Ultrafast Processes in Chemistry
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Module No # 09
Lecture No # 50
Vibrational Energy Transfer in Water

Right in the previous module we staring talking about solvation dynamics and then we went on to talk of solvation dynamics in water that is where we stopped. And we did not go into lot of detail but we said that if you take bulk water then the ultrafast solution dynamics that you see there is not single exponential it is tri exponential or bi-exponential with the Gaussian component and in Fleming's work they were actually been able to assign each of this components to different kinds of motion of water including rotational motion Librational motion so on and so forth.

So and your homework was to read that 1994 nature paper and understand we also said that in confine medium the solvation by water becomes slower by orders of magnitude and that is explain once again we did not go into much detail but it is explained mainly by Bagchi's model one of which is exchange between bound and free water. So today we will discuss a different aspect of water what we will do is we will show you the vibrational spectrum of water and then we will discuss the normal modes of water not isolated water but water as water liquid.

And there we will try to see what happens when one of the vibrational modes is excited how does the energy get dissipated? How does it get redistributed in different normal modes of vibration and liberation.

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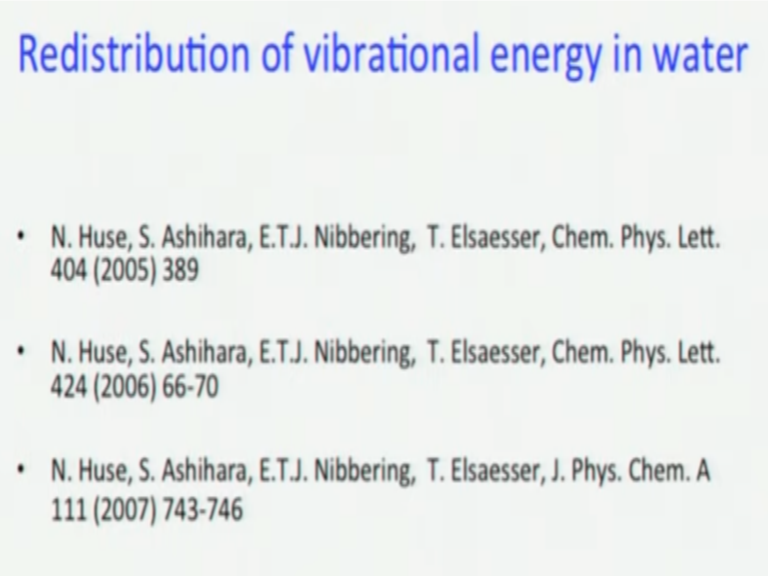

Redistribution of vibrational energy in water

- N. Huse, S. Ashihara, E.T.J. Nibbering, T. Elsaesser, Chem. Phys. Lett. 404 (2005) 389
- N. Huse, S. Ashihara, E.T.J. Nibbering, T. Elsaesser, Chem. Phys. Lett. 424 (2006) 66-70
- N. Huse, S. Ashihara, E.T.J. Nibbering, T. Elsaesser, J. Phys. Chem. A 111 (2007) 743-746

And this work is mainly by Elsaesser group and our present discussion will focus on these 3 papers that are listed here there has been more work so it is up to you to go and read more recent literature in this topic.

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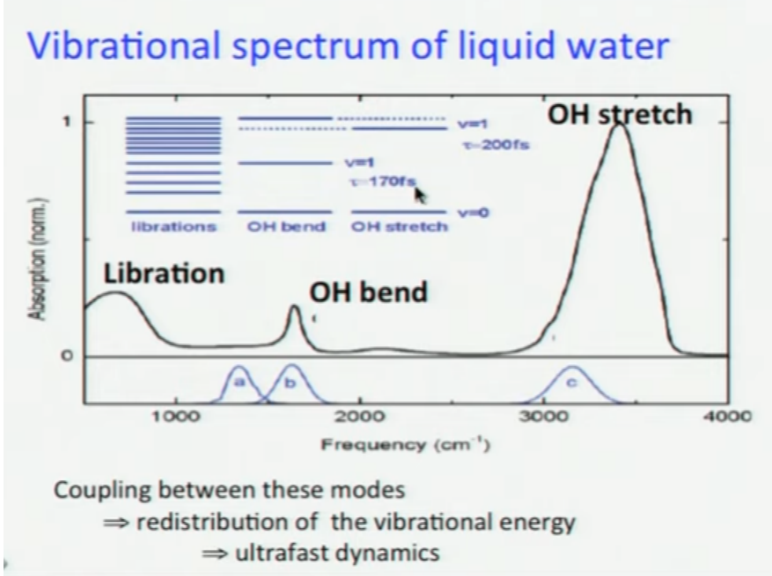

Vibrational spectrum of liquid water

Coupling between these modes

⇒ redistribution of the vibrational energy

⇒ ultrafast dynamics

So to start with let me show you a vibrational spectrum of liquid water and here the only difference between this and this vibrational spectra usually record this is that Y axis is absorbance not percentage transmittance as it usually is with IR spectrum. But this is a regular steady state FTIR spectrum. Now here you see 3 major features 1, 2, 3 and you see a broad feature here and a broad feature here what are they.

This one I think everybody knows the one between 3000 and 3600 700 centimeter inverse that is the OH stretch of water. That is the strongest signal and that is what predominates whenever there is anything that contains an OH group we always see this broad absorption that is very well known. The next one also I think is well known it is OH bend the third broad absorption here along with this even broader and less prominent feature is ascribed to liberation.

As we had perhaps talked about in the last module liberations are restricted rotation so you have water molecules want to rotate but then since hydrogen bonded a brought back. So it is sort of waging motion and you are familiar with waging motion molecule for IR so here not within 1 molecule but it is in the intermolecular couple system a particular water molecule wants to rotate but it is brought back because it is hydrogen bonded this kind of motion is called liberational motion.

Of course energy of this liberational motion would be much lesser than your stretch or bend and here it is this is actually called the L2 band the prominent liberation motion low frequency liberation motion. Here you have some high frequency liberation motion this is not very well defined but we will play an important role in our discussions and what are these A, B and C we will come back to that later in couple of slides.

So the question that we are trying to adjust trying to understand is this ultrafast dynamics involved in coupling of this modes generally what is the meaning of normal modes? That these modes of vibrations are independent of each other but in an correlated system associated system when you make 1 vibration happen it does affect the other vibration. So you can think that what happens when hydrogen bonding is stronger what vibrations will be effected? What happens when this bending takes place it affects hydrogen bond dynamics right.

The moment it effects hydrogen bond dynamics that is going to affect liberation motion as well liberation motion will be more or less depending on what happens to the hydrogen bond. So this is basically what we want to study? And the reason why you have coupling between normal modes is if you look at the energy diagram this is what it is? This one is OH stretch the biggest energy gap this is OH bend and this is liberational motion.

They might remind you of some asymmetric vibration but the energy gaps are really small as you can see this is the energy gap between 0 and 1 for OH stretch this is the energy gap between V = 0 and V = 1 for liberational motion much smaller. And the notable feature here is if you look at the energy of V =1 of the OH stretch manifold that has more or less as same as energy as V = 2 of OH bend right.

So what happens when they are close? What is it called? What are the symmetries of vibration of water? Now C2 the point group so what is the symmetry of this OH stretch? Symmetric stretch asymmetric stretch all that thing is there right. Now symmetric stretch is A1 what is bend? You better look up so what happens here is that since as an energy match and there is a match of symmetry as well you have something called Fermi resonance.

In Fermi resonance energy can then there is coupling between the modes and energy can get transferred between one mode and the other. So it is not unusual to expect that if you excite this OH stretch then energy will go into OH bend as well. And then liberation have so many energy levels it is it may be quite expected that no matter which one you excite there will energy transfer to liberations as well.

So finally when you make water molecule vibrate say excite a stretch that will that energy you give some energy for it to stretch that energy will be dissipated by exciting bending motion and liberations as well. And the times involved are always ultrafast because this V = 1 leaves for about 200 femtosecond this V = 1 for OH bend for about 170 femtosecond and we will see what happens when we look at the normal modes how they evolve okay.

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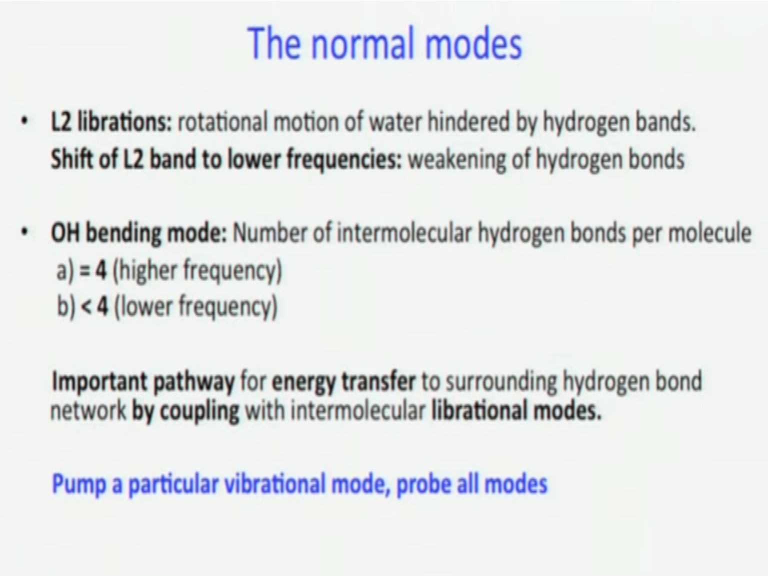

The normal modes

- **L2 librations:** rotational motion of water hindered by hydrogen bands.
  Shift of L2 band to lower frequencies: weakening of hydrogen bonds

- **OH bending mode:** Number of intermolecular hydrogen bonds per molecule
  a) **= 4** (higher frequency)
  b) **< 4** (lower frequency)

Important pathway for **energy transfer** to surrounding hydrogen bond network **by coupling** with intermolecular **librational modes.**

Pump a particular vibrational mode, probe all modes

So just a reminder L2 liberation is rotational motion hindered by hydrogen bonds. So if this L2 band shifts to lower frequencies what does it indicate? That means hydrogen bonds are weakened so these are the things that we are looking for. OH bending mode now OH bending mode generally we do not even pay attention to this in bulk water because each water molecule in any cases surrounded by so many water molecules but in a when you are going to make measurements in femtosecond timescale you need to take into account little more of a detail.

And if you are going to work with water clusters where you have small number of water molecules which you can prepare artificially then also this becomes important and this is what is actually known from this water cluster can do experiment. It is known that OH bending modes first of all depend the frequency of the OH bending modes it depends on number of intermolecular hydrogen bonds per molecule.

So if it is equal to 4 then you have a higher frequency vibration if the number of intermolecular hydrogen modes per molecule is less than 4 then you get a shift so the 4 is seems to be the sort of a magic number here it does matter whether you have well how many can you have per molecule that is another question? There is the reason why 4 is a magic number how many hydrogen bonds can be there for water they can be 4 right you cannot have more than that.

So if it is not 4 for some reason then if some hydrogen bonds are broken then there is one kind of lower frequency vibration and if it is 4 if whatever number of hydrogen bonds could be formed is found then you have higher frequency vibration. So this is something that is known so the important pathway for energy transfer to surrounding hydrogen bonded network would be of course by coupling with intermolecular liberational modes.

So experiment that is done is pump a particular vibrational mode and probe all vibrational modes so this is an IR pump IR probe experiment okay. Pump by a femtosecond pulse in IR not visible or UV and probe in IR as well. With that background we can come back to the earlier diagram and now I can tell you what these are this ABC these are the spectra of 3 kinds of excitation frequencies used.

When you excite by C and I will tell you what the wavelength is? Then you essentially excite OH stretch when you excite this by using B you excite OH bend when you excite by A you essentially excite liberation of course it might have been if you could excite here but then might have been limitation of the experimental setup okay.

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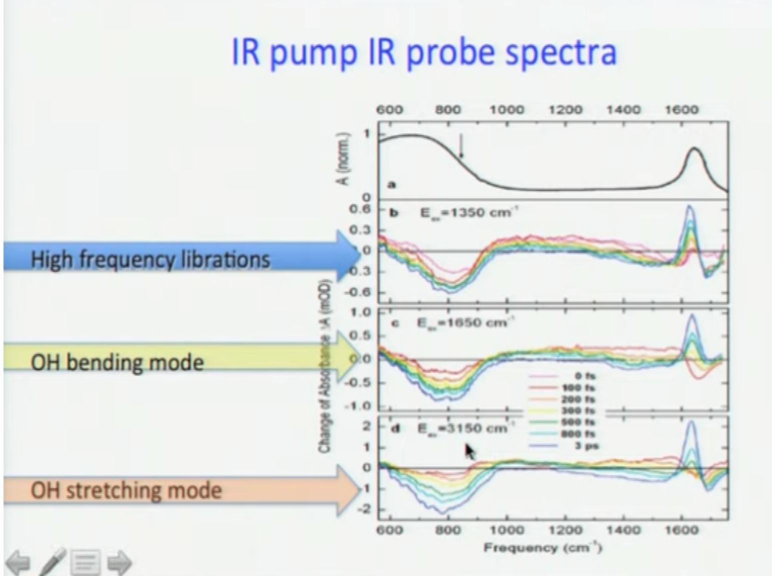

IR pump IR probe spectra

High frequency librations

OH bending mode

OH stretching mode

And these are the frequencies then 3150 centimeter and remember what i showed you earlier is spectrum not a here this is actually spectrum same scale and you will remember there are femtosecond pulse cannot be completely monochromatic there are always they spread of energies. So what we are showing here is the model frequency maximum of that spectrum higher spectrum.

So when you excite OH spectrum mode that has been done by using pulses which have maximum at 3150 centimeter inverse. OH bending mode is excited using 1650 centimeter inverse maximum pulses and high frequency liberations are excited by 1350 centimeter inverse okay. Another reason for not exciting low frequency liberation is that I mean where will the energy go?

You can only have liberation if you pump at low frequency liberation right only when you excite something at higher energy can that energy can go to lower energy modes. If you pump at lower energy mode that energy cannot you cannot have joining up of photon in this case at least okay. So remember this is a spectrum and this is truncated spectrum actually as I think the probe had a little bit of limitation and in case it makes no sense to probe the OH stretching mode the only thing that you can see there is a ground state bleach that is going to recover.

So here the study is focused on mainly 1650 centimeter what is that OH bending mode right and here you have all the liberations. So what do you have before going into each of this quantitatively if you see when you excite the OH stretching mode remember OH stretching mode is how much 3150 centimeter inverse. You get a bleach at 1700 centimeter inverse or so what does that mean?

Why would they be a bleach when you pump the why would there be a bleach for the OH bending mode when you pump at OH stretch you are pumping OH stretch and we see this is ground state bleach in OH bend why would that happen and this is not nanoparticles nothing we will talk about nanoparticles later this is just liquid water. What is the meaning of ground state bleach? In this case population at V = 0 goes down population at some higher vibrational level goes up there is an hint total population more or less is same.

Stretch we pump by stretch the what happens I have actually shown you the results already you have to connect with what I have shown you something that I have shown you depopulation of bend why? Remember Fermi resonance what happens in Fermi resonance? Is that direct energy transfer that means population of V = 2 yes population of V = 2 of OH bend takes place by direct energy transfer from the stretch remember? So a pump here right and that is V = 1 so this is energy transfer right so population of V = 2 will be there so naturally there is depopulation of this OH is bend energy transfer is taking place.

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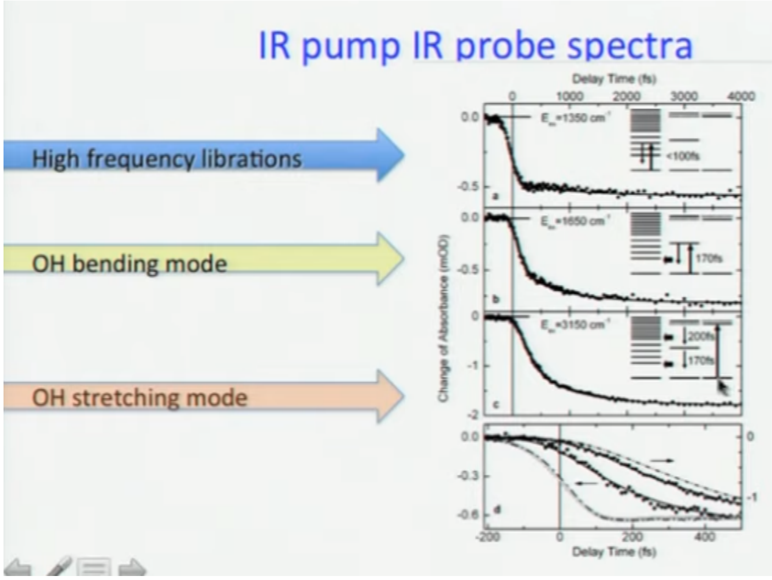

IR pump IR probe spectra

High frequency librations

OH bending mode

OH stretching mode

So it is excited well vibrated excited state phenomenon that would case the ground state bleach and here you see this transient absorption positive signal also coming for OH that is because of population of higher state okay. So there is this Fermi resonance this is this are clear signature of that. Now what happens here? There is ground state bleach of L2 as well and there is ground state bleach here little bit of growth here difficult to analyses the data but it happens.

So that means since there is a bleach of L2 vibration that means L2 vibrations are also they also get excited that means energy get transferred from stretch to bend and to liberation. So question is it direct or is it to stretch? Now what happens when you excite OH bending mode directly so here also you get a ground state bleach which is expected because you are exciting that particular vibration. And you get this excited state absorption that is also expected.

Once again you get a ground state bleach here and here you see there is a little difference you see a build up is stronger in high frequency liberational mode you see that little better. Which means when you make the molecule bend what is happening? Hydrogen bond network is effected and that is what will effect liberation as well that is what is taking place there is also sort of energy transfer.

And what happens when you excite high frequency liberations once again there is a ground state bleach here. And once again there is this lower frequency transient absorption remember what we said about this high frequency and low frequency business for bending motion? Yes if number of hydrogen bonds is less than 4 then you get this lower frequency absorption. So that is why this might seem a little strange there am I exciting lower energy liberations and I see a ground state bleach in comparatively higher energy bend that is because by doing this exciting this lower energy liberations high frequency liberation what you do always is that you it is moving like this so hydrogen modes will affected.

So there will be weakened that is why you get this phenomenon here so this is something very interesting because you might not at first glance expected right? You might think that you excite lower energy what will happen? This is what happens because we are not working with isolated molecules here it is a hydrogen bonded associated liquid. And again you see there we see a rise of high frequency liberation again we see a ground state bleach here.

Now qualitatively I think we understand what is going on quantitatively if you look at the traces this is what you see. When you excite high frequency liberations directly the rise is actually instantaneous this little bit of what looks like a slope that is because of the instrument response function you are not using a delta pulse anyway. When you excite OH bending mode do you see the rise? This one is instantaneous now compare this with this is instantaneous part and there is a rise.

Why is there are rise look at this energy diagram once again we excite the OH bending mode it is it leaves the 170 femtosecond and in this 170 femtosecond it can either come back to V = 0 or it can transfer energy to liberation. The rise time that we get here is about 170 femtosecond which means that almost all the energy that you provide in OH bending goes into liberational mode that is why that higher V states of liberation actually grow it is no longer just instantaneous a little bit of instantaneous part will always be there.

Because remember we are working with non mono-chromatic pulses so direct excitation is bound to be there and then you are exciting in this high frequency liberation as well a little bit but that rise is very prominent and rise is 170 femtosecond. When you excite OH stretching mode then you see that instantaneous part decrease even more and just to the I has not the growth become prominent and has not the growth become longer.

You can see it if you compare this here so here what happens is? In fact there are 2 rise times now analysis of this kind of data is always problematic now to fit a rise time itself is a non-trivial task. In order to fit kinetics to more than 1 rise time requires a lot of confidence because as you know increase a number of parameters it is going to fit better anyway. So your data quality has to be very good and you must be very confident about what you are doing must make sure that you are just not making up some story that is not right.

So there again model becomes important and 2 rise times here sort of okay because here you see 2 kinds of energy transfer one is from here to from stretch to bend and then from bend to here okay. So again we are again providing you an overall view of this paper please read the paper and see how did they analyzed? So what they have done really is that they have fitted then entire thing to a kinetic scheme so it is like a intermediate right A2, I2P when you do that you get a kinetic equation and that is what you have to fit your data tool you cannot fit to 2 rise or anything okay that is what they have done and they have extracted that 2 times the turn out to be 170 and 200 femtosecond.

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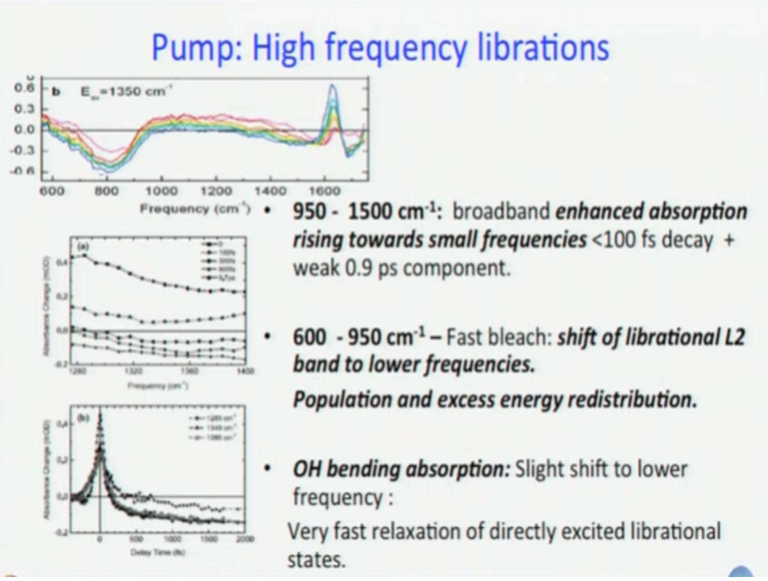

Pump: High frequency librations

- **950 - 1500 cm^{-1}:** broadband ***enhanced absorption rising towards small frequencies*** <100 fs decay + weak 0.9 ps component.
- **600 - 950 cm^{-1}** – Fast bleach: ***shift of librational L2 band to lower frequencies.***

  Population and excess energy redistribution.
- ***OH bending absorption:*** Slight shift to lower frequency :

  Very fast relaxation of directly excited librational states.

So this is the thing when you pump high frequency liberations okay I do not have to go through each part of it but when you pump high frequency liberation this is what happens you get a broadband enhanced operation rising towards small frequency which means again energy transfer is taking place. And here you get this less than 100 femtosecond decay that is limited by the laser pulse and a very week 0.9 picosecond component.

So that slow component is there it is not as we it is not there 0.9 picosecond means what 900 femtosecond okay you might not seem very slow but it is at least slower than less than 100 femtosecond. So what this means this broadband enhance absorption not easy to handle what it means is that when you excite the high frequency liberations then part of the energy goes right away and part of it goes little slower which may not be unexpected because there is always a period of this kind of librational motion.

600 to 950 centimeter inverse there is the fast bleach and that is because of and because there is a shift of librational L2 band to lower frequencies. See what is happening here something is rising is not it? Due to see the signal becomes more than 0 at the very end beyond 600 centimeter inverse. So why is there a bleach here? There is a bleach because due to high frequency liberations once thing that definitely happens is this hydrogen bond network is disrupted.

So like bending liberation also moves to lower frequencies if hydrogen bond is distracted that is why you see that bleach. And OH bending absorption there is a slight shift to lower frequency that we have already discussed why?

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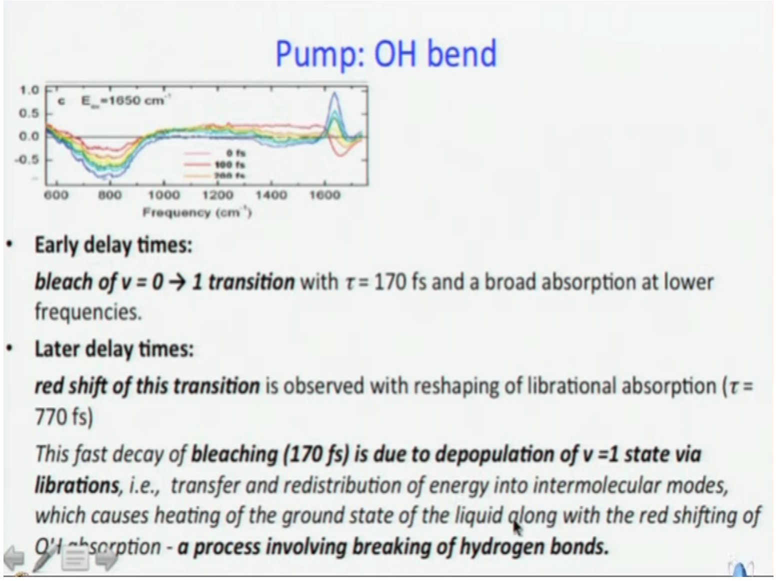

Pump: OH bend

- **Early delay times:**
  bleach of v = 0 → 1 transition with τ = 170 fs and a broad absorption at lower frequencies.
- **Later delay times:**
  red shift of this transition is observed with reshaping of librational absorption (τ = 770 fs)
  *This fast decay of **bleaching (170 fs) is due to depopulation of v =1 state via librations**, i.e., transfer and redistribution of energy into intermolecular modes, which causes heating of the ground state of the liquid along with the red shifting of OH absorption - **a process involving breaking of hydrogen bonds.***

When you excite OH bend then in early time you get a bleach of v = 0 to v= 1 transition time constant is 170 femtosecond broad absorption is lower frequency femtosecond broad absorption at lower frequencies later for longer times you see there is a red shift of this absorption and liberational absorption gets reshaped why does that takes place. Once again because of disruption of hydrogen bonded network okay and that is what is sort of discussed in this last paragraph.

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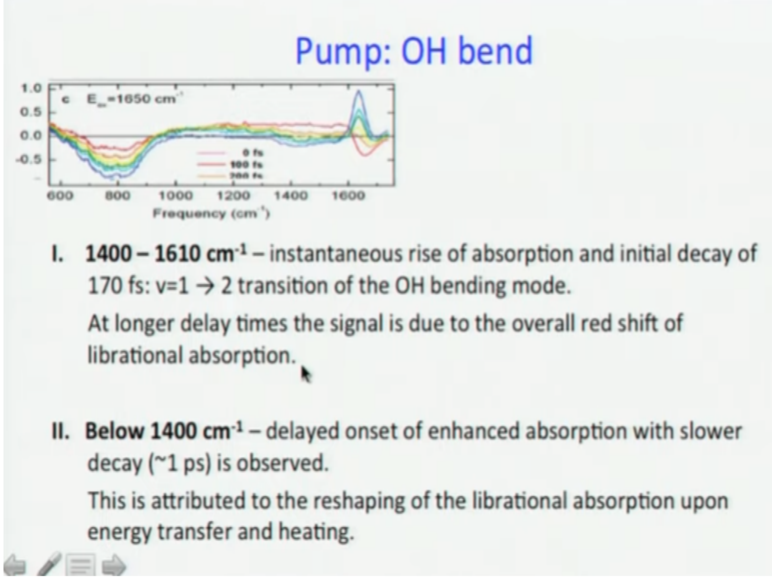

Pump: OH bend

I. **1400 – 1610 cm^{-1}** – instantaneous rise of absorption and initial decay of 170 fs: v=1 → 2 transition of the OH bending mode.
At longer delay times the signal is due to the overall red shift of librational absorption.

II. **Below 1400 cm^{-1}** – delayed onset of enhanced absorption with slower decay (~1 ps) is observed.
This is attributed to the reshaping of the librational absorption upon energy transfer and heating.

And finally when you excite OH bend you see an instantaneous rise in the 1400 to 1610 centimeter inverse 1400 to 1610 and initial decays 170 femtosecond as discussed already this is a v = 1 to 2 transition of the OH bending mode 1 to 2. Longer time the signal is due to overall red shift of liberational absorption okay.

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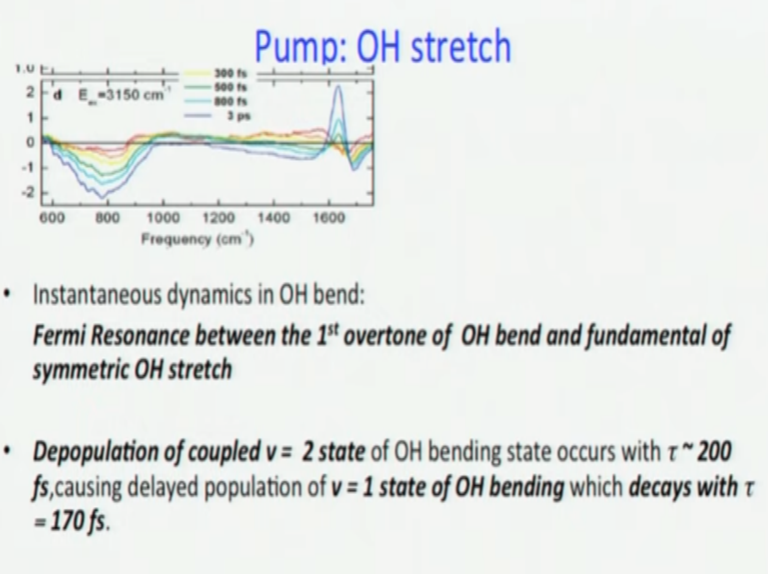

Pump: OH stretch

- Instantaneous dynamics in OH bend:
  Fermi Resonance between the 1st overtone of OH bend and fundamental of symmetric OH stretch
- ***Depopulation of coupled v = 2 state*** of OH bending state occurs with ***τ ~ 200 fs***,causing delayed population of ***v = 1 state of OH bending*** which ***decays with τ = 170 fs***.

And OH stretch I think we already discussed this Fermi resonance we do not have to go through it once again.

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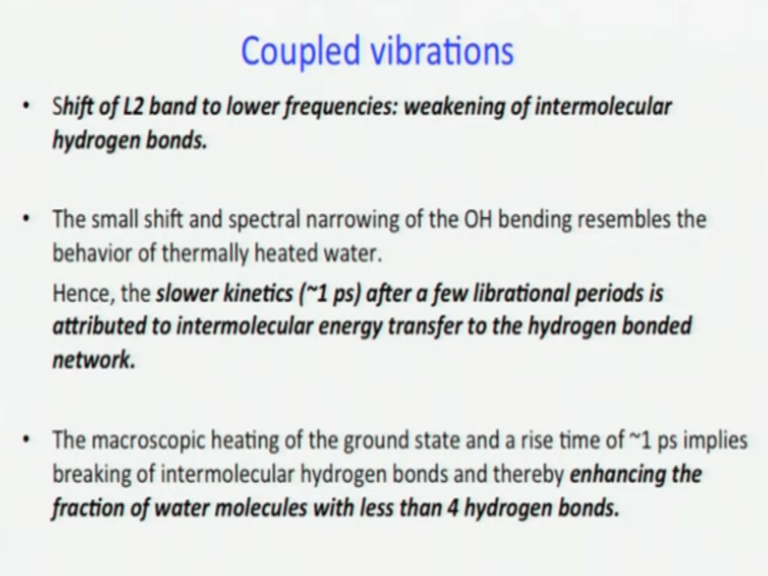

Coupled vibrations

- S*hift of L2 band to lower frequencies: weakening of intermolecular hydrogen bonds.*
- The small shift and spectral narrowing of the OH bending resembles the behavior of thermally heated water.

  Hence, the ***slower kinetics (~1 ps) after a few librational periods is attributed to intermolecular energy transfer to the hydrogen bonded network.***
- The macroscopic heating of the ground state and a rise time of ~1 ps implies breaking of intermolecular hydrogen bonds and thereby ***enhancing the fraction of water molecules with less than 4 hydrogen bonds.***

So finally the story that we get is that of coupled vibrations and this is I like this because it is good example of how one can use the pump probe technique to look at very intricate interaction that takes place in a coupled system. So there they have to looked at water so now water is ubiquitous that is the liquid of life but one can think of experiments that one can design similar experiments on things that are more complicated.

Of course IR experiment in presence of water if you want to look at motion of bio molecules for example this could be a good way to go. The complicating factor there is a bio molecules are always in water as it very strong absorptions because it is a solute anyway present in much more. So unless you have absorption is some other region it may be difficult to follow but it may not be impossible.

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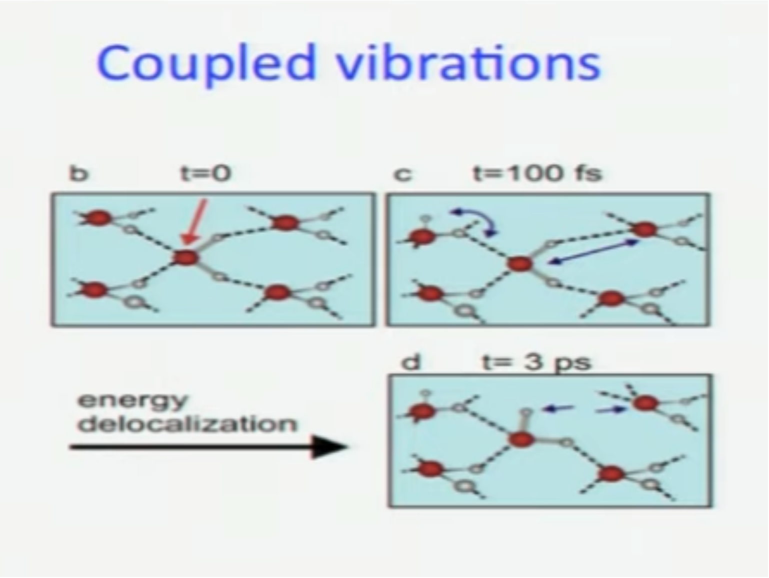

So finally this is the picture that has come out of the whole study you excite this I think this is taken from a movie that must be available in the somewhere on the website or in the associated content of the paper but excite in 100 femtoseconds this is the situation hydrogen bond if it put it very qualitatively what happens is that within the first 100 femtoseconds the hydrogen bonding network is weakened.

And then longer time 3 picosecond or so hydrogen bonds actually get broken and that is what shows up in this red shift of bending vibration frequency and in shift of liberational frequency as we have discussed. So that is the story of how energy migrates from one more to the other in associated systems like liquid water. So I do not know whether anybody as done followed this up later on it might be interesting to look at by forget biomolecules for the moment even water.

So water confined in an reverse micelle or water at the surface of a protein bound water what kind of energy migration do you have in case of bound water or inside a vesicle or maybe inside a cell that matter. But of course for that we want to do it inside a cell you have to work with an IR microscope not impossible but it we do not have it IR microscope coupled with femtosecond IR that is the problem.

But this paper is important because the thing is unfortunately in today lot of research is driven by impact factor which is completely wrong. And this paper is published in J Phys chem A which is least impact factor journal in J phys chem family it does not matter it is very good fundamental work and I think it is an indicator of lot of possibility that can open up in this kind of experiments for especially for water in confined environments and perhaps for other molecules as well okay. So that is what I think is one of the most important it is the work in this field in the last 10 15 years or so.