(Foreign language) Knowledge is supreme.

So this is what we had stopped... this is what we had stopped yesterday. Where said that due to the properties of laser light, intensity, monochromaticity, pulsed operation, coherence, and well directionality, you can do many things, you can do many kinds of spectroscopy, that you cannot do without lasers or at least you cannot do as well without lasers. And one of the things that we came... we ended with was we said that lasers can give you pulsed operation. So we are saying that using lasers you can actually measure fast processes. And the question we asked is how fast process do we need to measure in chemistry? And using this Eyring equation, which many of you are going to study, if you have not studied already, in this course on energetic and dynamics, using Eyring equation we reach the conclusion that the fastest process in chemistry takes place in about 170 femtoseconds. So then we stopped saying how do you measure time in femtoseconds. Because as you know it very well no electronics can measure such fast times in... well directly. So we need an indirect method. And the method we are going to use, builds upon the same kind of principle as what we have studied in the beginning of the course, time domain spectroscopy, FT spectroscopy. Okay so this is what it is.

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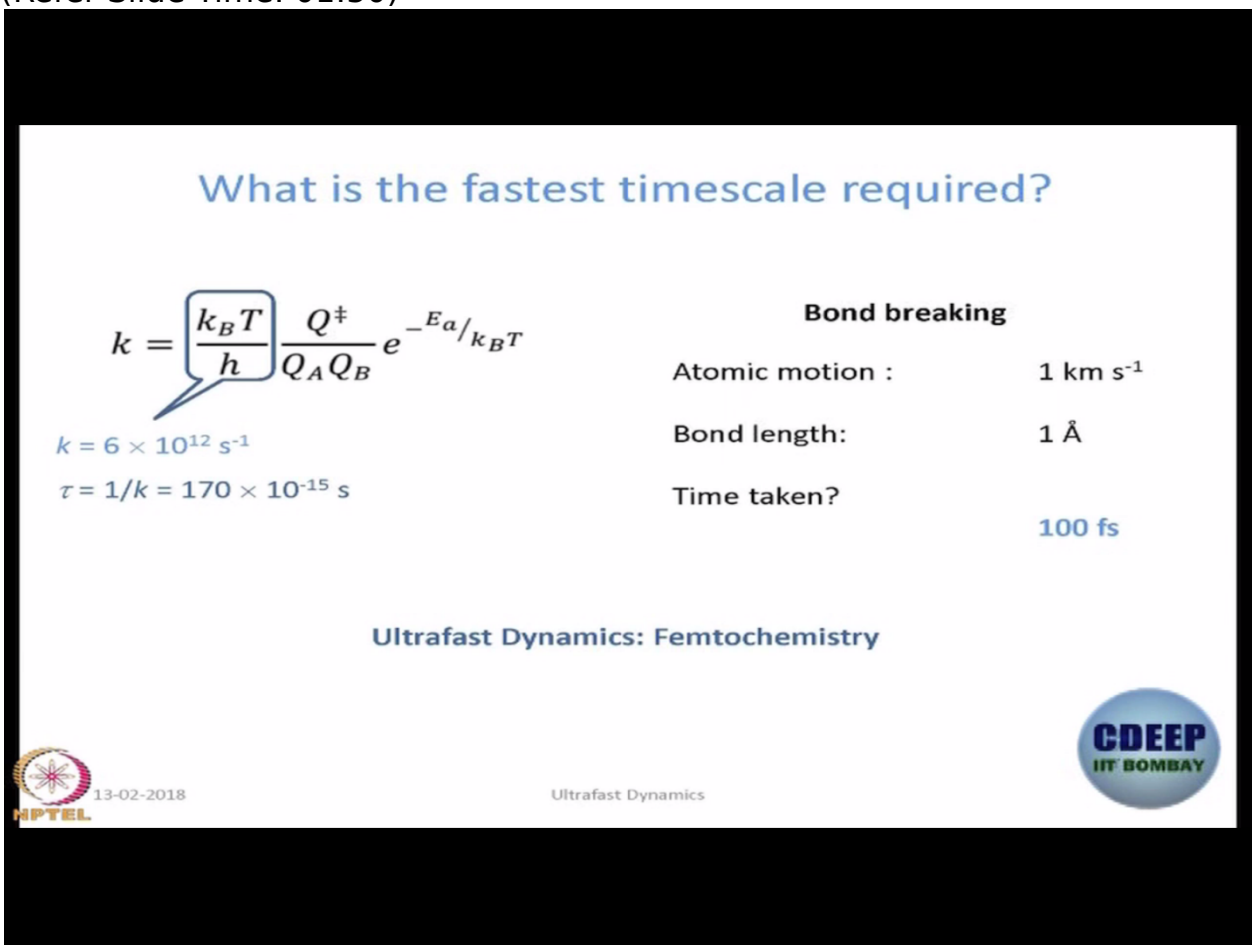

So first before trying to show you how exactly the experiment works. Let me pick the principle of the experiment. The principle is this. Let us say this is a ground state of the molecule, I will call this 1, let us say this is an excited state to which I can excite directly, this is 2, as we will see later on, if this is your, these are electronic levels, then this is called the Franck Condon excited state and then let us say a bond breaks, and this let us say is stage 3, which is the bond broken stage, okay, understand what I am saying. So if this the case, then the time I want to measure is associated with this 1, this I will just write Tau, this is the time that I need to measure, the time required for going from 2 to 3, are we clear, time for a bond to break, how do I do it? One way of doing it, well the only way of doing it, if you want to measure time, is to use an intense pulsed laser. When I draw something like this, it denotes a pulse, Y axis here is intensity of light and X axis is time, okay. If you want to draw a delta pulse, of course you draw it like this, but no pulse is really a delta pulse. Okay you excite with a delta pulse. Now let us think of the population of level 2. How does the population of level 2 evolve with time. Is there any population of level 2 at time 0, if these are electronic levels, no, right. Well initially the population is 0. Let us say this is where the pulse comes at this time. What will happen the pulse hits the molecule, all of a sudden population of 2 will build up, right instantaneously, okay. so at this time, what happens is population of level 2 goes to let us say this level. Okay I can call this something like P2 at time 0, so this is the definition of time 0, for these experiments time 0 means the time at which the laser pulse hits the molecule, clear. Now then the light goes on and goes off instantly, right. Now what happens? What happens to the population of 2. If you will… DK exponentially we have seen, right, so it falls like this, not much issue with that. And if this is the most efficient process, then we can say that time… ligament time associated with this will be the same Tau. Now let us ask a different question. How does the population of level 3 evolve as a function of time? Initially there is nothing, then comes time 0, the laser comes and hits… laser pulse comes and hits the molecule, do I get any population of lever 3 at that time, no. What about some time later, yes it starts building up, how, from here. What about sometime later it becomes a little more. So what you get is from time 0, you get a rise in the population of level 3, of course eventually it decays, okay. Now see, do these curves remind you of something that you have studied in chemical kinetics. Is this is not the kind of time evolution of population for the reactant and no intermediate, intermediate isn't it, intermediate, because it goes up, eventually it comes down, we are only showing the initial time, that is all. So my job is to find out, let us say if we can measure population of P3 in some way, my job is to obtain this curve. If I want to determine population of 2 in some way, my job is to determine this decay. Alright, clear. How do I do it spectroscopically. If you are doing spectroscopy, how… what is the easiest way of measuring population? What is the simplest relationship between concentration or population and a spectroscopic parameter that you know.

Lambert Beer's law, right. A = Epsilon CL okay so what you do is this. Now this is not enough, this beam I call it the pump beam, well basically I should have drawn here, so this light that comes in, to create the excited population, this laser pulse, the intense pulse, that is called the pump pulse. Now if I use a weaker light, weaker... a light of weaker intensity to probe an absorption of this or the absorption of this, this is called the probe beam. Let me draw the experimental schematic in the simplest possible manner and let's see if you understand what I am trying to say. Let us say, here is your sample. This is the pump beam an intense laser pulse. What does it do, it creates a population of level 2. Then let us say I use another much less intense beam and I put a detector here not here, this is the only thing that we need to understand here. I am monitoring the intensity of this probe beam, not the pump beam, okay. Let us say this probe is tunable, tunable means, I can select wave length, that you can do right? When we discussed absorption spectrophotometer, we said you start with white light then you put a monochromator and you get whatever wavelength you want. You understand what I am saying? This probe beam is tunable. I can get different wavelengths or different energies in the probe channel, are we clear. Now let us say the probe is tuned to an absorption of 2, that means it is absorbed by state 2, not by state 1 and not by state 3, that is possible, right. Then what will happen, if I monitor absorbents of probe here, then the absorbents of probe should follow exactly the same kind of decay as the population of P2, is it right. So we are talking about case A, then lambda probe is such, that it is absorbed by 2 and not 1 and not 3, are we clear. Yes Madhu, excellent question. What Madhu is asking, you are saying that pump is used to create an excited state population, now I bring in the probe, that is going to deplete the excited state population, right. Does that not affect the measurement. The answer is it does. So If I am to minimize this effect, what do I have to do. I have to use an intense pump and a feeble probe. Suppose this pump takes, say 10 to the power 20 molecules to state 2, and the probe takes only 100 molecules from state 2 to some higher level. Then 10 to the power 20 minus 100 is practically equal to 10 to the power 20, Madhu your answer, but that is a very important thing to remember when you do pump Rho spectroscopy, the probe light has to be sufficiently feeble, compared to the pump light, otherwise, you will have a second pumping, which will measure your experiment. OD = Epsilon CL, right. I have selected the probe in such a way that it is absorbed by state 2 and no other state. So time evolution of A will exactly follow time evolution of C of state 2 okay, and concentration and number you know, what the relationship is, that’s not such a big deal, NA divided by 1000. Similarly if I take case B, well the wavelength of the probe light is such that it is absorbed by 3, not by 1 and not by 2, then what will happen, the absorbents of probe will exactly follow the same shape as this one, clear, and the point to remember is that probe has to be me much more feeble compared to the pump, clear. can I go ahead? Now... so now in the discussion that we have had so far, what we have learnt is we have build the schematic of one way of following the time

evolution of states by using light. But the fundamental problem remains. The fundamental problem is this time has to be in femtoseconds, okay. How do I get time in femtoseconds. To do it what you do is, for the probe also you use a pulse. How we generate the pulse and all, we will not get into that, just believe me on this. Let us take this situation. Wavelength of the probe is such that it is absorbed by state 2 and no other state. Okay, now let's say this is my pump and this is my probe, what I do is, I put in two mirrors here, and this also I can do the same thing, I can put in two mirrors here and let me say, I put this mirror on a translation stage. A translation stage means, something that can be moved forward and backward that's all, nothing else, like a small cart that can move in a straight line. So this can move forward and backward. So using a tape, something as simple as a measuring tape, I can decide what the path difference between pump and probe will be, right, okay. So… and if this is movable and this is fixed, then what I can do is… or if this is moveable and that is fixed, does not matter, than what I can do is, I can vary the path difference between pump and probe, okay. Now… now think this is time 0. Let us say, it will be easier to understand, I think, if you can think the pump is fixed and the probe is moving. This is time 0, this is when the pump arrives at the sample. Okay suppose the path length of the probe is smaller than the pump, then what will happen, the probe will arrive at the sample earlier than the pump, okay. Let us say, the probe arrives at the sample here and at that time is there any excited state population, right, what will absorbents be in that case, 0, okay. So for this path length absorbents will be 0. Now let us take a situation where path lengths of pump and probe are exactly matched, there is no path difference okay, where does the probe, at which point of time does the probe arrives here, okay. Now what will happen, now you have a high population of the excited state, so absorbents will also be high, okay. So if I normalize and just draw it here, let us say this is the absorbents. Now suppose I change the path length in such a way that the probe pulse arrives at the sample after the pump pulse, may be at this time. Now what will happen, population has decayed from here to here, corresponding absorbents will also decrease. So like this by varying the path length in step wise manner, so remember it is exactly like your time domain spectroscopy, fourier transform spectroscopy. What you are doing is, you move the… so this is the moving mirror, this is the fixed mirror, right. You move the moving mirror to a particular position, stop there and make a measurement, that is how you get each of these points. Then move the mirror to another position, another path difference, make another measurement. This is how, what you can do is, point by point you can build up the time evaluation of absorbents of state 2, which is equivalent to the time evolution of population of state 2. And if you match the wavelength of the probe to the absorption of 3 rather than 2, then this is what you are going to get. So like in fourier transform spectroscopy, once again we use the speed of light to give us a time resolution that is impossible to achieve by using electronics, okay, this is the principle, tell me if you have understood or not.

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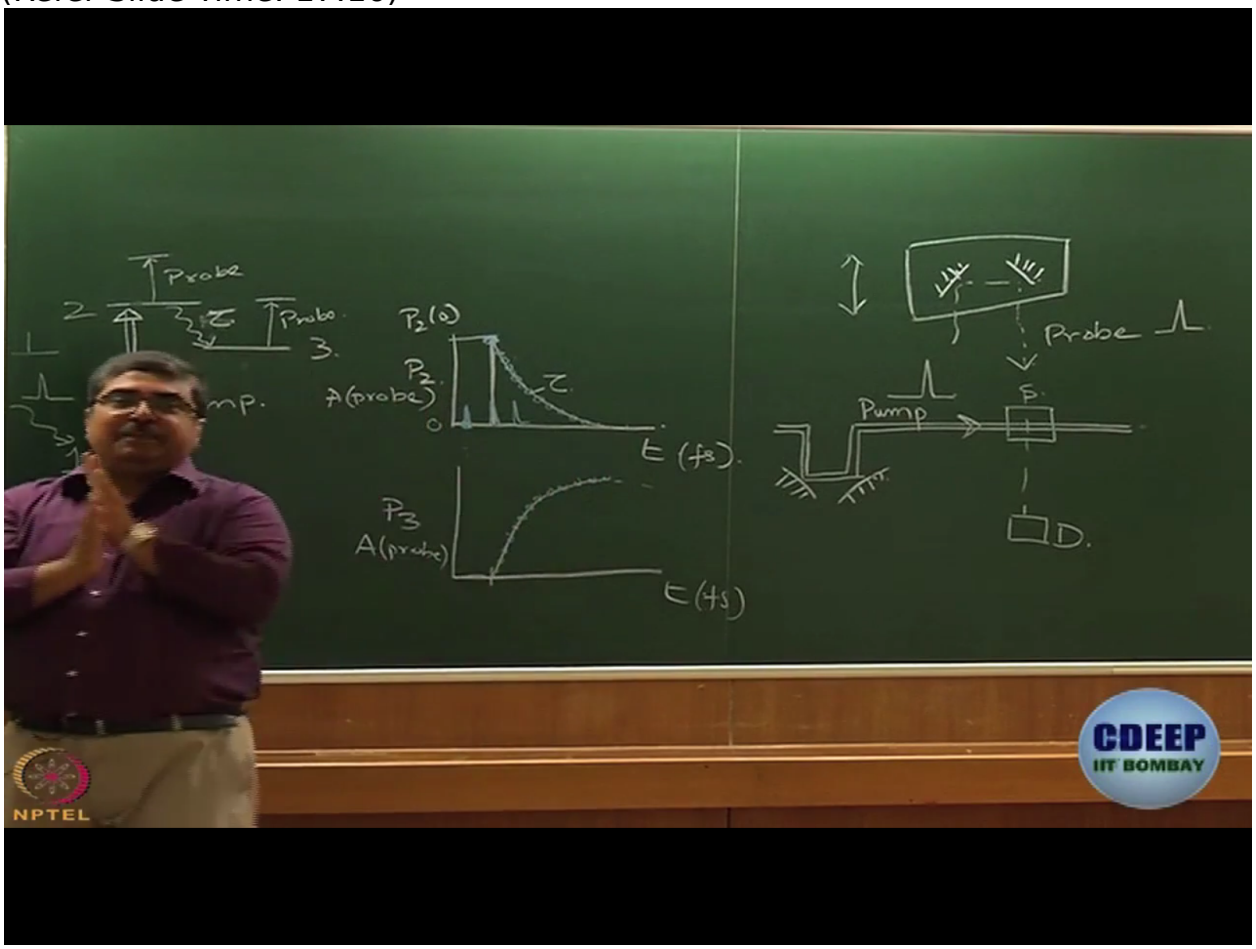

Alright this is from... this is a famous arrow of time drawn by Ahmed Zewail, this is taken from his nobel lecture. If you want, you can read the nobel lecture, it is available on the web.

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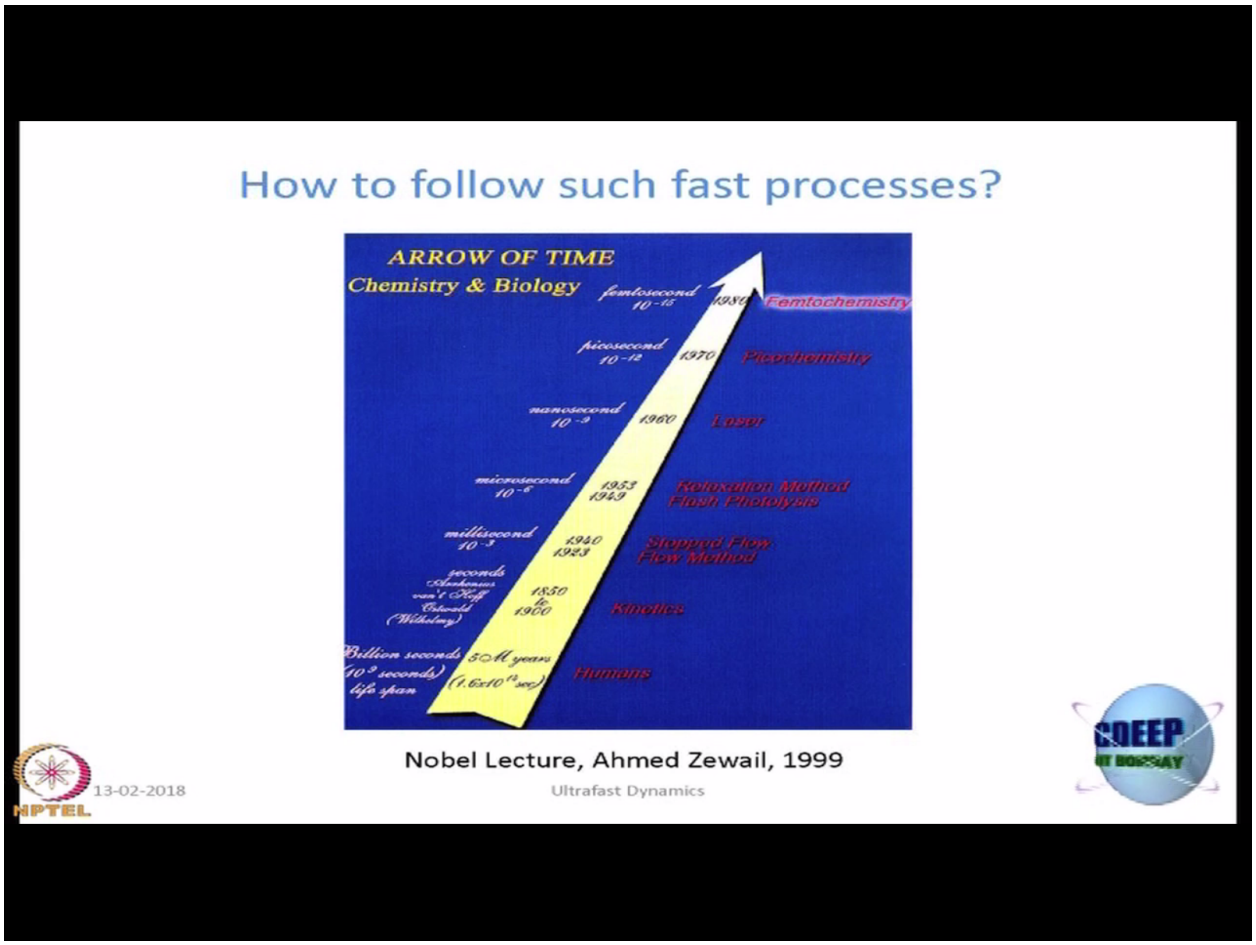

So this is what we are trying to do, okay. These are the two states, I am using pulsed excitation. This is where your pump is. X axis is time, don't forget. Now what I am saying is this, this is your pump, then excited state population decays in time like this, okay. Now this is your sample being pumped on one side and a pulse probe light also goes into the sample, and what you do is you actually detect the pulse probe light and here what I am showing is the pulse probe light energy is such that it is absorbed by this excited state and nothing else, okay. So since absorbents is equal to Epsilon CL, time evolution of this absorbents is going to map time evolution of concentration of this excited state, okay. Now what I am saying is this, you come back here by using a suitable optics, basically sets of mirrors, I can determine the path length, I can well… I can provide a particular path length for the pump beam, I can provide a particular path length for the probe beam, right. So what I am saying is I have adjusted the path lengths in such a way that the probe beam reaches the sample before the pump beam has reached, so this is a situation here. The pump beam comes at this time, probe beam has reached before. Now what will happen, there is no population here, right. So what will absorbents be, absorbents will be 0. Now let us say the probe beam has come here, absorbents will still be 0, and here still 0. What happens when the two path lengths are exactly matched,

no path difference is there. Pump and probe pulses arrive exactly at the same time, so that is the time when the pump has created the excited state population, which has not decayed at all, right, that is when absorbents of the probe becomes maximum. Now if the probe arrives sometime later, by that time the population has decayed somewhat, okay, so now absorbents will also decay accordingly, have we understood now. So this is how you build this decay point by point by simply varying the path length of the probe with respect to that of the path or the other way round, okay. I could do it the other way as well, I can delay pump, in fact in our lab the experiment that we do, there we delay pump and not probe, because generation of white light is a little touchy asset, we don't want to mess with that arm. What we are saying is that the intensity of the probe is such that it does not significantly alter the population of any state, it only goes and samples it. So when you do an absorption experiment, if you use two intense light, what will happen, your ground state population will go down and you will get problematic results. Here also the power of probe is typically kept at 100 or 1000 of the power of pump. So suppose I have 1000 molecules in the excited state, the probe will take may be 1, no more than that. so the population significantly… the population does not change significantly, instead of 1000 it is 999, that's all. So this decay that you see is due to the decay of the excited state population, by radiative pathway, non-radiative pathway or whatever, alright. It is simply the decay of the population that would have been even if there were no probe. All the probe does is that it gives you a handle of seeing what the population is at different times, okay. If you use, suppose you use the same pulse, pump and probe, say same intensity, then there will be a problem, yes in fact the entire thing will get messed up and you will not be able to interpret your data. So you have to ensure there is no double pumping. How do I know what is the population there, I cannot go in the molecule and count, so all I can do is I can measure the absorbents and that absorbents is proportional to population of that state, that is the purpose of the probe, it lets us see how much, how many molecules are there or how much population is there in a particular stage, but we have to use a feeble probe so that double pumping doesn't occur. Any other question? If not this is the end of this part of the discussion, we will go on after this to the actual experiment of Ahmed Zewail, okay, right.

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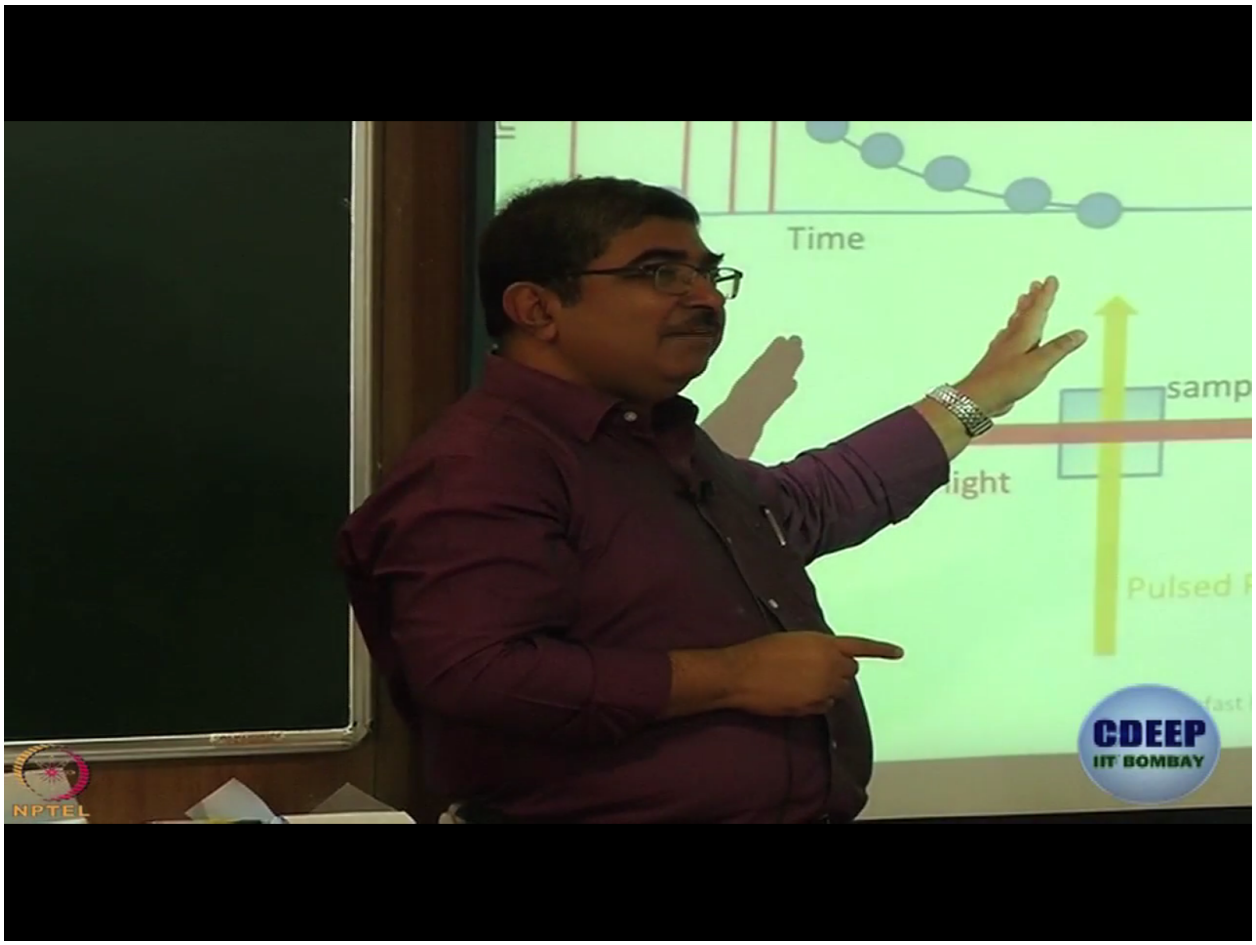
Time
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