Ultrafast Optics and Spectroscopy
Dr. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru

Lecture - 02

Welcome to part 2 of module 1 of the course Ultrafast Optics and Spectroscopy. In part1, we have given an introduction to the subject and in this part we will continue the discussion on the ultrafast time scales and capturing events in that timescale.

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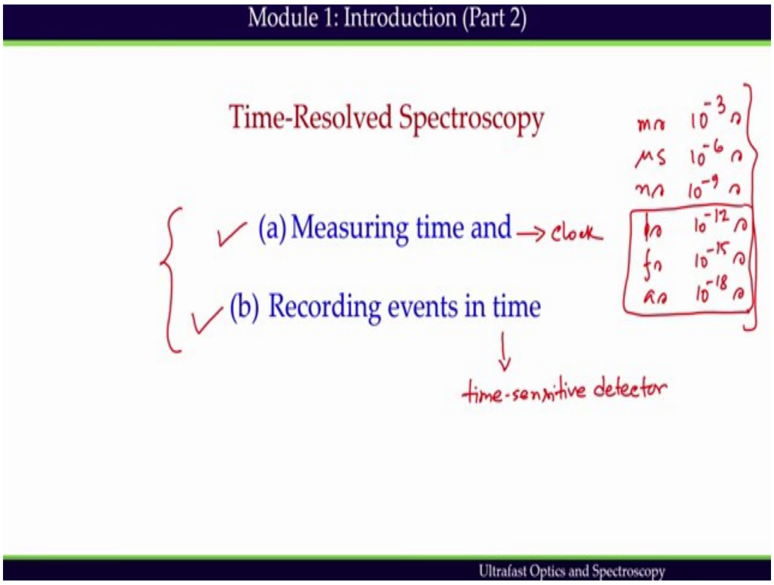

Ultrafast spectroscopy is an advanced time-resolved spectroscopic technique. A time-resolved technique monitors how a system evolves as a function of time. Ultrafast spectroscopy enables us to capture events mostly microscopic both physical and chemical in very rapid timescale. In general time scale in time resolved measurements may span from hour, minute, second, milliseconds, microsecond, nanosecond, picoseconds, femtosecond to attosecond.

So, these are the different timescales we are introducing millisecond 10 to the power minus 3 second; microsecond 10 to the power minus 6 second; nanosecond 10 to the power minus 9 second; picosecond 10 to the power minus 12 second; femtosecond 10 to the power minus 15 second and attosecond 10 to the power minus 18 second. So, these are the relevant time scales in one might be interested in time resolved spectroscopy.

However, when we say ultrafast spectroscopy we in general consider this portion of the time scale; picoseconds, femtosecond and attosecond. Modern ultrafast spectroscopy includes time resolved measurements only in picoseconds, femtoseconds and attoseconds time regime. Like anytime resolved measurement if we consider anytime resolved measurements that will include two important measurement elements.

The first one is in any time resolved measurement we measure time either directly or indirectly and then we record events in time. So, measuring time I need a clock, for this I need a clock and recording events in time, what I need? I need a time sensitive detector. So, these are the two devices I need for measurement of time and recording events in time and these are the two elements would be present always in any time resolved spectroscopy including ultrafast spectroscopy.

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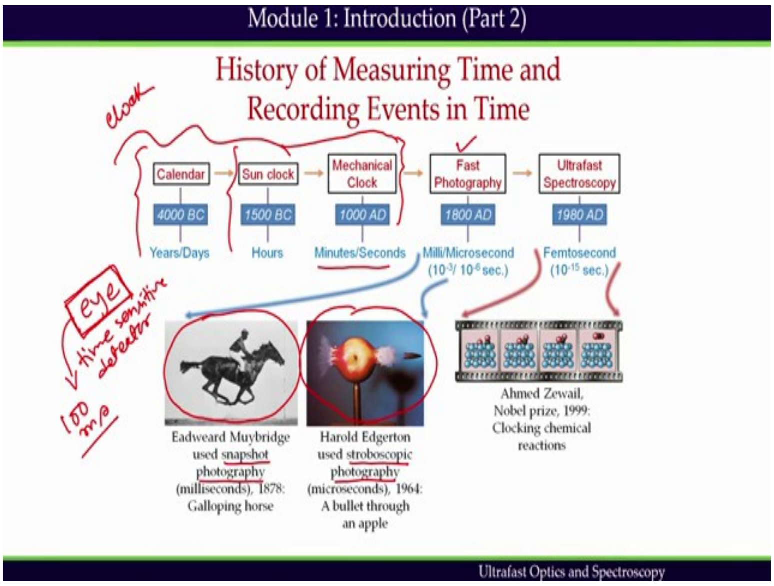

Our interest in measuring time and recording events in time has a long history as schematically depicted here. It is first reflected in ancient development of calendars in about 4000 BC. So, we developed calendar a long time ago and calendar was kind of time measuring device which helped us to understand processes in terms of years and days.

Followed by sun clock in about 1500 BC, the sun clock was developed. These early developments permitted us to record yearly and hourly activities events with the help of our eyes. So, when we have used sun clock or calendar, these are the clocks we have used. So, these are the clock that is the time measuring device and to monitor the evolution of the events we have used our eye that is the time sensitive detector we have used; time sensitive detector.

Then, development of mechanical clock in about 1000 AD enabled us to major events in duration of minutes and seconds. So, we developed this mechanical clock and that enabled us gave us second and minutes and second and minutes time resolutions. Before 1800 AD, however, our ability to record the timing of individual events in progress was essentially limited by the response time of human vision; blinking of an eye approximately 100 millisecond.

As I told you that all these clocks we have used and as a time measuring device, but the detector time sensitive detector is eye and we can use this time sensitive detector as long as the event is slower than the response time of eye; response time of eye is 100 millisecond. So, any event which is slower than 100 millisecond can be captured with the help of our eye. Recording any event faster than the response time of our eye was beyond our scope at that time.

Snapshot photography in which time sensitive detector is placed in dark and is exposed to time evolving event for a very brief time using a mechanical shutter of a galloping horse done by Muybridge in 1878 was the first atom to record events without eyes in millisecond domain. So, that was the first the fast photography was discovered in 1800 1878 and the galloping horse picture was recorded with the help of the camera. This fast photography was nothing, but a snapshot camera the; it is more like an SLR camera nowadays.

The response time of snapshot photography however, was limited by mechanical shutter speed which is a few milliseconds. Anything faster than milliseconds was beyond the scope up capturing using snapshot photography in 1878. So, what does it mean? I have camera or detector kept inside a darkroom let us say and I have a shutter which is separating outside and the darkroom. And I have to pull the shutter and close the shutter quickly and I can capture the image on the CCD camera or any time sensitive detector. So, the response time of this kind of snapshot photography depends on how quickly I open the shutter and close the shutter, that was the limitation and it was millisecond at that time in 1800.

Then, the fast recording technology was shifted from mechanical to optical resulting in stroboscopic photography performed by Edgerton in for the first time in 1940; 1964. He recorded an image of a bullet passing through an apple. This image was recorded with the help of not by fast not by this snapshot photography. This was used; this photography was over here snapshot photography was used but, this was done by stroboscopic photography. Stroboscopic photography and snapshot photography they are little different.

In snapshot photography what we do? We have camera kept inside the dark and we are separating this darkroom from the outside world with the shutter; and, we open the shutter, close the shutter. We expose the camera for a very brief time to the event. But, in stroboscopic photography, we keep the event in a darkroom and, we keep the; so, the event is going on in a dark room I have camera pan to the event in the darkroom. So, I cannot see anything and then I use a flash of light, a very brief flash of light and I will be able to capture the event that is called stroboscopic photography.

So, we had to move to a stroboscopic photography because the time resolution which was achieved with the help of snapshot photography was millisecond and with the help of stroboscopic photography we have been able to get microsecond time resolution; this is microsecond, this is millisecond. Stroboscopic photography was performed using a brief flash of light while the event occurred in dark and photographic camera was kept exposed to the event in dark as well.

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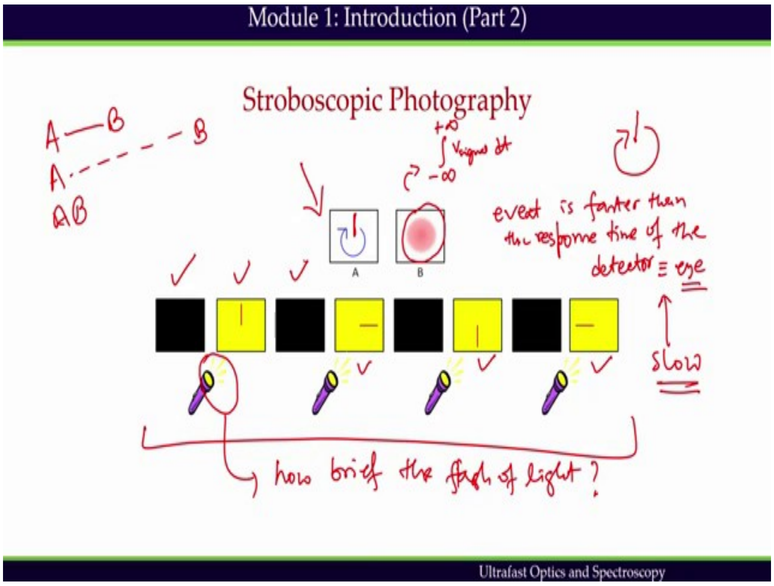

A schematic illustration of capturing frames of a rapidly rotating dial which is A, this dial; A this dial is rotating like this way. And if it is rotating; if it is rotating very fast then what happens generally we experience at home all the time when the fan is rotating very fast, we see a blur image. It cannot distinguish each blade. So, if it is rotating very fast then we get a blur image by our eye and in that case event is faster than the response time of the detector. In this case detector is our eye.

So, if the event is faster than the response time of the detector then I can use the same detector, the slow detector we call it; generally, we call it then slow detector a slow detector can be used, but in that case I have to use stroboscopic photography where I have to keep the rotating dial in dark, then I have to use flash of light at a certain interval. So, in this interval we see a frame, then again dark, then again flash of light I see the rotating dial, again I see rotating dial, again I see rotating dial and that is the way we can capture the image. And, this stroboscopic photography is at the heart of ultrafast spectroscopy.

So, a bare eye captures only a blur image mathematically it is called time averaged signal. So, when I capture a blur image with a slow detector I am just capturing this minus infinity to plus infinity V signal dt over the time I am just integrating the whole signal and whatever I am seeing is depicted here in frame B. However, if bare eye a slow detector is kept exposed to the event in dark and a flash of light is used at a certain time interval, different frames of the event can be captured which together represents time evolution dynamics of the rotating dial. This idea depicted in the bottom frames presented here.

The discovery of stroboscopic photography helped us realize that if we need to capture events using a slow time sensitive detector which means the period of the event is faster than the response time of the available time sensitive detector such as human eye, we have to use faster flash of light. So, now, we are that time resolution of this process will depend on how brief the flash of light we can prepare, because if the event is much faster very very fast then we have to have even faster flash of light. So, the duration of the flash has to be controlled and selected depending on what kind of event we want to monitor.

This realization, this stroboscopic idea; stroboscopic photographic idea, this realization has revolutionized the technology of synthesizing faster flash of light. By 1980s the flash of light with several hundred femtoseconds duration became available and today flash of light with several tens of attoseconds duration is available. Our interest in capturing events with rapid flash of light at ever increasingly shorter time scale has given birth to the modern ultrafast science and spectroscopy.

With this, it is now seemingly important question how rapid flash of light is required to observe a chemical event. So, let us say in the rotating dial experiment instead of rotating dial I have an molecule, a molecule like A-B molecule and this molecule is vibrating. Let us say this is a stretching mode. This molecule is vibrating just like a breathing mode A-B, A-B bond is vibrating like this way. And, if this is vibrating first thing I have to know if I want to employ stroboscopic photography, then I have to use flash of light even faster than the period of this vibration.

So, first thing we have to understand is that how rapid flash of light is required to observe a motion; atomic motion or electronic motion in molecule with the help of stroboscopic photography.

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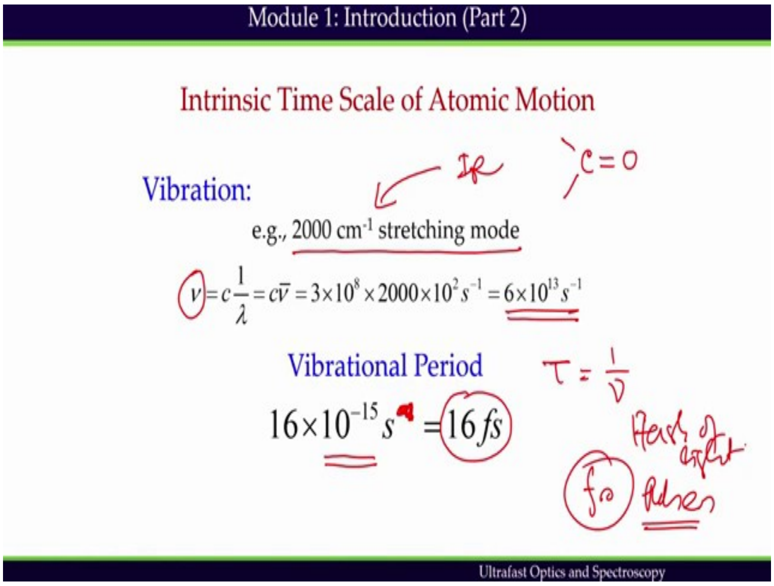

So, we need to know the intrinsic timescale of atomic motion. First we will look at the intrinsic timescale of atomic motion; the timescale of chemical reaction is the time scale of atomic motion of a molecule. I can think about A-B they are coming closer, forming chemical bond. So, this is nothing, but vibration. So, I have to find out how much, how long does it take to extend the bonds, stretch the bond like this and then recompress. How long does it take?

If I consider 2000 web number stretching mode, this is can be obtained from IR spectroscopy; a particular stretching mode can have a particular value, the excitation value. So, if it is a 2000 web number stretching mode then I will be able to convert this 2000 wave number to its frequency. This is the frequency we get and once we get the frequency vibrational period can be obtained with the help of this equation 1 by nu and this gives me 16 femtosecond; 16 multiplied by 10 to the power minus 15 second, this is second.

So, 16 femtosecond; so, what does it mean? If I take 2000 wave numbers stretching mode; 2000 web number stretching mode could be let us say sometimes it could be C double bond O. This kind of functional group if we have in a molecule that kind of functional group will be vibrating. And this kind of functional group will vibrate with 16 femtosecond period which means that it will stretch, recompress, this whole time would be 16 femtosecond.

So, this is the time scale where the vibration occurs which means that if I want to monitor this vibration then I need femtosecond pulses and this pulses are not are nothing, but flash of light; a sophisticated flash of light.

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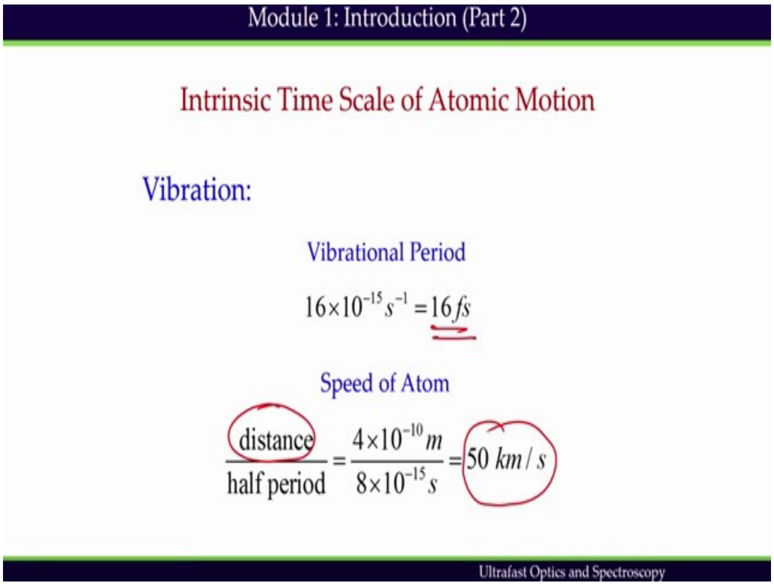

If we look at the vibrational period 16 femtosecond one more time and if we try to find out what is the speed of atom during the vibration, then we have to assume that the critical distance travel by atom during dissociation is 4 angstrom. Let us say I will assume that once the two atoms are having 4 angstrom distance, I will call it the molecule the bond is dissociated, the bond is broken.

And, the if the bond is broken then I can find out this for this distance what is the velocity of the atom to dissociate the bond and we find that it is 50 kilometer per second; per second it is traveling 50 kilometer to dissociate the bond. This is the typical speed of atom during the vibration, during the molecular dissociation.

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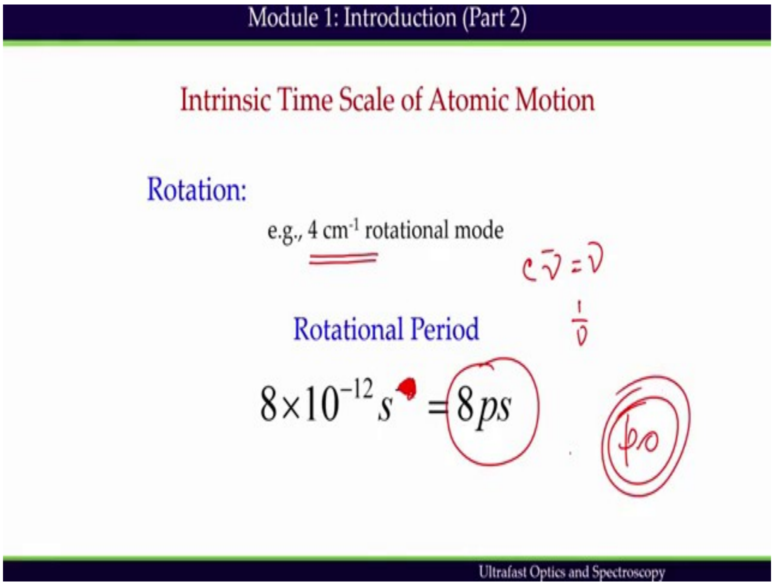

Then, we will look at the typical time scale for the rotation. Let us say I have CH 4 molecule. CH 4 which is having C then 3 hydrogens are organized here and 1 CH bond here. So, with respect to this CH bond this 3 CH 3 this CH 3 group can rotate and if this is rotating what is the time scale of this rotation? That is exactly what we are trying to find out.

So, those kind of rotation having energy 4 wave number. If we have 4 wave number then very easily I will be able to convert to it is frequency and from frequency I will be able to get the time period. And, the time period for the rotation we get is, this is second. Time period we get is 8 picosecond which means if I want to find out a molecular rotation like this and if we want to monitor how it is rotating in a molecule, then I need to have picosecond timescale; picosecond flash of light.

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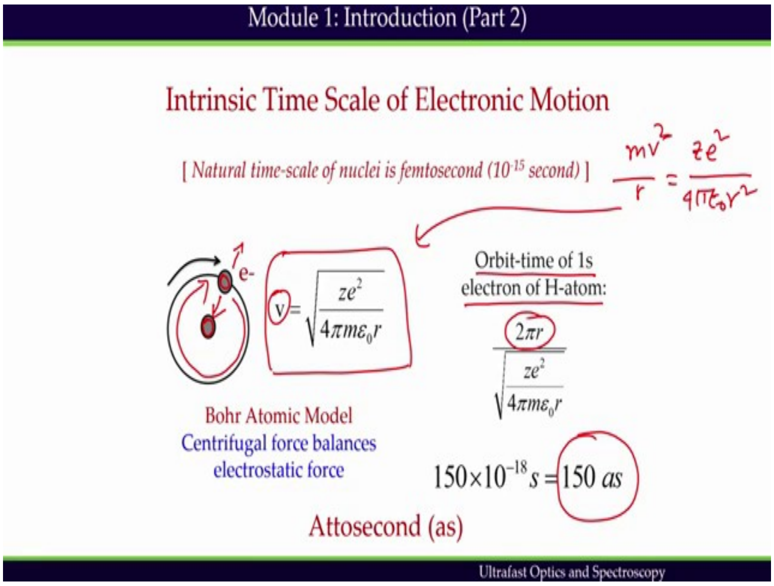

Next we will look at the intrinsic time scale of the electronic motion. In order to estimate intrinsic time scale of electronic motion in atom, we shall use Bohr atomic model. Although this is the simplest atomic model we have, but we can use that to find out or predict what kind of intrinsic timescale of electrons we have in atoms. So, if we consider Bohr atomic model which we have, we have a nucleus here and we have an electron orbiting the nucleus.

And, when it is orbiting there are two forces which is centrifugal force; centrifugal force given by mv^2/ r, centrifugal force which must be equal to its columbic electrostatic force $4\pi\varepsilon_0 r$ which means columbic electrostatic force is acting along this way and centrifugal force is acting along this way. They must be equal to stabilize this atom and if they are equal then I will be able to get a velocity. Just from this equation I will be able to get this velocity.

And, from the velocity if I know the typical hydrogen atom radius then I will be able to find out the distance it travels for the one orbit. And, from the distance and the velocity I will be able to get the time orbit time of 1s electron in hydrogen atom and that is given by 150 attosecond. 150 attosecond is the orbit time of the 1s electron predicted by Bohr atomic model. So, in order to record intrinsic electronic motion in atoms and molecules we need flash of light with attosecond temporal duration.

Here we must note that not every nuclear processes, not every nuclear process occurs in femtosecond or picosecond timescale and not every electronic process features attosecond timescale. For an example, chemical reactions which are driven by mass diffusion occurs in microsecond timescale. However, it is quite clear at this point that in order to record a fast chemical event in time using slow detector or using stroboscopic photography we need even faster flash of light.

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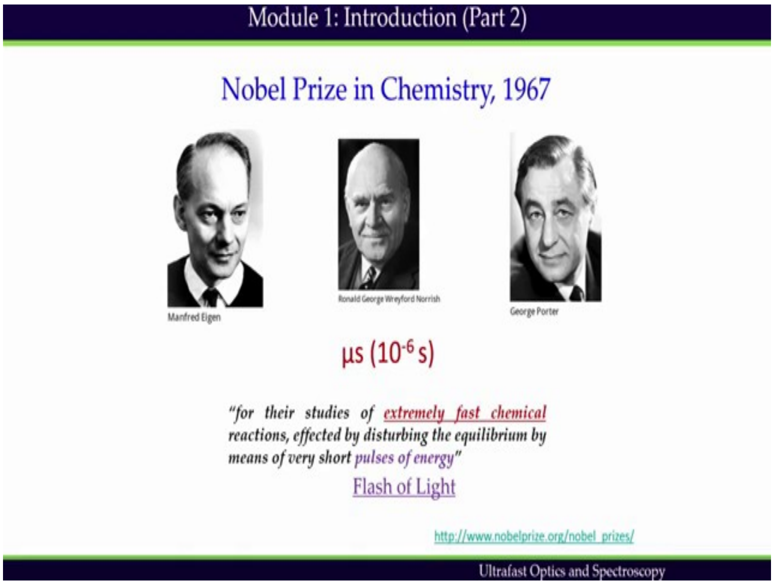

The introduction of the flash of light to chemistry with microsecond time resolution came near 1950s with the development of flash photolysis by Norrish and Porter. With the advances made with lasers the time resolution improved continuously over the years reaching picosecond in 1970s, femtosecond in 1980s and attosecond 2000.

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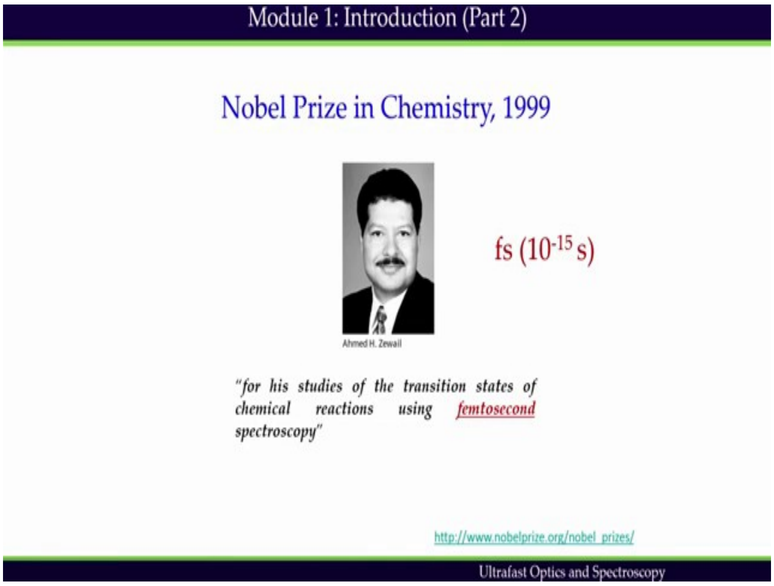

The 1999 Nobel Prize in Chemistry was awarded to Ahmed Zewail for his studies of the transition states of chemical reactions in the femtosecond time domain.

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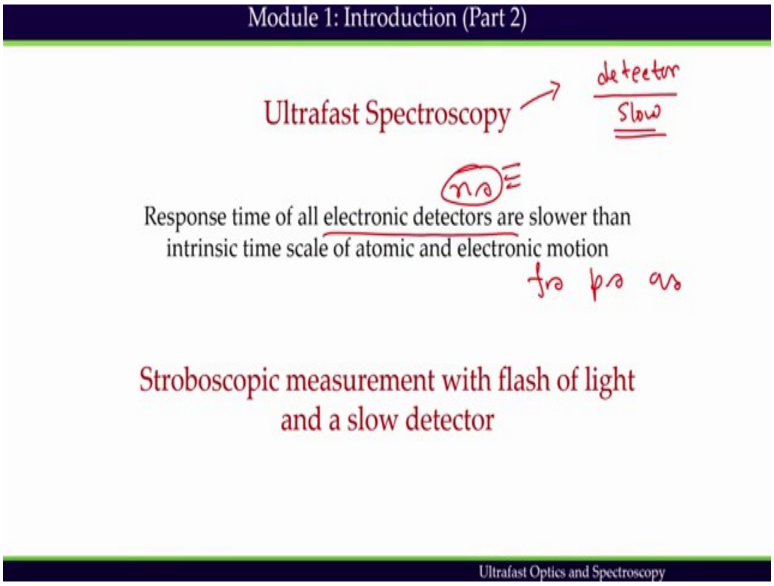

So, before we end this module we will point again to an important issue. If the available time sensitive detector is slow let us say I have; so, for ultra fast spectroscopy what I need? I need a detector and we see that this detector is going to be slow because the response time of all electronic detectors are actually nanosecond which is much slower than femtosecond vibrational motion, picosecond rotational motion or attosecond electronic motions, intrinsic motion.

If the available time sensitive detector is slow, we have to follow the approach of stroboscopic photography to capture a fast event. This means that we need to use rapid flash of light, duration of the flash of light must be shorter than the period of the event to be captured. What is the typical response time of the fastest time sensitive detectors which we have?

The response time all modern time sensitive optical detectors such as photodiode, photo multiplier tube, power meter, CCD camera all of them measure voltage or current using electronics and the response time of the fastest electronics is a few nanoseconds or if it is the best electronics then I can have several hundred picoseconds,that is all. We cannot have femtosecond or attosecond time resolution or picosecond time resolution with the help of electronics.

Therefore, all time sensitive detectors are slow detectors when it comes to measuring intrinsic time scale of nuclei and electrons. Therefore, only a flash of light provides a well defined time window for the time resolve measurements with a slow detector. How a slow detector can be used and what kind of interpretation we have that is all about this course.

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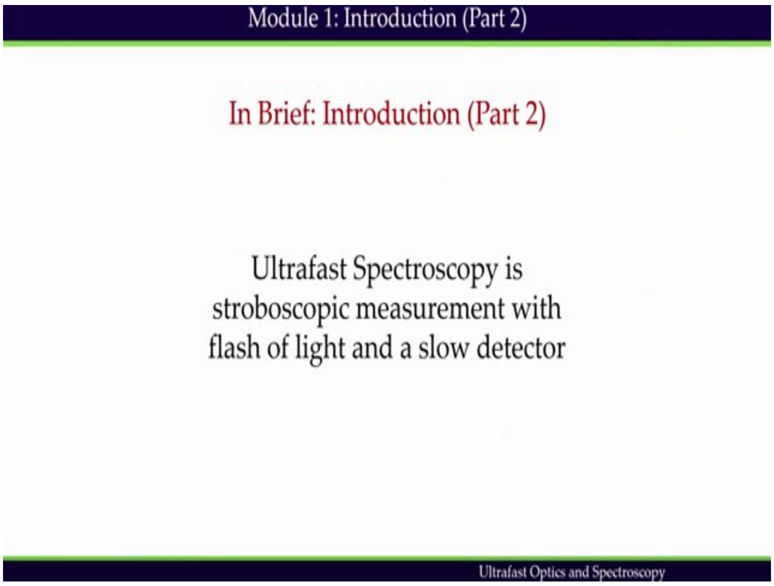

So, with this we have come to the end of this module. In this module again we have gone over different relevant timescales and one important concept which we have introduced is that stroboscopic photography is the only answered to the problem we have. The problem is that we have slow detector and we have very fast event so, in order to observe that we need flashes of light with duration shorter than the period of the event.

We will meet again for the next module.