Ultrafast Laser Spectroscopy
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Lecture-64
Two Dimensional Infrared Spectroscopy: Introduction

Today we move on to the last or maybe second last topic that we will discuss in this course, as we said in the last module, we want to discuss two dimensional IR spectroscopy. And then we want to discuss a little bit of surface sum frequency surface nonlinear spectroscopy. Now looking at the number of lectures already delivered and the number of hours prescribed for NPTEL course, I am not really sure whether we will have time to go into this surface nonlinear spectroscopy bit, but let us see how far we get.

So, today, what we essentially we want to do is we want to start learning what happens when we add one more dimension to the pump probe spectroscopy technique that we have studied. And our discussion will be limited to the infrared region. But then after this, if you read papers on say 2D electronic spectroscopy, the principles are pretty much the same. So, I hope that nobody will have any difficulty understanding 2D electronic spectroscopy as well after this course.

But we will limit our discussions to 2D IR spectroscopy and today we will get introduced in this module, we are going to get introduced to this topic. Before proceeding further, let me acknowledge the contribution of my friend Dr. Sukhendu Nath from Bhabha Atomic Research Center. Sukhendu has set up a two dimensional IR spectroscopy spectrometer in BRC and he is real expert.

I have learned 2D IR spectroscopy from him and some of the material in the slides that I am going to show you are actually from a presentation that he had made in our department. The other 2D IR spectrometer that is there is in IISER Pune by in the lab of Professor Bagchi. So here goes, what is the meaning of 2D IR spectroscopy. Before that, let me remind you of something that we had studied about 10, 12 modules ago, we talked about vibrational spectrum of liquid water.

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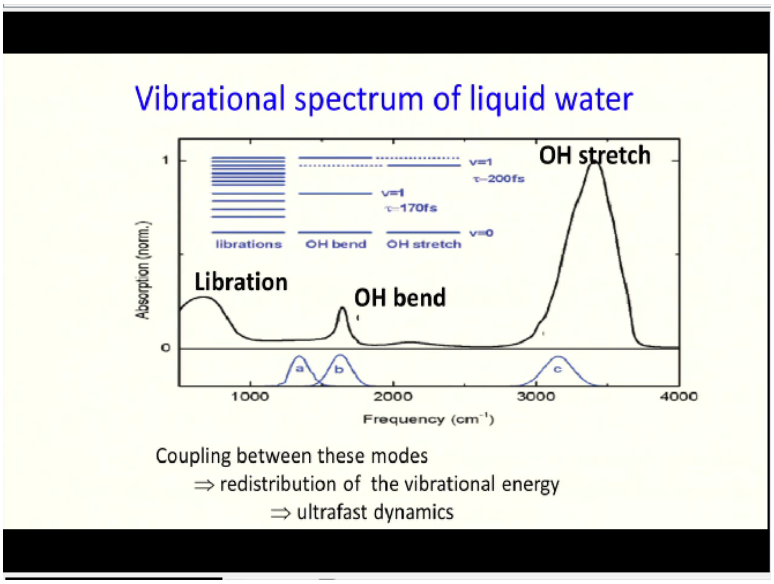

And we had said that when we talk about liquid water, the molecules are all associated to each other by hydrogen bond. So, first of all the librational mode comes up, which is not there for isolated water molecule. And we saw that these modes are all coupled, meaning if you can excite one mode, then the vibration energy gets redistributed in an ultra fast timescale into other modes as well.

I hope we all remember this discussion that we had made. So, 2D IR is sort of the next step of what we have studied in the course of discussion of this topic.

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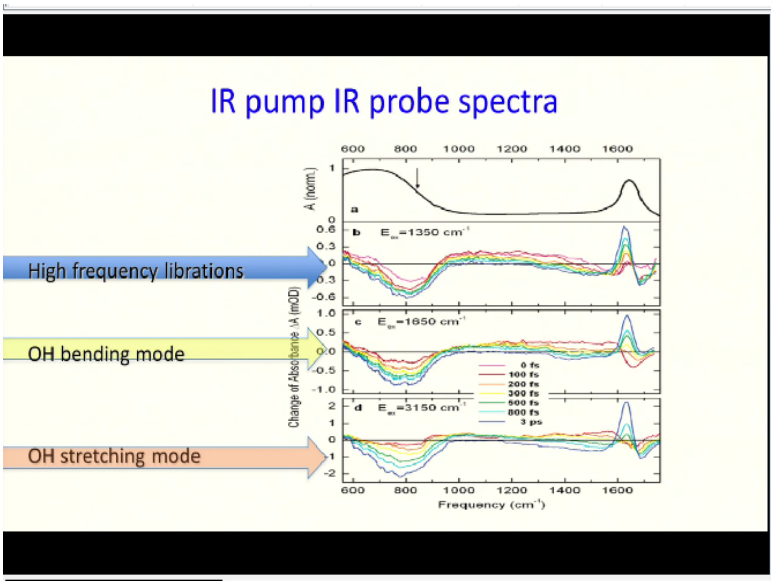

There if you remember we did an IR pump, IR probe, we learned an IR from IR probe spectroscopic technique.

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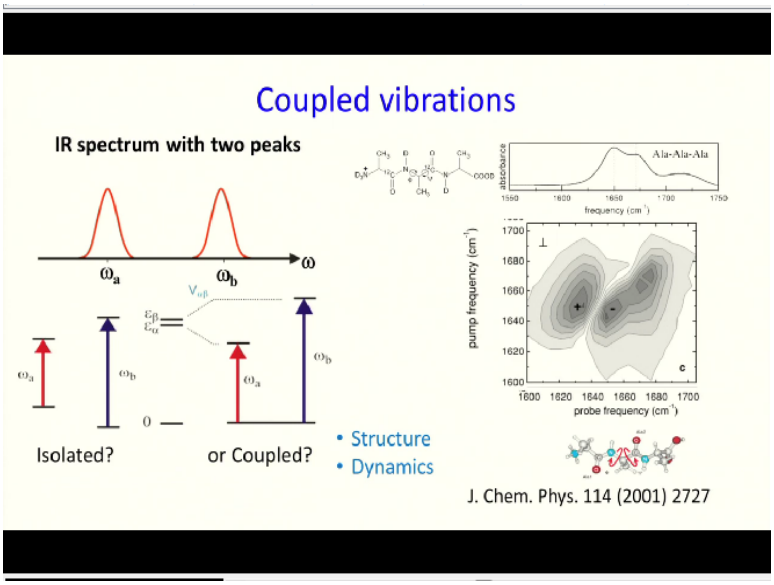

Here what is the how do we add another dimension and what is the advantage. The advantage is we get an idea of coupled vibrations. In the example discussed earlier, we had to look at the time constants and then from there we had to get an idea of what kind of coupling is there. Here we see we get another very useful and interesting feature in the spectrum that comes up if you add one more dimension, but let us take it slow. Let us go step by step. Let us say, I have an IR spectrum where there are 2 peaks, the blue omega a and omega b.

Now, there are 2 possibilities. One is that omega a and omega b arise from 2 different isolated normal modes of vibration of the molecule. I am talking about non associated isolated molecule now, right as you know molecules have these normal modes of vibration and each normal mode can be modeled as harmonic or anharmonic oscillator. Now, let us say we have oscillators that are not coupled with each other.

Then we expect to get 2 events like this due 2 transitions like this. But from the spectrum can we say that the picture is what we have drawn already and not this one. How do we know that the vibrations are not coupled. In a coupled system, when you excite one vibration, energy can be

transferred to the other. It is actually 2 quantum numbers are required one for each oscillator. This is something we elaborate upon later.

So looking at the spectrum, there is no way in which we can say whether we have a case of isolated oscillators or coupled oscillators. If you read this paper in published in 2001, we will see that they had studied IR spectra of trialanine and they are isotopic substitution. So, the IR spectrum of trialanine turns out to be something like this, and here they are focused on a particular region of the spectrum 1550 to 1750 centimeter inverse.

This is where the so called amide 1 stretch, amide 1 vibration shows up. Now, there are several amide bonds here, it is possible that the amide bonds vibrate by themselves or maybe they are coupled. How do you know from the spectrum, can you tell what is happening here, you cannot, but if you do 2D IR spectroscopy, and here I am jumping the gun a little bit and showing you a 2D IR spectrum already.

What you see is that this 2D IR spectrum is actually three dimensional plot on one axis we have pump frequency on the other axis we have probe frequency, there is a third axis pointing out of the projection towards you or towards me, that axis gives you the intensity or absorbance whatever you choose to plot. So, whenever we have a three dimensional plot and we have to draw it on a two dimensional paper or two dimensional surface, it is most convenient to show it as contour diagrams.

These contour lines essentially join all points where absorbance or intensity is the same. And what these contour lines look like they represent is that they represent hills. So, this contour line outside is has the lowest magnitude, the point inside has the highest magnitude as you go from out to in you see you can get a hill or you can get a trough if the sign of the absorbance is negative. In this course at this stage we are familiar with negative absorbance what we are really talking about is delta A, as you know, for ground state bleach.

And for stimulated emission, you actually get negative delta A signals. So depending on that, usually it is color coded to show whether it is plus or minus, and then you get contour lines like

this to represent the three dimensional surfaces, three dimensions, remember our pump frequency, first dimension, probe frequency, and delta A or delta T or whatever you choose to plot is a third dimension.

So, this is conventionally called a 2D spectrum. Those of us who have studied NMR spectroscopy might be familiar with 2D NMR spectroscopy. In fact, that came first the idea of 2D IR and 2D electronic spectroscopy borrows heavily from the understanding developed already from 2D NMR spectroscopy okay. So, if you studied 2D NMR, you would know that by 2D NMR, one can actually understand what kind of coupling is there between different nuclei.

And from there, one can predict structure, function and so on and so forth. That is why 2D NMR is very useful in elucidation of structure of complex molecules like proteins. So, in IR spectroscopy, what one can do and what has been done in this paper that we are citing is that actually coupling between different normal modes have been worked out and from there, it has been shown that one can talk about structure and not only structure the advantage is that, since this vibrational coherence is all decay in ultra fast timescale.

One can talk about ultra fast dynamics of evolution of structure by looking at how this coupling changes as a function of time, that is the appeal of 2D IR spectroscopy to the ultra fast community okay. Now, let us go back to basics once again and start from something that we have discussed many times in this course and that is pump, probe spectroscopy. Here remember we are using ultra fast pulses.

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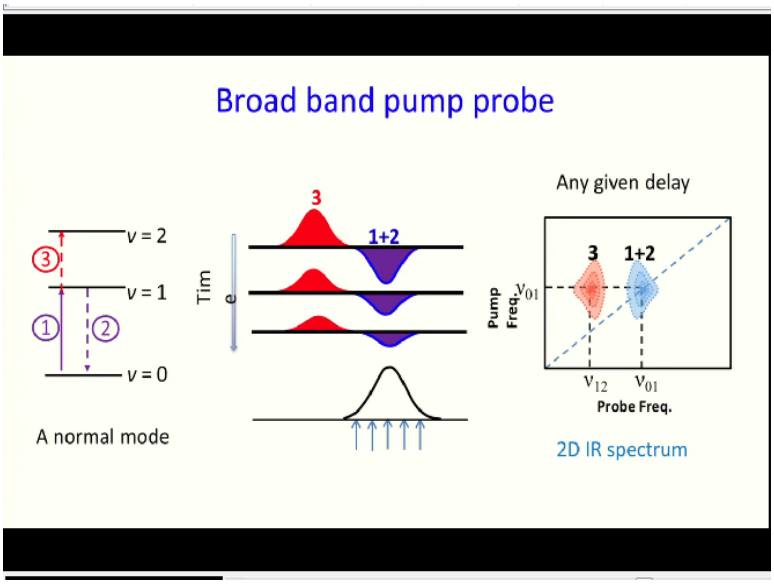

So spectrally there is a lot of width. Bandwidth is significant for ultra fast pulses as we know. So, we are talking about broadband pump probe spectroscopy. And for the purpose of the present discussion, we are talking about broadband pump probe spectroscopy in the IR range. Let us say these are the energy levels of your particular normal mode in a polyatomic molecule. For our purpose we will only talk about v = 0, v = 1, v = 2, one can talk about v = 3, 4, 5.

But, at least to start this is enough. So, as we know in ground state at room temperature, only v = 0 is populated for all practical purposes. So, suppose I pump this, we call this process 1 and corresponding band that we are going to show we recall band 1, the pump v = 0 to v = 1. If you do a pump probe experiment, and if one is a pump, then what I can do is I can probe different regions.

So, this is the broadband pump that I am using. And the probe that I can do is first of all, I can prove the same region. What is it that we will get if we probe to 2 is essentially the same spectral region as 1. So, what we can get is that we get contribution from downstate bleach of v = 0. And we can also get stimulated emission from v = 1 and they add up to give you a negative signal as we know.

So we expect a negative signal like this. What happens if you probe v = 1 to v = 2 region. Let us call that region, region 3. There we expect a positive signal, is not it. Now, there is going to be a transient absorption. Now, if we vary the delay between pump and probe, then we expect that this

signal is going to decrease is going to become smaller and smaller at sufficiently long time is going to become same, the something that we know already.

But now the additional dimension that comes is that since it is a broadband pump, let us say, we have the capability of exciting using narrower band light, spanning the range of the broadband absorption of 0 to 1, then what happens. Then, I can record these transient spectra for each of these pump wavelengths. And I can plot for any given delay let us say, I can plot a 3D plot like what we have discussed already.

Pump frequency on one axis probe frequency on the other intensity or absorbance on the third axis represented by contours. So, what do we expect. What happens when we pump at 1, pump at 1, let us say the frequency is nu 01 we expect a negative signal for probe frequency of nu 01 as discussed already, we expect a positive signal for probe frequency of nu 1 to a nu 01 corresponds to the frequency matching the energy gap between v = 0 and v = 1 nu 1 to is the frequency corresponding to the energy gap between v = 1 to v = 2.

Of course, if this is a harmonic oscillator, then nu 01 will be equal to nu 1, 2, but for anharmonic oscillators are going to be different. Okay, so what do I see. Do I see a point here and a point here. Not really because the thing is this think of the pump axis. So, when I scan from say lower frequency to higher frequency of pump, whatever signal I get here, it is going to go up from this side to that right on frequency lower to higher, lower to higher.

Absorbance is increasing, and then going through a maximum. So, whatever is the intensity that I get a nu 0 =1 magnitude of it, remember, we get a negative signal at nu 01 magnitude of it is going to go up and go down along this axis, not very difficult to understand. And then, if you look at the probe axis, this is the probe axis here also for any given pump, the magnitude of signal goes up negative sense here.

And then goes down until it becomes 0 and I am saying go up and go down and only talk about magnitude. So, what do you expect you get a distorted well, you get a three dimensional not really Gaussian not necessarily Gaussian distorted Gaussian kind of shape. So, at center wavelength of

nu 01 we expect this kind of a shape, the negative signal due to here blue means negative, red means positive.

Negative signal due to rousted bleach of one and transient well stimulated emission denoted by 2 okay. So we get a three dimensional surface and at nu 1 2 at the intersection of nu 01 pump and nu 1 2 probe we get a similar signal but positive okay, what is the difference between the maximum point in the positive signal and the negative signal. Not very difficult to see from here to here, the difference in frequencies okay.

So that would give you the difference in frequencies of nu 1 2 and nu 01 modal frequencies okay, that is not very difficult to understand okay, but that has already introduced us **to** 2D IR, this is the simplest possible 2D IR spectrum that one could think of.

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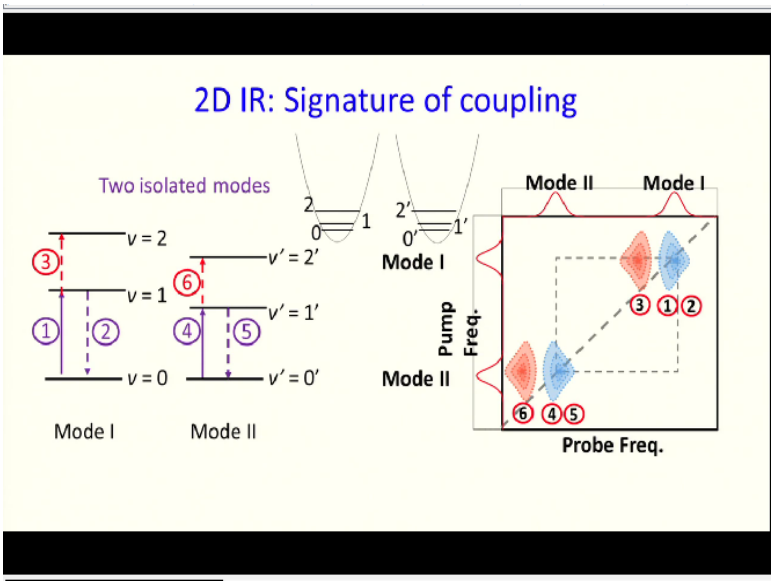

Now, let us make the situation little more complex, because, as we said earlier the appeal of 2D IR lies in the understanding of coupling between normal modes of vibration. So, if coupling has to happen, then you should have 2 normal modes. So, now, let us see what kind of 2D IR spectrum we expect, when we have not 1 but 2 normal modes of vibration. To start with let us talk about 2 isolated modes, 2 isolated modes denoted by these 2 potential energy surfaces.

Since the quantum oscillators, the energy is quantized. And here we are shown v = 0 v = 1 v = 2. And just to ensure that we do not forget that this mode is different from the other one, we have represented the vibrational quantum numbers in the second mode as 0 dashed 1 dash 2 dashed. So we have drawn it here, it might look like the modes are similar, they do not have to be, the shapes can be different.

The energy minima have to be different. This is not 2 scale diagram. But now, if we zoom in, forget about the parabolas for the moment, look at only the vibrational energies and zoom into the first one. We already know what kind of transitions we can expect for the first normal mode. And it is not very difficult to figure that we expect very similar kinds of transitions for this second normal mode as well.

Here, instead of 1 we have written for 4 for the 01 pump, the instead of 2 we have written 5 for this v dash = 1 to v dash = 0 dashed transition and we have been 6 instead of 3 for v dash = 1 to v dash = 2 dash transition okay, so what kind of 2D IR spectrum do we expect when the modes are isolated. There is no coupling whatsoever they do not talk to each other okay, this is what we are going to get.

Right now we have not shown any peak here, but for the sake of understanding I have shown these spectra where the mode 1 and mode 2 are okay. Now when we pump mode 1 okay, which means we pump here then what do we expect to get we expect to get a negative signal for 2 which will occur in this region and we expect to get a positive one for 3, which will occur also in this region.

This will be at lower frequency because for anharmonic oscillator v = 1 to v = 2 gap is smaller than nu = 0 to nu 1 to nu = 1 energy gap. So, we expect this kind of a feature that we have discussed already, negative signal due to downstream bleach of 1 stimulated emission of 2 positive signal for transient absorption pathway 3 fine, but now say we have the capability of scanning the pump wavelength.

So, we do not have to pump necessarily at mode 1. We can pump mode 2 also which means we can pump here. What do we expect to see, we expect to see an exactly similar feature not here, but

here in the region of mode 2 frequency, again we expect to see a negative signal and a positive signal not very difficult to understand okay. So, in a low coupling case, we can expect to see modes along the diagonal.

This diagonal here represents the pump frequency equal to probe frequency situation. So, we expect as many positive and negative pairs as the number of degenerate sorry, as the number of non degenerate vibrational normal modes, we expect along the diagonal as many positive and negative pairs as the number of non degenerate vibration normal modes in the molecule okay. This is what we expect when coupling is not there.

Now, let us say coupling is there, which means, if I pump one normal mode, then it can transfer the energy to the second normal mode as well and cause transition of the second normal mode from v dashed = 0 to v dashed = 1 state, to discuss such a situation, first of all, this is one way in which we can show coupling, okay, by a dual energy minimum kind, double well kind of potential with a potential barrier.

Now, what I have drawn here is symmetric double well, but the most general case would be an asymmetric double well, this would be lower or higher. The way I have drawn it here it should be lower. Now, what happens since the system is coupled, you cannot really talk about the 0 1 2 vibrational quantum numbers and 0 dash, 1 dash, 2 dash vibrational quantum number separately to designate any particular energy state we need to specify both the quantum numbers as it shown here.

So, the lowest energy quantum number will be 00 dash, which means this is how it is populated, this normal mode is in the 0th state, this one normal mode is the 0 dash state and then what one can do is using light of suitable frequency one can do a promotion to 1 0 dash state, 1 0 dash state would mean that this normal mode has undergone a promotion this has not okay. So, what is 0 dash means the second normal mode continues to be in the 0 dashed state.

But the first one goes to higher energy one state or you could have the other way around 01 dash, 01 which simply means no transition in the first normal mode 0 dash to understand the motion in

the second normal mode, okay. So, these states are basically the same as the isolated ones we have just had to redesignate them. So that we show both the quantum numbers together. Similarly, one can understand what the meaning of 20 dashed and 02 dashed is.

But that is not all as a result of coupling, one needs to think of some other states as well. One state that arises is 11 dash state where both the normal modes have been excited to 1 dashed, it is not necessary that only one normal mode is excited right. One can have both the normal modes in the excited state. That is 11 dash normal mode, is important to understand that the 11 dash normal mode can be produced in 2 ways.

You cannot go from 00 state to 11 dash state directly. And once again, for those who have studied NMR spectroscopy, I would like you to think what happens when you talk about 2 nuclei. Suppose you have alpha, alpha, you cannot go from alpha, alpha to beta, beta by itself, because that would require in a single transition, you cannot go from alpha, alpha to beta, beta, right, because 1 photon can only bring about 1 transition.

That is called 1 photon rule, I think we have talked about this earlier in this course as well. So, in 1 photon transition, you cannot go from 00 dash to 11 dashed. So, only one normal mode can undergo excitation when 1 photon impinges on the molecule So, you cannot go from 00 dash to 11 dash, but one can go from 10 dash to 11 dash right, because 10 dash to 11 dash essentially means the first oscillator escaped well sorry the second oscillator is kept, what am I saying 10 dash to 11 dash means already the first oscillator is in the $v = 1$ state.

Now 1 photon comes and all it has to do is to promote the second oscillator from 0 dash to 1 dash state. 10 dashed to 11 dash essentially means promotion of this second oscillator from 0 dash to 1 dash state 1 dash level when the first start oscillator is already at $v = 1$ okay, so we will call this pathway, pathway 7. And it is important to understand that the energy of this is equal to the 0 dash to 1 dash transition.

What else can we do, we can do the other thing from 01 dash, we can go to 11 dash also, if you want to go from 01 dash to 11 dash, then what we are doing essentially is that already the second

oscillator is in the 1 dash level. Now, the first oscillator is in 0 level, 1 photon comes and promotes it from 10 dash to 11 dashed state we call that pathway 8. Now, let us think how this 2D IR spectrum is going to change if at all if we pump either mode 1 or mode 2.

Let us say we pump mode 1, in addition to pathway 2 and pathway 3 the other pathway that is available is this right because what the pump has done is that the pump has populated the 10 dash state. Now, the probe if the frequency is right can bring about a 10 dash to 11 dash transition, that is a transient absorption. So we expect a positive going signal and where do we expect the positive going signal.

Remember, we have pumped mode 1. So, this is the pump frequency. And the positive going signal, as we said earlier, should appear in the same frequency as this 0 dash to 1 dash transition because that is a transition that is taking place here. So, we should get something that comes here, where pump frequency is that of mode 1, but the probe frequency is the same as that of 6 okay, the other thing that happens is that the moment you have this 10 dash to 11 transition.

The other thing that happens is that the second oscillator will not other thing the same thing, the second oscillator gets promoted from 0 dash to 1 dash level. Yeah, 10 dash to 11 dash, as we said essentially is 0 dash to 1 dash promotion, when the first oscillator is in v = 1 level. So, 0 dash to 1 dash promotion, it is manifest in 2 things, one is transient absorption that is 7. Second thing is again, ground state bleach.

So, here we get another positive negative signal, but this time it is of diagonal okay, we have pumped mode 1 and we have got in the probe, a signature that we expect when we pump mode 2. Similarly, if we now well and this is delta 23 as we have discussed earlier. Now, if you pump mode 4 what will happen, again same thing will happen we will get another cross diagonal peak in this position.

Because pumping mode 4 is going to bring about a transient absorption here in pathway 8, which is 01 dash to 11 dash, 1 dash remains 1 dash, the first oscillator goes from 0 to 1. So, pump wavelength will be for mode 2 probe wavelength, we get the feature, where we got it for pumping

at mode 1. So, the significant nu feature that we get if you perform 2 dimensional IR spectroscopy is of diagonal peaks.

As we have seen in the discussion so far of diagonal peaks do not arise if coupling is not there, if you have of diagonal peaks that means the 2 modes have coupled very similar to 2D NMR spectroscopy and that gives us an idea about if we extrapolate further and interpret a little more that can give us an idea of the structure okay. So, take home messages that off diagonal peek in 2D IR spectrum is a signature of coupling great.

Now after all this is an ultra fast dynamics course, so, it is logical to ask can we follow some kind of a dynamics using this of course, we can, we are doing pump probe remember. So, what we can do is in addition to scanning the pump frequency, we can also vary the delay time between pump and probe like what we have discussed so many times earlier. Let us take this example.

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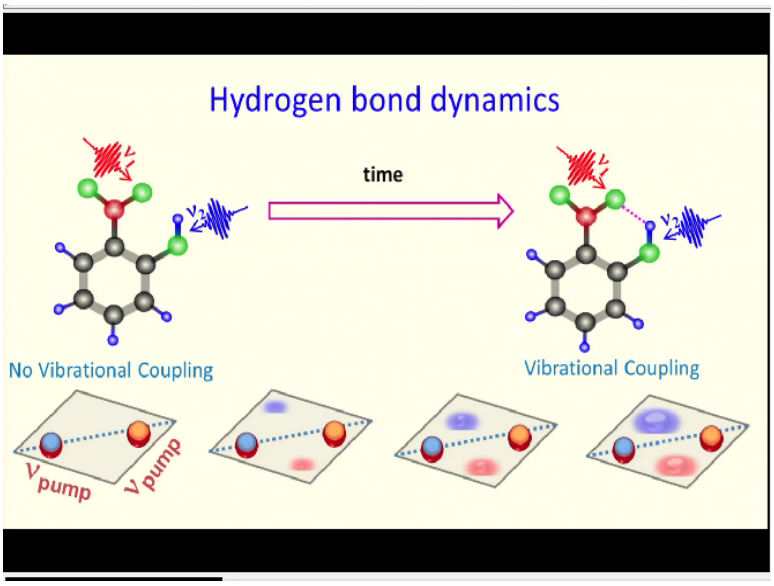

Where we have this situation, let us say we have this molecule, this C double bond O, let us say or well some molecule that can do hydrogen bonding, let us say initially there is no hydrogen bonding, nu 1 is nu wavelength of this vibration nu 2 is the wavelength of this vibration. So, if there is no coupling, no hydrogen bonding, then we expect this kind of a spectrum, only diagonal peaks. If hydrogen bonding is there, then we expect off diagonal peaks, this is something that we know already from our previous discussion.

Now, see, if the situation is such that the hydrogen bonding is not there in ground state, we excited and then in the excited state, the hydrogen bond gets formed. Then what happens then with time we go from this non hydrogen bonded non coupled structure to hydrogen bonded coupled structure. So, times 0 we expect to have a 2D IR spectrum without of diagonal peaks. With progress in time, the off diagonal peaks slowly emerge.

And the dynamics of emergence of the off diagonal peaks gives us the dynamics of formation of hydrogen bond. So this is an introduction to the 2D IR spectroscopy technique. Well, this is an introduction and this tells us what we can do by 2D IR. Next day, in our next module, we are going to learn what happens, rather, how are we supposed to do it. We understand that 2D IR spectroscopy gives us additional information.

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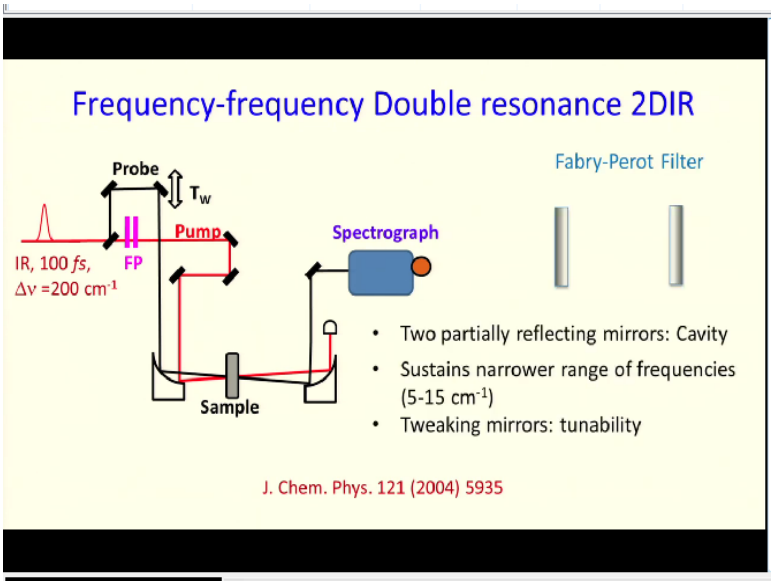

But we have to do a frequency domain as well as time domain measurement. How do we do it. We will start with the simplest technique, frequency-frequency double resonance, 2D IR and we learned something about Fabry-Perot filter, but then we will move on to a little more complicated technique. So, in the next module, we are going to discuss techniques of 2D IR spectroscopy.