaller than the pitch of the screw, because you can turn it by may be half a degree also precisely, okay. So that way mechanically the good thing is the time resolution here depends on our ability to, machine an accurate screw, and use what is called a stepper motor. Do you what stepper motor is, or do you know what a motor is, right DC motor, how does a DC motor work? You have a magnet, right, you apply potential difference, and then you get circular motion. Is it continuous or is it discrete? It is continuous, moves like this, right, that's a regular motor, but then in many devices like say your printers, how do the printers go, if the printers, in the printer if it moved continually then it would be difficult to print, right. So in printers, the movement is in steps, that is what uses, what is called step motor. I will not discuss how a step motor works, that's a little too complicated for this. so you can use a step motor, you can use an accurate screw, and easily get resolution of femtoseconds, okay. We adjust have to be able to move our retroreflector in a very-very precise manner, that is machining. Fortunately machining is something that human beings have been at for several centuries, so we are good at that. Any other questions, no.

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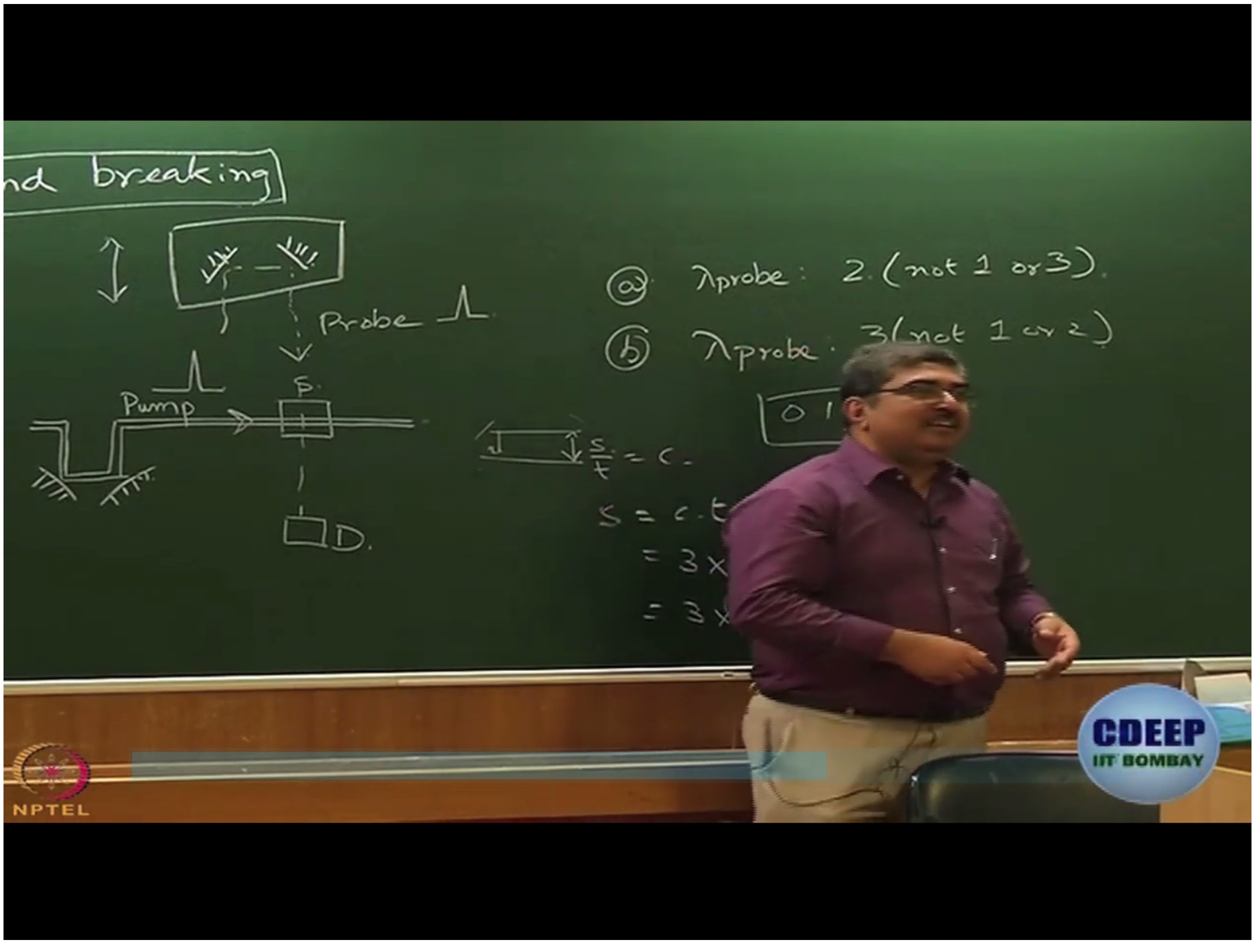

Then I will quickly discuss another experiment of Professor Zewail, which is also interesting, but before that, what is… what are the properties of laser that have been used in the experiment, we just discussed. One is monochromaticity, second is pulsed operation, third intensity, intensity right, because unless you have an intense pump, you cannot do this experiment at all, intensity. So several properties of laser makes it useful for this kind of experiment. Now we are going to talk about another experiment where all these properties are important, in addition to one more property, what is that, a laser is a coherent source of light. Well same… same group, similar experiment, but different system. System here is sodium iodide, okay. So what we have learned so far is how much time does it take for the bond to break. Now the question we try to address takes us to a finer degree of understanding. Now how many of you have studied this transition state theory in B.Sc., right, transition state theory, remember. So in transition state theory, it's all about vibrations, right. How does the bond break, is it that the bond is sitting there, happily sleeping, all of sudden it breaks, no, right. So what happens is there is a low frequency vibration, right, and then this vibration is the one that has to be activated, until the bond breaks. So if that is the case, what I should be able to see, if I can do the right experiment, is that I should be able to see that vibration. So you understand what we are trying to say here, on all the chemistry that we have learned, we have said, you cannot see the transition state. Is it right or wrong, right. Conventional or organic chemistry, in organic chemistry everywhere we said, the transition state is something that is… that seems to be like a fragment of our imagination. The entire theory is there based on it, but how do you see a transition state. Can you actually see the auscultation, you can. This is how it is done. Now one thing I need to tell you is that, when you take a femtosecond pulse, it is actually not very monochromatic, it is broad band, why, because if the pulse is small, say 5 femtosecond, then the uncertainty in time associated with it is also no more then 5 femtosecond, right, very small uncertainty in them, that brings in a large uncertainty in energy, same uncertainty principle the kind of argument, okay. So since it's a broad band pulse, what it does is, when it performs an excitation from an electronic level, you understand that each electronic level is associated with many-many vibrational levels, right, this as well as that. So actually the transition takes place from many vibrational levels to many vibrational levels. So what you have in the excited state is not one wave, but many waves, and you are doing a coherent excitation, that means at 0 time, at the time of pumping all these waves are in phase, okay. What do you call such a collection of waves, louder. A collection of waves, all of them… all of which are in coherence to start with, what do you call it? You add a lot of sign wave, it's a packet of wave, so wave packet, right this is a wave packet, a collection of waves. And then I think you know that when you have many waves, what happens is initially the intensity is large, then it falls off, and if there are too many waves, they don't get back again, that is what a wave packet looks like. So this wave packet is produced. Now in sodium iodide what happens is this. This is the potential energy surface of NA+ I-, ionic, there is also a potential energy surface of NA + I, sodium + iodine. Everybody has done flame test and there we have seen yellow color of sodium, that is not NA+, right, that is sodium NA, right. This is why it happens, because there is a possible… it is possible to go from this NA+ I- potential energy surface to NA+I neutral potential energy surface. So what you do is, you excite is and then the wave packet oscillates between the ionic and the covalent potential energy surfaces. Can you see it. First of all what kind of shape do I expect, if I tune my probe to that of NAI, NA+ I-, then I expect a decay, if I tune it to that of NA, neutral, then I expect a rise, right. But if there is an oscillation between two, then what do I expect to see. The rise will not be like this, it should be something like this, that is what you get. So here what you see is, not only do you get the time required for breaking of a bond, you can actually see, how it is breaking. So like that horse we talked about, whether the four hooves come off the ground at the same time or not, you can actually see this auscultation between NA+ I- and NAI surfaces. So this low frequency vibration, that is central to transition state theory, this is your low frequency vibration and you can see the period is about 1 picosecond, okay. This is of course complicated. So we will stop here. You can read this part from Atkin's book. I do not expect you to have understood everything today. Please read, come back, and ask questions. Next day we start discussion another kind of spectroscopy, which has become very important only because we have lasers and once again, all these properties, monochromaticity, intensity, coherence, everything is important for that kind of spectroscopy and that is Raman Spectroscopy, next day we discuss Raman's spectroscopy.

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