Ultrafast Processes in Chemistry
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Module No # 09
Lecture No # 49
Solvation dynamics – Part 2

So now let us see if you can understand how to follow solvent dynamics using ultrafast spectroscopy. And as we are going to discuss by the end of this module this sometimes solvation can be ultraslow as well.

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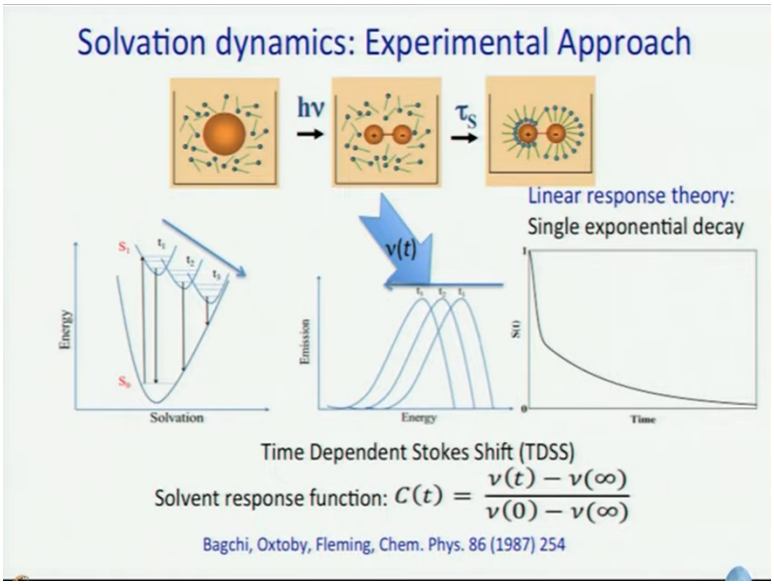

And fast or slow study of solvation dynamics can give us some useful and interesting information. So the way one studies solvation dynamics is you start from what we have discussed earlier. You start with the molecule which has near 0 dipole moment and we excite it and the molecule should be such that there is charge transfer in the excited state ultrafast charge transfer.

So this is the situation in the ground state your molecule with no dipole moment and solvent molecules are oriented in whatever way they are oriented around them around this solute molecule. Upon excitation charge transfer has to take place. Now this excitation takes place in ultrafast time attosecond. There is not enough time for the solid molecules to reunion. That is what I think Prajit was saying in the earlier module.

Then given enough time this solvent dipole would reorient around the 2 poles of the newly created solute dipole and you would get a happy situation like this. And as we have discussed due favorable dipole-dipole interaction you are going to get a stabilization of the excited state. Now see incase this molecule is fluorescent then what is the situation? If you can record emission spectra at different times after excitation and we have discussed earlier in this course how one can do that.

One can do it either by gated emission or one can record steady state and time resolved data and construct the time resolved emission spectrum from there we are going to come back to that in a moment. But the point is at time t = 0 you get emission at some particular maximal frequency. As time passes there is going to be a red shift because the energy gap between the ground state and the excited state and ground state would keep decreasing because of stabilization of ground state and the fact that the corresponding excited state is of higher energy than the state that we actually excited the unsolvated state.

This is something we discussed in the previous module so what you get is a time resolved stokes shift time dependent stokes shift TDSS as it is called of the emission spectrum. So in this case one works with the maximum emission maximum of this time resolved emission spectra and from there we will construct this solvent response function C of t which is given as Nu at time t. Nu means it is said the maximum of emission spectrum at time t minus the emission maximum at time infinity.

Time infinity means you do not really have to measure up to time infinity. It means the time after which there is no further stokes shift. And that is the contagious issue I will come back that in a moment. Denominator is Nu 0 - Nu infinity when Nu 0 is the emission maximum at the instant of excitation Nu infinity is what we have discussed already. Now see what are the problem associated with this.

How do you know Nu Nu 0 how do you know Nu infinity that is what the problem is? Because if the life time is say tens of nanosecond life time of the excited state and solvation time is some 1 picosecond 2 picosecond then there is no problem. Because you would go from the higher energy unsolvated state to the completely stabilized state which will persist for few nanosecond. So you get Nu infinity without hassle.

The problem arises is if solvation time is comparable to the life time which we are going to show is the case in many cases. Then you do not know whether solvation is complete or not. If solvation is not complete within the time scale of the measurement, then Nu infinity is not determined accurately. That is one problem the second problem is how to determine Nu 0?

The easiest way of doing it is a well to feed the decays to multiexponential fitting functions and then construct the time resolved emission intensities by putting t = 0 now this is the problem with that. The problem there is what is the time resolution of your experiment? What is the instrument response function? If you are going to do if you can excite with the attosecond pulse attosecond detection and do this experiment perhaps you will get the accurate value of Nu 0 every time.

Otherwise Nu 0 is subject to errors associated with the full width of maximum of instruments response function. Now different people have proposed different ways of determining Nu 0 all of them have some pros and some cons. One way of determining Nu 0 is sometime is you will have considered the emission spectrum in nonpolar solvents that may or may not be correct because even the ground state energy may not be exactly the same.

The energy gap between the ground state and the locally excited state may or may not be the same between polar and nonpolar solvents. First approximation they are but not always. Another way that has been done is that the solvent has been frozen. And you perform measurements at liquid nitrogen temperature. This seems to be a good result. When a solvent is frozen then there will be no re-orientation so you look at the same excited state that you are going to excite anyway.

The only hesitation about that is that the polarity of the medium as we have seen for DMABN can be temperature dependent. So no method is 100% fool proof you have to work within whatever limitation it might have ok. Now let us come back to the section itself. What does it denote? Nu t - Nu at t - Nu at infinity / Nu at 0 - Nu at Infinity. What is the significance of this fraction? Ok Nu 0 - Nu infinity what is that? That is the total stroke shift.

What is Nu t - Nu infinity? Stokes shift that is yet to happen. So this fractions you have CFT is the fraction of solvation that is yet to happen ok. As has been discussed very nicely in this golden paper it has been sighted I do not know how many thousand times it is a very famous paper where

Bagchi Oxtoby and Fleming 1987. What they have discussed is that due to linear response theory it is the simplest case scenario you expect this C of t to decay exponential.

However most of the time you do not get a simple exponential decay you get something like this ok because there are different modes of solvation that are there. This is not a simple phenomenon as we are going to represent very briefly about water there are different things that happen. That is why you usually do not get there are cases in which you get single exponential as we are going to show. But many times you do not get a simple single exponential decay of your solvent response function.

So generally C of t is fitted as a multi exponential function and each of the time constant is called solvation time. And the challenge is it possible to assign each of the solvation time to some kind of mode of motion of this solvent molecule ok.

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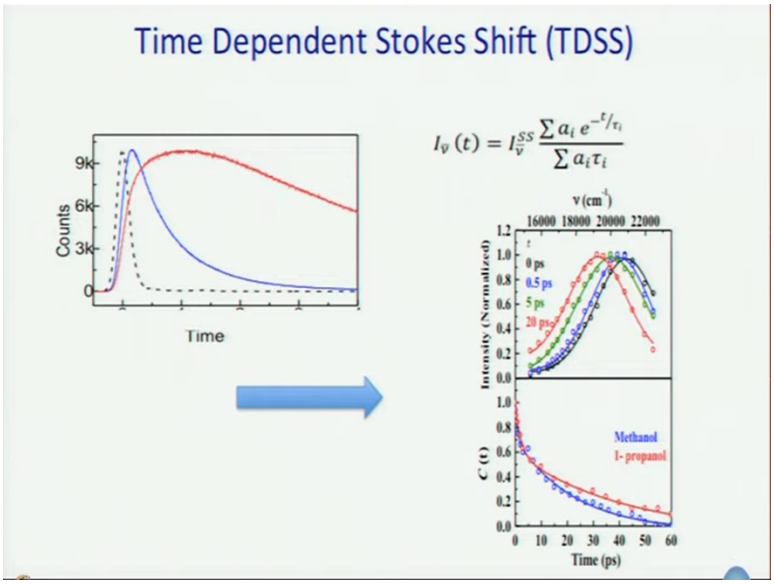

So let me show you some example of time dependent stokes shift data from our own lab. Here what do you expect? If solvation takes place then you expect we have talked about what the signature of an excited state process is. In this case solvation is taking place of the excited state so it is also an excited state process. So you expect a fast decay in the blue end which corresponds to the in this case un-solvated local excited state. And you expect rise time in the red end because that corresponds to the solvated excited state that is being formed.

So this is a typical kind of curve that you would expect ok. So what you do is? You fetch this kind of time resolves fluorescence data to multi exponential function and you generate the intensity at some particular wave number by I Nu bar SS multiplied by sum over I ai e to the power -t / Tau i / sum over i ai Tau i. It comes it comes from the fact that what is this I Nu bar SS that is the emission intensity at a particular wave number.

Now emission intensity at a particular wave number is essentially integral of time resolved intensity from 0 to infinity it comes from there. There is a standard integral which turns out to be sum over ai Tau i which is the total intensity and you get this kind of an expression. Now when you do this you are going to get time resolved emission intensity for different frequencies. And when you plot them against frequencies for different times you get this kind of a picture.

This is an example of time resolved emission spectra and here we see from our lab an example of how C of t changes with time. We can see decays, however it does not decay single exponentially one thing you can see we are not told you what the molecule here? Molecule is here does not really matter. But one thing you can see is here the solvation is faster at least a long component of solvation is faster for methanol than for 1 propanol. The reason is understandable 1 propanol is more viscous than methanol.

So similarly there can be many other reasons many other factors that can influence solvation dynamics ok. So to start with let us talk about solvation dynamics in nonaqueous solvent. Of course nonaqurous solvents can be classified into 2 parts aprotic solvents and alcohol.

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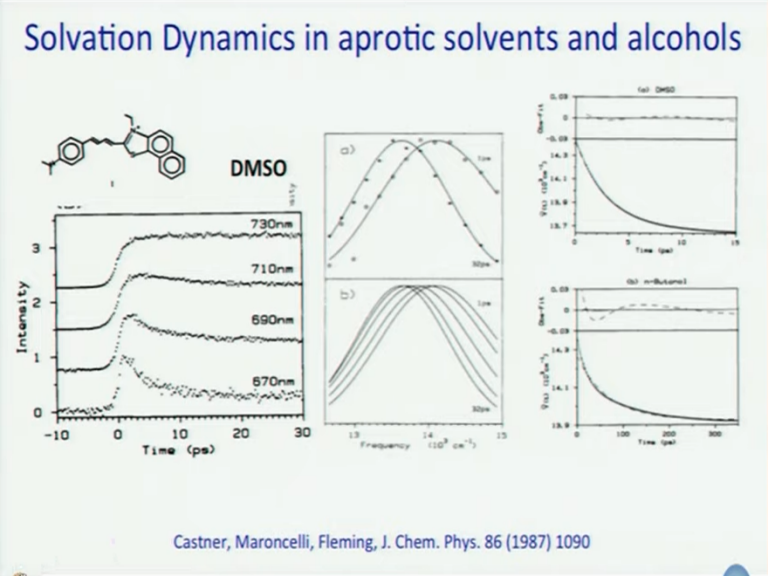

In 1987 from ground Flemings group has made significant contribution to the field of solvation dynamics. And not only Fleming his students later on went on to become independent researchers they have also done significant work. So you can think Fleming school comprising Castner, Maroncelli all this people have contributed big time. The other players are Mark berg well of course it is everyone Biman Bagchi, Kankan Bhattacharyya these people have done lot of work. Ahmed Zewail towards after getting noble prize got interested in the field of noble solvation dynamics will not real ly talk about his work here but you can read it.

And there are many groups in India which who have studied this. Nancy Levinger has done significant work on solvent dynamics in things like reverse micelles. So that is something that I leave for you to read yourself. It is a very interesting body of literature that has been created starting from say 1985 1987 until now. A new infinity has now been reached even now plenty of this going on using solvation dynamics.

So this particular work Castner, Maroncelli and Fleming used this kind of a probe and let me show you the decays fluorescence decays in DMSO. So as you see in the blue end 570 nanometer you have fast decay that almost gets over within 30 picosecond. The red end of the spectrum 730 nano nanometer you see a distinct rise and here you see a long live excited state that is di-solvated state that is being formed ok.

So this is the signature of solvation that we were talking about. From there the constructed the time resolved dimension spectrum and here in this early work they did not really bother working out C of t this simply plotted Nu at time t against t. As you understand you can rearrange that equation right and you can still get the solvation time.

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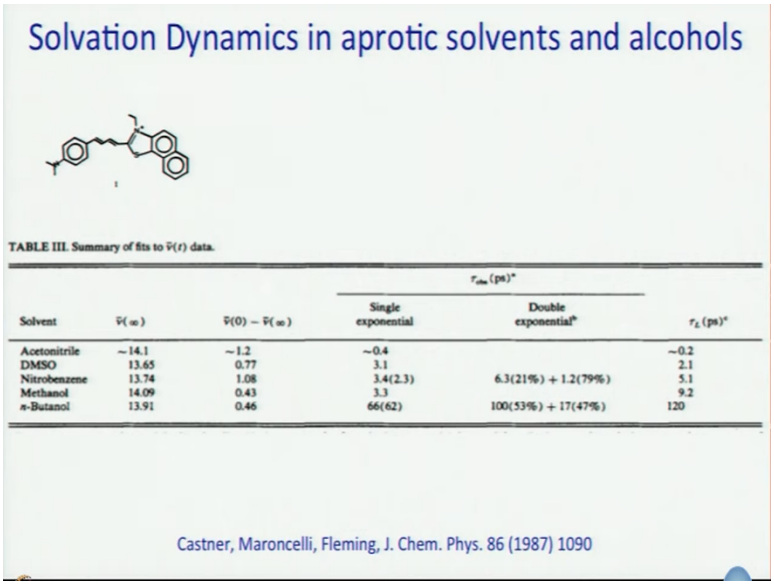

And these are the solvation parameter that they obtained. So as you see for acetonitrile linear response theory holds very nicely. This is a single exponential decay associated with 0.44 400 femtosecond decay sorry that is for acetonitrile. For DMSO it is the same thing but the decay is slower 3.1 picosecond. So you see acetonitrile and DMSO are they protic, aprotic what kind of solvents are they? Both are aprotic solvents still there is an almost order of magnitude differences in solvation time.

That depends on the polarity of the solvent bi-enlarge. So here you see a signature of polarity. Then when you go to nitrobenzene things get a little more complicated because you get double exponential nature of decay. First one is 3.4, 2.3 is I think calculated theoretically and second one is 6.3 picoseconds. So if you look at Nu bar infinity and better look at Nu 0 - Nu infinity here also you see a lot of difference.

I think this is in 1000's of centimeter inverse or something. This is one 1200 this is 770 this is 1080. So even the extent of stabilization not just dynamics depends on the solvent and even that has a story to tell. From there the moment you go to aprotic solvent methanol has 3.3 nanosecond

single exponential solvation time. Butanol has a 66 is it nanosecond 3.3 picosecond 66 picosecond and 100 picosecond.

So of course for butanol which is a more viscous solvent you get slower solvation time and due to viscosity different kinds of modes get decouple that is why see not 1 but 2 difference solvation times. This is only 1 example of solvation in aprotic solvents Maroncelli especially has done of very thorough job I remember this JCP paper of 1994 or 95 where I think there are several probes a 30 40 solvent.

So that paper I think 4 pages of that paper were just tables like this a small table. So exhaustic work has been done in non-aqueous solvents to understand the factor that contribute to solvation dynamics polarity, viscosity, hydrogen bonding everything matters. Having done this the next question that will last is what about solvation in dynamics in water? Now this is a very important at fundamental question that has been dealt with significantly after the report that I am going to show you.

Because after all the entire life is waste on the water right. So understanding what happens in water is an interesting question that has persist then water is not a simple liquid right. Sometimes figuratively we will say something is as simple as water there is a completely wrong sentence scientifically. Perhaps we should say as simple as hot water because in hot water some hydrogen bonds are broken.

Water itself is an abnormal liquid as you all know it should not have been a liquid in the first place because H2S is a gas oxygen and Sulphur oxygen is lighter. The reason is why the water is liquid is hydrogen bond. So all the life processes are dependent on this extraordinary liquid that is water it is important to study solvation dynamics in water in many different forms. So the first report of this came in 1994 once again from ground Fleming's group. And the importance of this work is highlighted in the fact that is published in nature. Here similar TDSS studied were performed using Coumarin 343.

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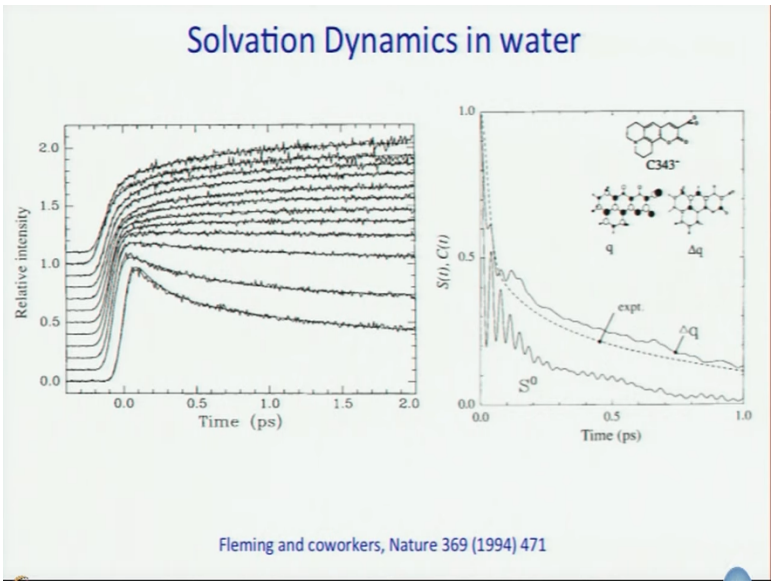

So this is this has become one of the most used fluorescence probes after this study ok. So there are coumarin 120 is 1 343 is 1. So using this Fleming and coworkers got this kind of time resolved decay. This is all femtosecond optical gating experiment ok. You can see fast decay in the blue end rise in the red end and you can note the full scale of the experiment 2 picosecond. Of course this is zoomed in picture they did not do the experiment for much longer time.

And having done this they obtain the C of t and saw how it evolves in times. There is lot of data in this we are only giving you an overview expectation is that you are going to ready this paper is extremely important should be read in detail. I am not presenting the even the numbers here. So here this is the experimental time evolution of C of t and the other things that you see are theoretical fit and all that. And this is how the oscillation takes place that is shown using molecular dynamics.

So crux of the matter is that it is multi exponential. In fact there is an initial Gaussian component it is not exponential all the way. And what Fleming and coworker did in this paper is that using experiment as well as molecular dynamics they could attribute the difference solvation times to different kinds of motion of water reorientation, liberation. What is the meaning of liberation? Liberation means restricted rotation so remember when you take water in isolation that is what we are used to thinking it is just HOH.

But water is not present in isolation in this liquid state as we know it is associated liquid that are hydrogen bond. So when a water molecule tries to rotate very often what happens is this hydrogen

bond with the next water molecule call hinders the rotation. It cannot rotate all the way it comes back. So that becomes a kind of an oscillator emotion which is identified as a low frequency vibrational motion. It is not fully rotating this kind of a motion back and forth.

So that of course has energy that is much more than rotational emotion but significantly less compared to vibrational motion. In the next module we will actually show you the spectrum of the water IR spectrum where you will see what kind of wave numbers are associated with this liberation. So this different mode of water how they contribute to solvation that is what it is worked out in this paper please read it so this was 1994.

The next year the same group Fleming's group published a paper in Faraday journal of chemical society faraday transaction. So what they show the experiment that they did there is that they took 2 probes C3 43 and C420 and they perform the experiment not in a just water but in cyclodextrin in aqua cyclodextrin solution ok. cyclodextrin has we might have said earlier I do not remember if you have is a macro molecule that looks like a ice cream cup without a bottom.

And the reason why cyclodextrin is interesting is that the out outer circle of cyclodextrin is polar the inner surface is nonpolar. So it can be used to solubilize non polar solutes in water non polar molecules in water. It is used very frequently in draft formulation and all that. So in cyclodextrin Fleming groups found that solvation gets slow down significantly. This is a comparison of the time evolution C of t between water and cyclodextrin and these are the associated solvation times.

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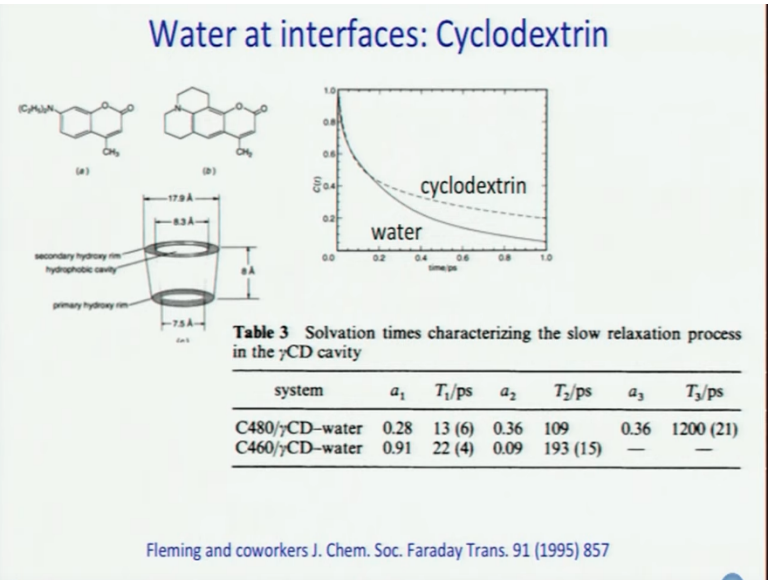

So you see that in addition to the picosecond compound that was there first of all they did not observe a less than picosecond components. This is was the TCSPC of the experiment. And more importantly hundreds of picosecond components and in one case what they have observed as the nanosecond compound came in. So you have slowing down the solvation by order of the magnitude.

And this paper sparked a series of work that has resulted in publication of I do not know how many thousand of paper. Half of my PhD thesis was inspired by this one so the explanation initially was actually not correct. What everybody thought was your bound water and free waters. So free water rotates quickly free water moves quickly and contributes to the first component of solvation. Bound waters moves slowly and contributes to the slow component of solvation that is not quite right.

Has as, been illustrated later mainly by the group of Bimen Bagchi. There is a dynamic equilibrium remember, I talked about dynamic exchange of solvents in the previous module or may be in this module. So what they showed is that the bound water is actually you can think frozen.

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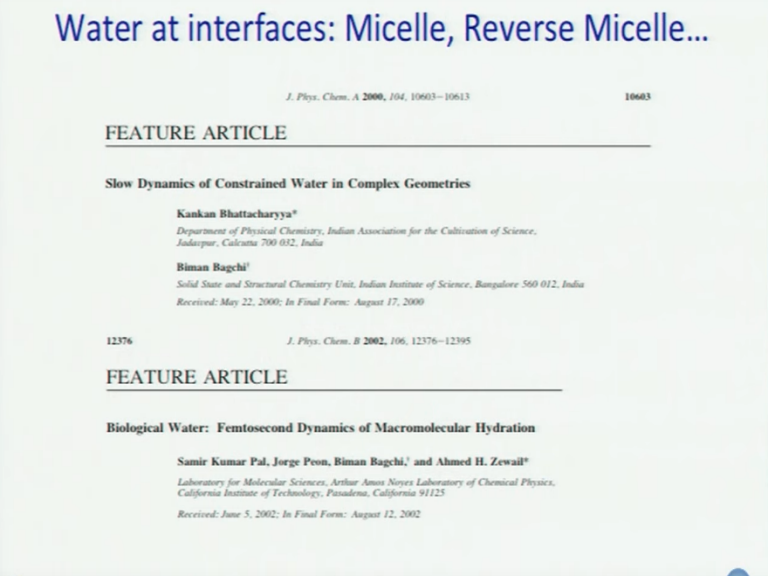

It does not participation in solvation as such. However there is a dynamic exchange between bound and free water. It this always the free water that is reorienting around the newly created dipolar moment but there is an exchange and if you remember your lessons from chemical kinetics if there is some equilibrium associated with that you have to take that into account be forward and backward constant. And this exchange is what is associated with slow component of water.

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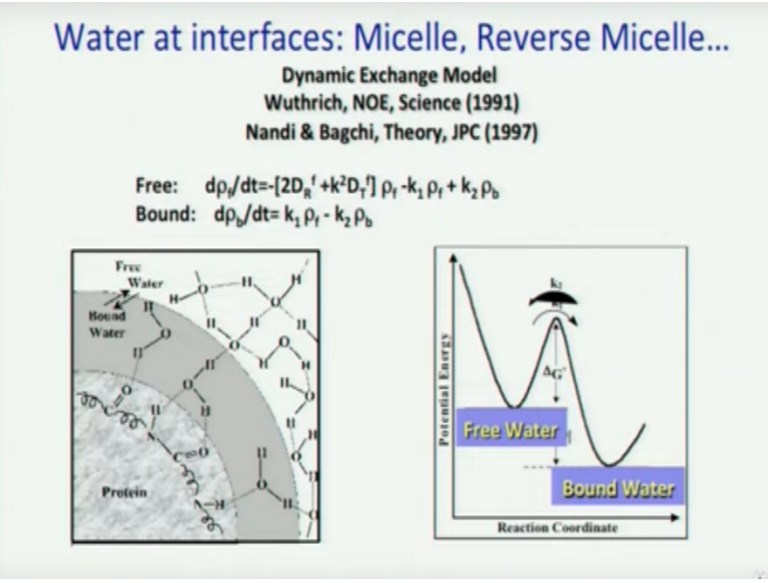

That is a something that is that came out very nicely in this Nandi Bagchi theory. And this is the cartoon representation of let say a protein to which water is hydrogen bonded and here you have the regular network of free water. There is a dynamic equilibrium between bound and free water.

When they consider that there is when they could arrive at this long solvation time. So if you look at the energies this is the situation for free water this is the situation for bound water.

There is a variant crossing back and forth. This k1 and k2 could be considered when you build the kinetic scheme for solvation that is what causes slow solvation ok. So now let me take a detour with this from the main agenda of the course the title of our course is ultrafast processes. Now we have arrived at something that is not ultrafast which is not ultra-slow maybe but definitely not ultrafast slow.

The question to be asked is so what? I mean why would we even interested in slow solvation. Well slow solvation has in the last 20 22 years emerged as a marker at bound water as we have said and what has been shown later on is that you can actually use it by combining with confocal microscope capable of performing life time measurements FLIM in this can give you an insight into really small volume like never before. So in the next 3 minutes or 4 minutes let me present to you a brief summary of work done in one group that of professor Kankan Bhattacharyya in IACS.

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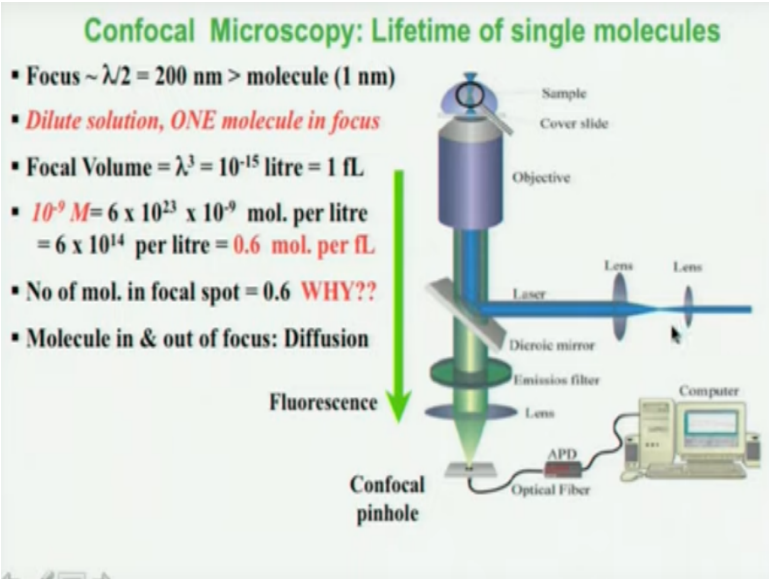

In which they used confocal FLIM set up so this is lifetime imaging microscopic set up. When I say confocal what it is essential means is that this is where you are sample is right. So the excitation light is focused on to a particular point in the sample focal point as you know cannot be less than Lambda by 2 in diameter that is the diffraction limit. And then there is Dichroic mirror that sends

the this is the laser light this is the fluorescence light the dielectric mirror sends the fluorescence into this objective of the microscope after which the direction takes place.

Now if you have work with sufficiently small concentration you can look at single molecules by this technique. So suppose you use an excitation wavelength of 400, nanometer. What is the resolution you have 200, nanometer? Now suppose you use this microscope to study something like a cell. What is the size of a cell?

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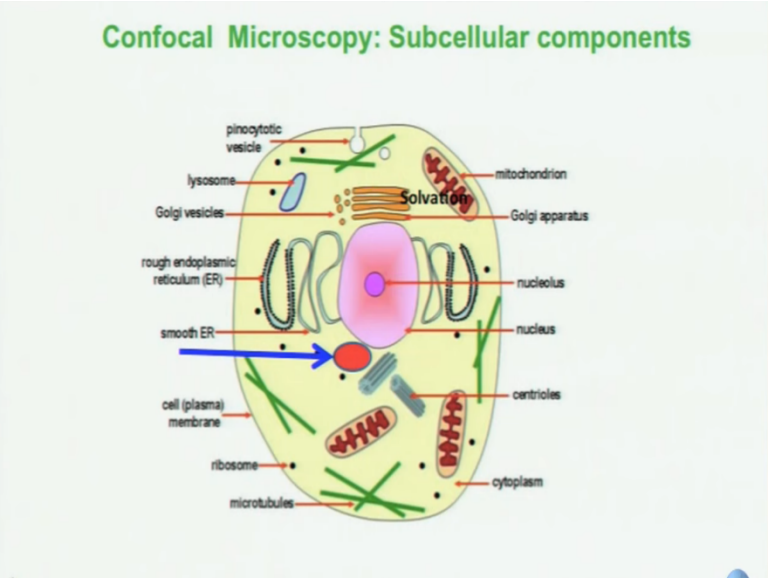

Microns you can see cells very easily under a not very sophisticated optical microscope. So the thing is since the cell are like 20000, 30000 times larger than the resolution that we have in confocal microscopy. You have the capability to look at not only the cell has a whole but also at different parts of the cell. If you have a fluorescence probe that goes an mitochondrion. You can look at mitochondrion selectively. If there is something that goes and minds to some microtubules, then you can look at microtubules selectively.

If there is something that will go and mind to say lysosome you will be able to see lysosome selectively. And this technique has to be used very effectively Y groups like for example Yamuna Krishnan who migrated from NCBS to Chicago few year ago gave a talking in our institute last year. So, one can look at different components of cell by using selectively by using confocal microscopy.

Now if your confocal microscopy is capable of measuring lifetimes you can measure life times at different location of the cell. Does not always have to be a cell of anything of that dimension and if your system is fitted with a grating and detector typically AMCCT then you can measure fluorescence spectrum as well. In our set up we currently cannot do it. So if you have an AMCCT and a grating combination as well as a life time measurement accessory FLIM then you can study solvation dynamic in different parts of the cell as well. And that is what has been done by Bhattacharya group this is one example.

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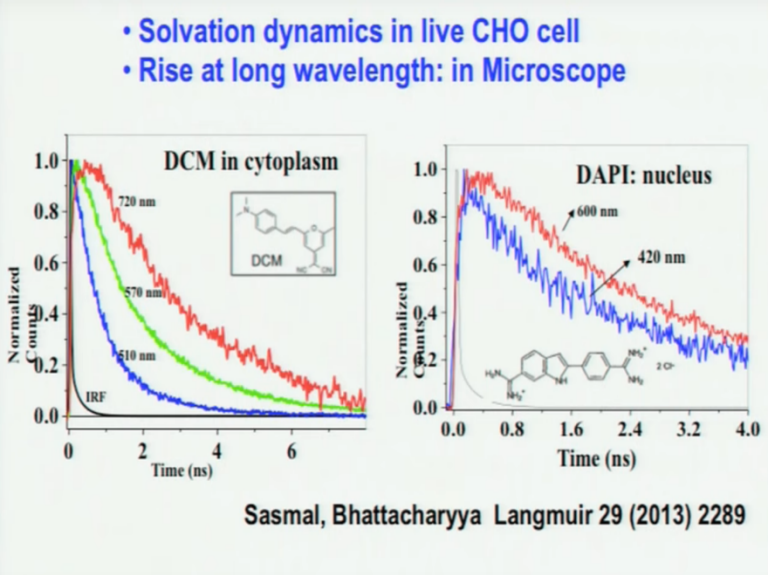

What they did is they worked with CHO cell. What is CHO? Chinese hamster ovary there are difference cell line that we worked with this is Chinese hamster ovary. So there you see they used 2 dyes. One is DCM this is DCM the other is DAPI this is DAPI. So DCM is known to localize in cytoplasm will not get into the detail of why that one can study. DAPI is known to mind to nucleus.

So what you see here is that if you look at the decays fluorescence decay they are definitely wavelength dependent. And then if you record the emission spectrum as well you can get an idea of solvation times in different parts of the cell using DCM you get the solvation times in cytoplasm. Using DAPI you can get the solvation time in nucleus. Using something else you can get a life time of something else.

The good things is here even if there is a distribution of DCM between say 2 different parts of the cell you can using confocal microscopy look at say cytoplasm once and record all your data there.

Then look at say golgi body another time record all your data in golgi body. So coupling this time resolved emission spectroscopy with microscope gives us this very powerful technique of looking at dynamics in different parts of a very small volume like that of a cell.

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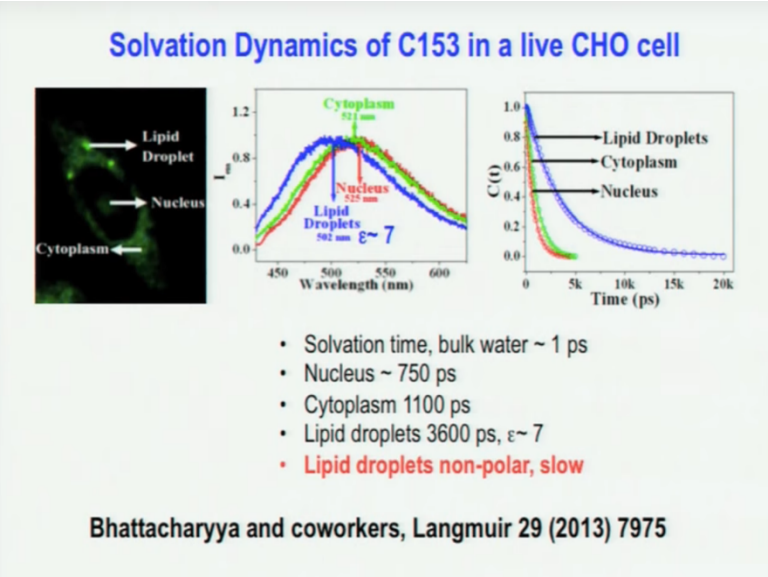

And this is what a typical confocal image looks like and here looking at this image one can identify things like lipid droplets, this is nucleus, this is a cytoplasm and recording fluorescence decays at different parts of the cell like this. What Bhattacharya group was able to do is that they were able to work out the C of t of different parts you see. This is the decay of C of t in the nucleus this is the one site to cytoplasm, and this is what is there in lipid droplets. So if you look at the times in the bulk water it is about 1 picosecond, in nucleus it is about 750 picosecond, cytoplasm little slower 1100 picosecond, lipid droplets 3 times slower 3600 picosecond ok.

And what has been proposed is that using these you can in fact later on this technique has been expanded to differentiate between cancerous cell and non-cancerous cell. So this is away in which one can extend this time resolved ultrafast technique to think of applications in biological systems or even in micro heterogeneous materials ok. I think we will stop here today and next day we will talk about since we are talking about water now next day will what we will do is we will talk little more about water.

We are going to revise something that i think we did little hurriedly Nibbering work you remember in science 2003 science 2005 we are going to talk about that little more detail. And we continue

with the work from the same group in which they have shown how vibration energy gets redistributed into different modes of water. Today we talked about liberation and all we will come back to that but from a different perspective in the next module.

Then after that have I talked about ESIPT at all in this course. Did i talk about excited state intra-molecular proton transfer. Then for the sake of historical accuracy we will do that. Since we are talking about photo acid anyway then what we will do is we will move over there is one debate that I would like to present if we get time that is ok maybe we can do that as an extension of ESIPT ESPT. Then we will move over from molecules to nano clusters and then nano material.