Ultrafast Laser Spectroscopy

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Lecture-65
2DIR: Techniques

Hello, welcome to the last module of this course. Well in the previous module, you might remember we have said that we are going to have to learn, but then taking stock of how much ground we have covered and how much time we have, it appears to dent that we call it a day with this module itself. Because if you want to discuss to 2d IR spectroscopy or terahertz spectroscopy or nonlinear spectroscopy, for that matter in any more detail, we will need at least 10 more modules.

We do not have scope for doing that. Secondly, let me apologize for the quality of this video. Because right now this has been recorded from my home because of this deadly disease worldwide. Like most of the people, we are also locked down. And so the quality that you see here is nothing like what we have experienced so far. So, apologies for that. Please bear with us in this difficult time.

And there is another reason why I thought let us not prolong it any further. Let us call it Asia. So, today, we will complete our discussion with a brief introduction to the techniques of 2d IR spectroscopy. And once again, before I begin the module, let me acknowledge my friend, Dr. Sukhendu Nath of BARC, from whom I have learned whatever little I know about 2d IR spectroscopy. So, what we have said so far is that in 2d IR spectroscopy is all about coupling.

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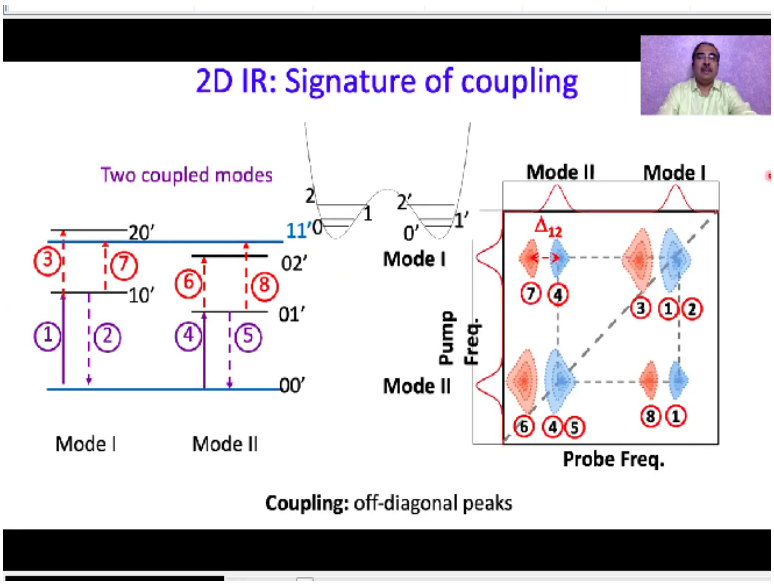

If you have coupled vibrational modes, then they show up as off diagonal peaks in the 2d IR spectrum, very much like NMR spectroscopy, for example, there also in 2D NMR off diagonal peak show up when there is coupling between nuclear spins. Here instead of nuclear spins, we talking about coupling between vibration and normal modes of polyatomic molecules.

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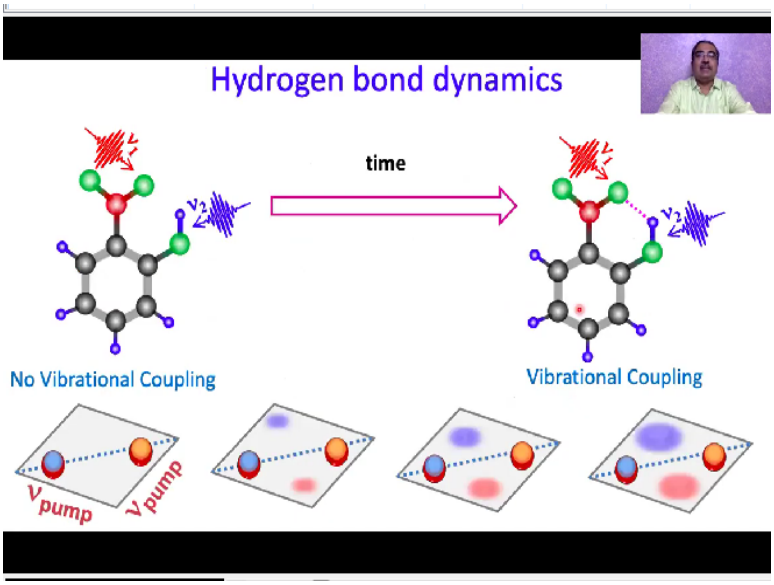

We have also said that one can perform studies of time evolution of these off diagonal peaks. And that gives us an idea of dynamics of coupling or decoupling. For dynamics of coupling, we see an emergence of the off diagonal peaks with time, for decoupling we see a disappearance of these off diagonal peaks with time. Now the question is, how are we going to do this? There are 3 techniques that we want to talk about very briefly.

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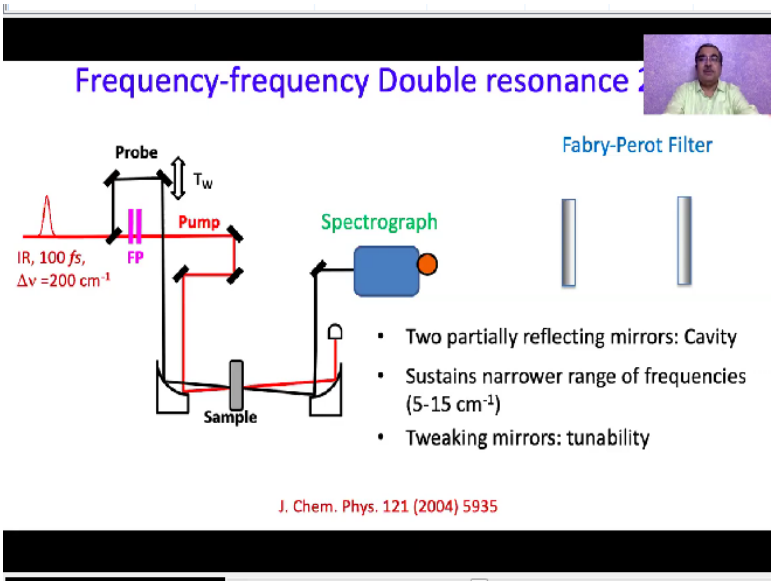

The first is very simple. It is called frequency-frequency domain 2d IR spectroscopy, or frequency-frequency double resonance 2d IR spectroscopy. And the setup here is very simple and it is absolutely same. Well, almost absolutely same as something that we are very familiar with, the pump probe spectroscope. So, what we have here is that we have an ultrashort IR pulse, let us say 100 femtosecond time duration.

And of spectral width of 200 centimeter inverse, this beam is split into 2 parts. One is pump, the pump pulse goes through a reflective optics and is made incident on the sample after which it is stopped locked. And the probe pulse goes through a retro reflector, which can be moved by a computer control delay stage. And then it is also focused using a parabolic mirror onto the same spot of the sample where the pump is made incident.

And the probe pulse goes through a spectrograph on an array detector to give the probe spectrum. So, far it is exactly the same a as broadband pump probe spectroscopy. How do we get the second dimension? The second dimension remember is pump frequency. We get pump frequency by introducing one more piece of optics here. And the piece of optics that is introduced is very fundamental to lasers. It is called Fabry-Perot filter.

A Fabry-Perot filter is nothing but a pair of almost parallel, partially reflecting plane mirrors. So, whoever has gone this far in this course, would know for sure what happens when we have 2 partially reflecting plane mirrors. Well the form a cavity, remember laser cavity that is a very fundamental discussion that we performed here. So, we have studied that when we have this kind of a cavity, the cavity length determines which frequencies can be sustained.

And if we change the cavity length a little bit by tweaking the mirrors a little bit, then one can have tunability. So, remember we are working with femtosecond pulses here. So, the spectrum is always broadband, okay. But what we can do is that out of this broadband we can select a narrower band, say a 5 to 15-centimeter inverse spectral width by introducing this by Fabry-Perot filter.

By tweaking it of course, the tweaking is not by hand everything is computer controlled, one can choose a narrow range of a pump frequencies as well. Now, the job becomes very simple, decide which range of pump frequencies you want, set the Fabry-Perot filter accordingly and then scan a T w, T w is the w's for wait, T w is the wait time that is the conventionally used term for the time associated with the delay of the probe beam in a 2D spectroscopy.

So, the probe here is subjected to a variable delay T w. So, for every value of T w one gets a 2D IR spectrum right. So, very simple. Now, what is the limitation of this technique? Limitation is how small a band you can generate out of this Fabry-Perot filter okay, that is what will determine the spectral resolution okay. Otherwise, it is a very simple technique. But then, towards the beginning of this course, we spent a significant amount of time talking about why time domain spectroscopy is more advantageous okay.

We actually did it in a little more detail in the NPTEL course on molecular spectroscopy that were offered a couple of semesters ago. So, as we know, when we do IR spectroscopy, nobody does frequency domain anymore. I mean, I am talking about regular IR spectroscopy that you do for sample characterization run of the mill. Even then, the spectrometers that are used are always FTIRs, Fourier transform IRs, which means the data are recorded using an Michelson interferometer in time domain.

And Fourier transformation takes us over to the frequency domain, for further understanding please refer to lectures from the earlier NPTEL course on molecular spectroscopy.

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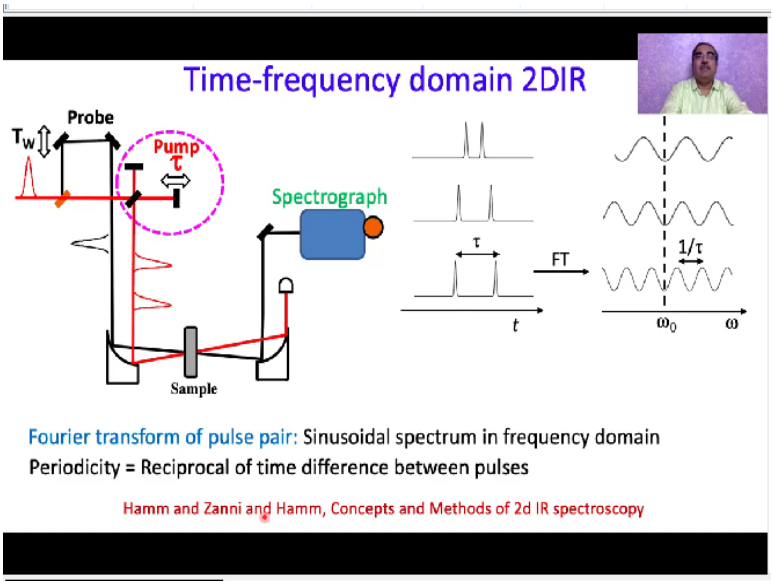

So, the question is can we do it here? Can we use say time frequency domain 2d IRs here, actually we can and it gives, there are some advantages associated with it, but the moment we try to do it the experiment becomes a little more complex. So, let us see what we have in a setup in which we want to do time frequency domain 2d IR spectroscopy. We start with a similar ultrafast IR pulse split it into 2 parts as usual.

One part is probe shown in black lines. The probe is focused by a parabolic mirror now to the sample and is routed through a spectrograph onto an array detector, that part is exactly the same, the pump is different. The pump what we have is we have a beam splitter, 50% of the pump pulses are sent in this direction to hit a plane mirror in normal incidence, because incidence is normal, it retraces its path and comes in this direction.

And if that is the only thing that is there, then you get this pump pulse coming here. But then remember this bit of optics here is really a beam splitter. So since 50% of the beam in this direction, it transmits 50% of the beam and that 50% is incident normally on another plane mirror 100% reflecting there and this plane mirror is mounted on a variable delay okay. So, since once again the incidence is normal the beam retraces its own path and comes back.

Now see if the path difference is 0. If the path length is exactly the same on the 2 arms, then the 2 pulses combine and we get pump pulse here. If however, there is a nonzero path difference, that means, the path lengths in the 2 arms, 2 arms means one generated by reflection from the beam splitter, the other because of the transmission. If the difference is nonzero, then what happens, then the pump does not consist of 1 pulse anymore.

Rather, it consists of a pulse paired 2 pulses separated in time. So, why would you want to do that, you want to do that because if you take a pulse pair with a variable time separation between them tau, then Fourier transformation of such a pulse pair turns out to be a sinusoidal spectrum in frequency domain. So, what we have done is we have generated a lot of colors at the same time. So, now, we do not need that Fabry-Perot filter Fabry-Perot filter anymore, we had do not have to look at individual pump frequencies one by one.

Rather, we generate a whole range of pump frequencies with varying amplitudes, varying electric fields okay. Moreover, the periodicity, what is periodicity, the separation between the 2 peaks, the periodicity turns out to be 1 by tau. I am avoiding all the mathematics here. All the mathematics involved here. Please bear with me for that. Unfortunately, I have written the name of the book a little wrongly it is not Hamm and Zanni and Hamm.

That is one Hamm too many, the book concepts and methods of 2d IR spectroscopy is written by Zanni and Hamm, it is considered to be the textbook for people who want to study 2d IR, please study this book, if you want to know more about these techniques, alright. So, coming back, what happens if I increase tau, if I increase tau then the periodicity changes, because periodicity is the reciprocal of the time difference between the pulses.

So, as we change tau, we get different shapes, different sinusoidal shapes. So, we basically get different well maybe the same range of frequency, but the contribution of each frequency changes depending on tau. So, suppose we now use the same spectrograph and diode array detector right and record the spectra as function of tau. Then what happens?

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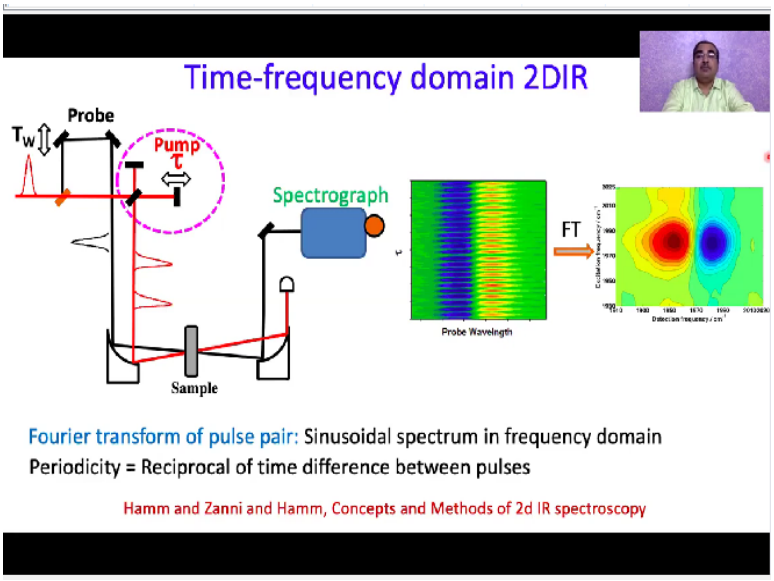

Then we get a plot like this on x axis, we have the probe wavelength, on y axis, we have tau the separation between the pulses and z axis is the feed. So, now what one can do is one can Fourier transform the y axis, the tau axis and that will give us the 2d IR spectrum with which we are now familiar right. So, the good thing about using it is that this time frequency you know with 2d IR technique is associated with all the advantages of time domain measurement.

You do not need to work with a small range of frequencies at a time, the entire range of frequencies is incident at the same time, right, I talk about pump frequencies. So, all those techniques and all those advantages that are there for the time domain technique () throughput advantage, all these advantages are there in this kind of a techniques. So, this is a more elegant method, than frequency-frequency domain 2d IR.

However, this is not all, because 2d IR spectroscopy actually has many facets, which unfortunately we do not have time to discuss in this course anymore, but, it is not just recording spectra, polarization, coherence these are very important things that come up here, because excite you pumps let us say using a vertically polarized paths, then we generate all these vibrations that are all coherent and then the coherence takes place. What is the time for this decoherence, what is the time for this dephasing?

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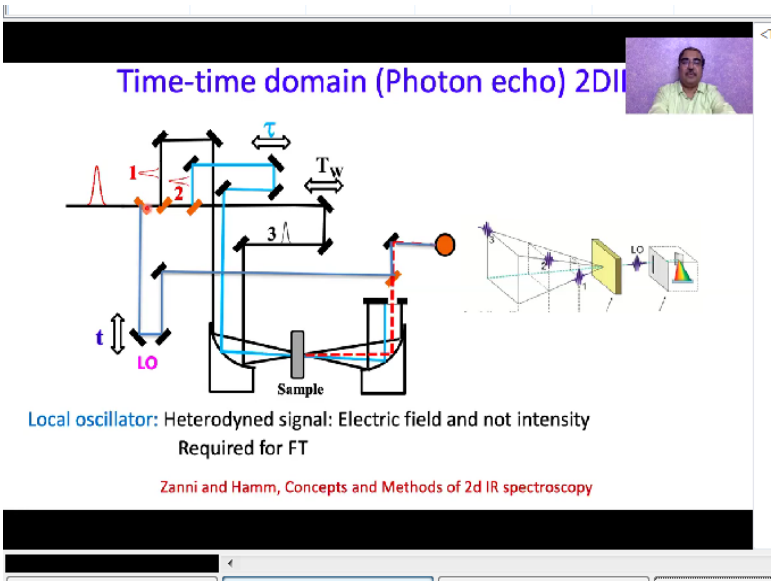

That is something that can be followed very elegantly using the time-time domain 2d IR technique is also called photon echo technique. Once again, photon echo itself would require maybe 4 or 5 modules, if you want to discuss in detail, the technique as such is discussed in a our regular textbook , so, whoever is interested please go through that book and put it very simply, once again, we resort to what I hope most of us would know from our earlier experience with NMR spectroscopy.

And NMR spectroscopy one technique that is used very frequently is to measure the relaxation times, one uses pulse radio frequencies well, one uses pulse radio frequencies to record spectra as well. But record relaxation times one uses pulse sequences. So, let us do a quick recap on NMR spectroscopy without showing any slide, whoever wants a more detailed treatment. Please refer to the lectures on this topic in the earlier NPTEL course on molecular spectroscopy.

So, what happens is, if one wants to measure let us say transfer relaxation time, then first in 90 degree pulse I will talk about NMR right, a 90 degree pulse is made incident on the sample, the purpose of this 90 degree pulse is to flip the bulk magnetization into the xy plane from the z plane. And then if you wait for some time, the fanning out effect takes place dephasing. Then a 180 degree pulse applied to turn this fan exactly by 180 degrees right to flip the fan.

Then what happens is if you wait for an equal amount of time, then the dephasing effect is exactly modified and then we see what is the extent of decrease in magnetization due to the spin lattice relaxation, that is how a spin echo works and we can explain it by using classical analogues. Unfortunately, photon echo does not have a classical analog. So, it is not very easy for us to explain it without resorting to quantum mechanics and mathematics of which as you said, we do not have the time.

So, let me just tell you what is there in the setup. So, this is only well it is not even the tip of the iceberg. It is only an introduction. I sincerely hope that you will be encouraged to read further and understand this technique in much more detail. So, what we have here is this, as you see, there are more retro reflectors, more taus, let us see one by one. We have the femtosecond IR pulse, it goes through a beam splitter, which sends a part of the beam in this direction.

We are not shown it yet it will come, the other part is transmitted or the transmitted beam, one part is deflected by another beam splitter. Recall this beam number 1, this another beam splitter, which produces beam number 2. And beam number 3 is the beam that is finally transmitted through this a third beam splitter that is shot. So, let us go one by one. What is the path of beam number 1, goes up, it is this mirror it is this mirror.

Falls on this parabolic mirror and is focused on to a point on the sample and then see that beam is blocked, this horizontal black thing that is shown here, that is basically a beam stop. So, pulse number 1 goes to the sample and is stopped, not detected. What about pulse number 2 is this mirror comes this way, it is this mirror, here, here, well, there may be more optics in between actually, we are not showing everything here, it is just a schematic.

Then the same parabolic mirror focuses it on to the same point on the sample as beam number 1. And then it goes through an, even beam number 2 is stopped, not the detected okay, as you see, beam number 2 can be associated with a delay time of tau which is variant, beam number 3 similarly is associated with another delay time T w. So this is really the probe beam okay. So beam number 3 falls on the same parabolic mirror.

And is focused on to the same spot on the sample. And then beam number 3, remember beam number 3 is a probe beam that is also stopped. So now that is a very strange situation. We have 2 pump beams, they are stopped. Understandable, the probe beam is also stopped. So what is it that we detect, that may be a question. Well, before answering that question, well, what we detect is this dashed line. This dashed line goes, hits this mirror and is directed to the spectrograph.

In fact, you do have a spectrograph here, I have not shown it here. But you do have a spectrograph CCD array here, because the spectrograph what it essentially does is that it performs a Fourier transformation and gives you the delay time of frequency domain. But the question is what is this dashed line. That is the photon echo, before going there let me show you another figure which is of utmost importance.

Well the figure is taken from a paper on not 2d IR spectroscopy, but 2D ah UV spectroscopy well 2D electronic spectroscopy that I referred to a little later. See, looking at the schematic here, you might think that everything is in the same thing it is not. What happens is that these beams are aligned in the so called boxcar geometry. Think of the square and think of this point. It says it, the 3 beams propagate from 3 the 3 points of the square, see beam number 1, 2, and 3, all coming from these corners of the square.

There are 4 corners, these 3 come from 3 corners. The good thing about boxcars geometry is that if 3 ultrafast beams are made incident on a sample in this way, then we have studied a little bit of nonlinear spectroscopy, nonlinear effects take place and we get a fourth beam emerging along this dotted line, the fourth line from well the line from the fourth point of the square drawn to the same point on the sample, right.

That is the vector sum well linear combination of the K vectors well that is associated with light whose K vector is a linear combination of the K vectors of beam numbers 1, 2 and 3, okay, that is the photon echo signal. So, what happens here is that beam number 1 is sort of like the 90 degree pulse of NMR. It comes and creates a coherence over a period tau de-coherence takes place and then the second beam comes and flips it sort of just like 180 degree pulse.

Then once again coherence takes place. And what you have is a photon echo. Very similar to spin echo in NMR. And it is a photon echo that is detected by the detector okay, now there is a problem here. If you go through in the same (()) book if you see the expression for photon echo what you find there is not intensity but the field and you might be wondering already what this yellow is, is this we need to know the field and not the intensity.

If we look at intensity, intensity is the mode square of filed, the moment you do mode square the phase information is completely lost. In fact, we need phase information here in order to proceed. So, to do that, now comes the roll off this beam splitter here, but this beam splitter does is that it creates another pathway for yet another beam, beam number 4 and this beam number 4 is called the local oscillator, but the local oscillator does is that okay.

This is the path from here to here. Here, here, here, now it is combined with the photon echo and goes into the detector along with the photon echo. And when this mixture goes in heterodyning takes place, we will not discuss heterodyning in any great detail here. Just believe me when I say that, by virtue of heterodyning, we get information of electric field and not just the intensity, and this is something that we need for the subsequent Fourier transformation.

Without heterodyning, we cannot really do it. Heterodyning is a technique that makes use of the local oscillator. For want of time, unfortunately, we will not be able to get into this any further but I will refer to some other work where heterodyning is discussed in some detail okay. So, this oscillator is associated with its own delay time. So what you have is a little more complex Fourier transformation involving all these delay times.

That is what finally gives you the 2d IR spectrum. So, why would we do, because, as I said, there is more 2d IR, we talk about polarization, we have not talked about polarization rather, but polarization is an important thing, depolarization is an important thing. So, all these things can be understood when we incorporate this little bit of complication in this technique right.

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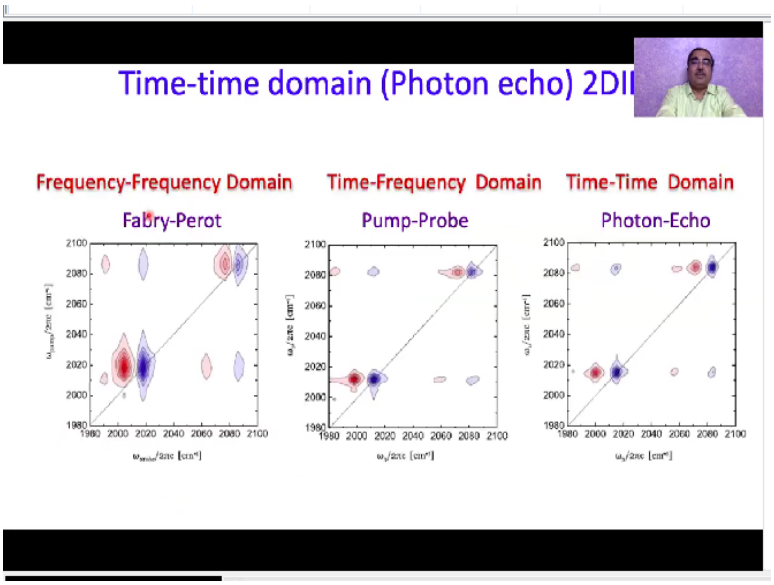

So, to conclude this discussion, let me show you an example. I will not tell you what the sample is, but this here are 2d IR spectra of the same sample recorded by 3 different techniques. As you see they are qualitatively similar, quantitatively they may be a little different because every technique is associated with its own strengths and own weaknesses. So, that is all I wanted to say about 2d IR.

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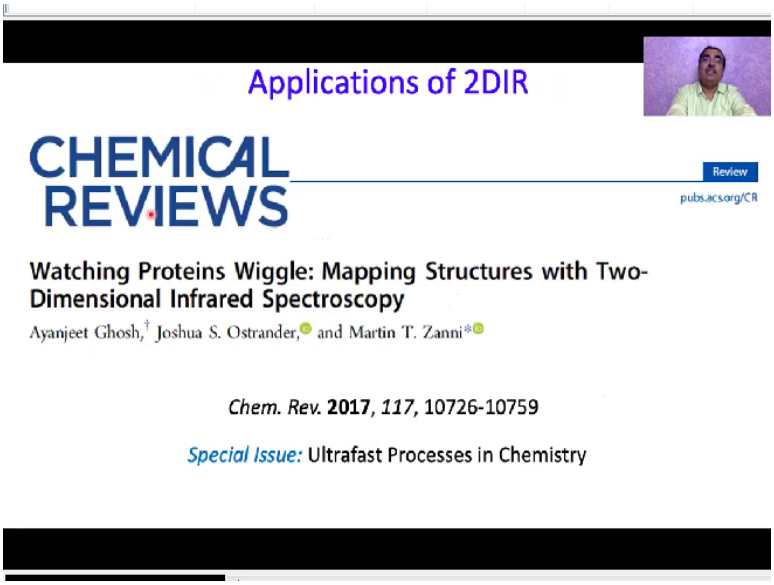

Unfortunately, we did not get time to talk about applications. I suggest that in addition to reading Zanni and Hamm's book, please go through this paper published in chemical reviews. Here there is an ample discussion of how one can study the dynamics of well, movement of chains of proteins,

for example, using 2d IR spectroscopy. And this chemical review issue itself is very special, because it is a special issue on ultra fast processes in chemistry.

I am going to refer to another paper of this in a moment. So what I suggest is that in fact, read all the papers published in this particular issue of chemical reviews, published in 2017 right. So, much for 2d IR.

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Let me tell you that well, this is the book of Hamm and Zanni, please go through this book, let me tell you that this 2D spectroscopy is not limited to IR. In fact, there is a lot of promise in 2D electronic spectroscopy. A lot of people like Shaul Mukamel and others had done a lot of good work on different types of 2D spectroscopies. This perspective article is a good reading material for 2D electronic spectroscopy okay. So, this is what we could say and actually we could not say this course.

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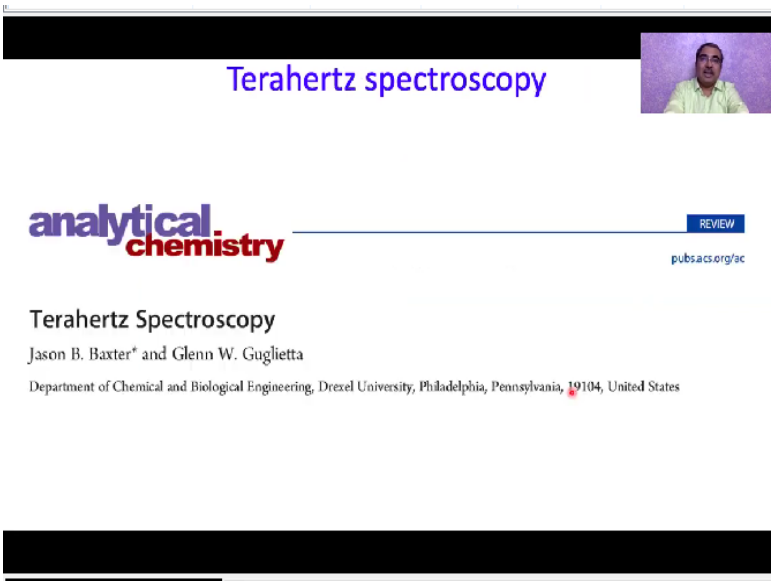

And we will have loved to talk more about 2d IR spectroscopy. I would love to discuss terahertz spectroscopy, which has become very, very interesting over the last maybe decade and a half not only from the point of view of fundamental studies, but also for applications like explosives. Whoever is interested, please do read reviews and reverse on terahertz spectroscopy.

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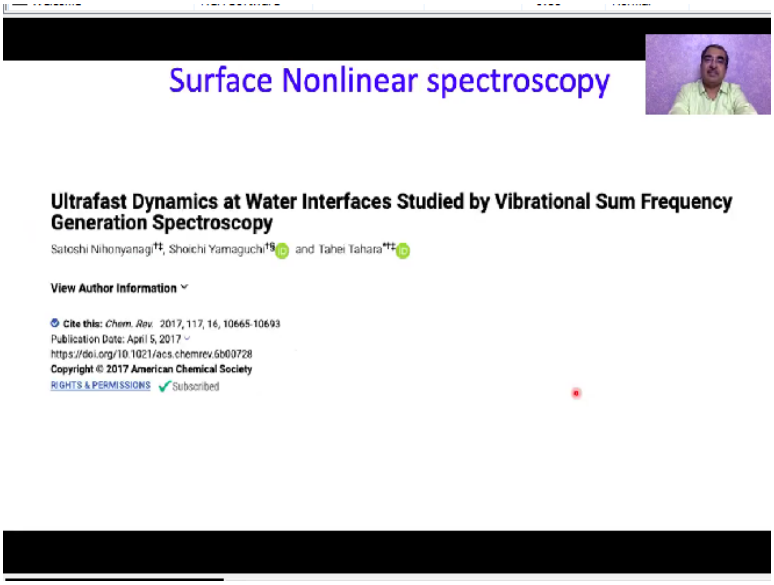

And finally, I would like to refer to this paper by Tahara and co workers on ultrafast dynamics at water interfaces studied by vibrational sum frequency generation spectroscopy, nonlinear spectroscopy at surfaces using heterodyne. So, that they can talk about phase. So, they do not only have to talk about intensities from that they have generated a wealth of information about many kinds of interfaces.

Unfortunately, we could not discuss all this in any great detail because that would be too much. Maybe later on, if NPTEL agrees we can have a half semester NPTEL course on these advanced aspects of ultrafast spectroscopy. There we can talk more about multi dimension 2D spectroscopy, we can talk about terahertz spectroscopy, we can definitely talk about surface nonlinear spectroscopy. But let that be the story for another take. For now, I hope that we have learned something new in this course.

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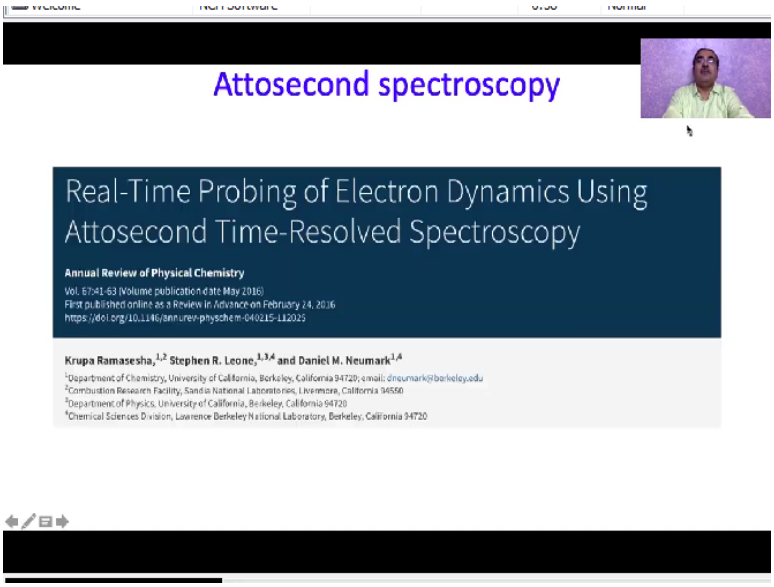

And I hope that it has been a pleasurable experience for all of us. So, with this, we come to an end of this course. And it is time for us to say goodbye.