Advanced Chemical Thermodynamics and Kinetics
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Lecture - 34
Introduction to solution phase reactions dynamics 04

Hello everyone. So, we started our discussion on Reaction Dynamics in Solution, and today we will be discussing about the effect of solvent in a two important reactions.

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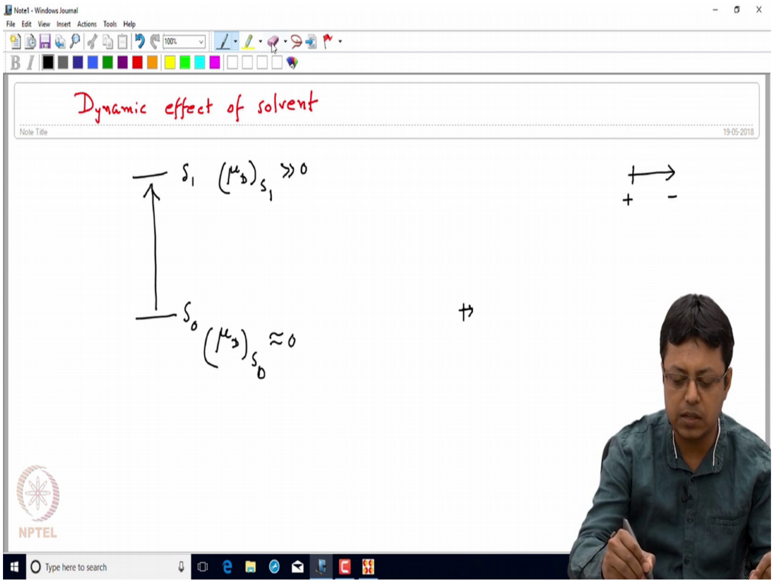

So, again this effect we can say that this is actually a dynamic effect of solvents, dynamic effect of solvent. So, by dynamic effect let us first give you an example what do you mean by dynamic effect.

Now, suppose I dissolve molecule in a solvent and usually it is assumed that the when we excite electronically a molecule, suppose these are elect elected this is the electronic excitation that I am showing already these notations are familiar to you S 0 and S 1. And suppose some molecular I am exciting and what happens when you excite the molecule it say since it is an electronic excitations, the electron cloud is now actually a moved from a one molecular orbital to another molecule orbital as you have already talked about.

So, the electronic configuration chains and you can have different electronic configuration, and out of that actually one is your singlet configuration in the excited state which is the allowed transition. And then what you see here in that electronic state there is a charger distribution. Now, usually in the ground state for most of the molecules the electrons are all paired up and that charge redistribution that or the dipole moment is very much a very minimum, in the sense that a dipole moment it will be close to 0.

So, we can say that the mu the permanent dipole moment you are talking about here the permanent dipole moment in the ground electronic state. So, we can actually write it as mu d in the S 1 state S 0 state is almost equal to 0, but what happens in there when it goes to the excited state due to a huge charge redistribution we can actually have a nonzero dipole moment in the excited state.

Now, what happens is again, so this is related to what we discussed when we are talked about electronic transition the photochemistry part. And we said that there is a principle known as Franck Condon rule and the essence of it is that the electronic transitions are so fast that the nuclei do not have enough time to reorganize themselves. It is not exactly Franck Condon principle this is an answer that we use in many cases, but the point here is that vibrational degrees of freedom are kind of frozen during the electronic transition, and what happens all of a sudden these molecules which you are exciting optically by shining visible or ultraviolet light there these actually creates a excited state permanent dipole moment, and then these solvent molecules around it try to rewrite due to this new created dipole.

Now, we can actually draw a picture something like that. So, suppose in the ground state I have a very very small dipole moment. So, by so usually the notation for the dipole moment is shown as an arrow and we put a cross here some people that you do not write this cross here. So, it just to show you the positive and negative end there are also other conventions. So, we can actually show it to just I mean in this old, this is most likely the old convention of the dipole moment and then this convention we can use just for our purpose.

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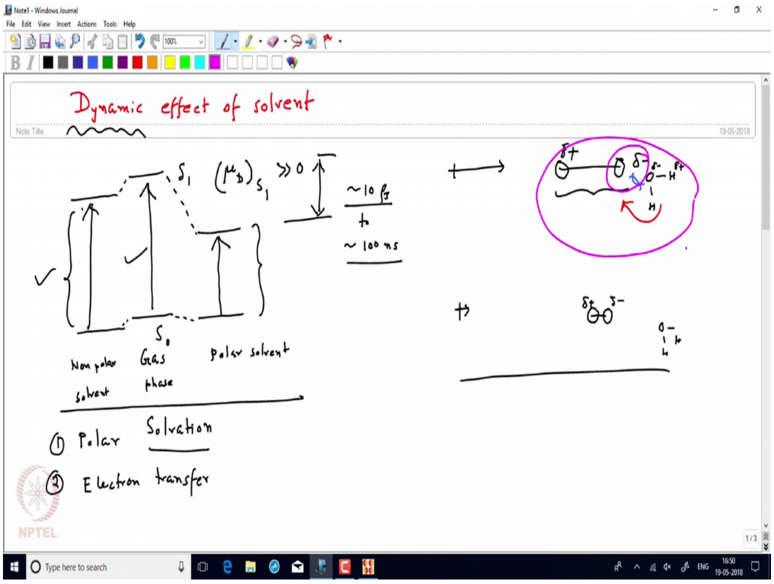

Dynamic effect of solvent

① Polar Solvation

② Electron transfer

So, from ground to excited state, so as you can see the dipole moment was very small in the ground state and in the excited state we have a huge dipole moment. And or we can actually show it as very small charge redistribution. Suppose I have two ends in the molecule where I have small positive and negative charges separated by a small distance and in the excited state I have a huge change in the dipole moment. So, you can just use the similar notation. So, I have delta minus and delta plus and in the excited state their situation is something like this delta plus and delta minus.

Now, I see that there is a big change in the excited state I mean there is a huge dipole created and suppose momentarily when that dipole was created at time 0, which is very fast because if it is an electronic transition. So, then what happens we can find the molecules let us say actually the molecules we are doing this experiment in water. So, momentarily we may found that suppose initially there was a water molecule which was in this position along the molecule, and then since we have a large dipole this molecule has not changed its position. So, the negative end which is the oxygen end. So, water molecules are also polar molecules and you see that this is an very much unfavorable orientation for this molecule and due to that what the water molecule will try to do is that it will try to reorient itself. So, that these are each end will actually face the negative end of this newly created dipole.

Now, if we do this experiment in polar solvents. So, what happens is that the polar solvents will actually stabilize this excited electronic stays much more than if we do it in a non-polar solvent. So, in a non-polar solvent there will be little change, but in the polar solvent there will be huge change. And usually since the ground state the dipole moment is almost 0. So, the ground state stabilization in any solvent will be very negligible. So, we see that we have actually drawn a few figures here. So, I will just write it once again.

So, this is the electronic states in the gas phase this is what the excitation will be in the gas phase. This is in some say polar solvent and this is in some non-polar solvent. So, non-polar solvent the excited state stabilization, the way I have shown it is little bit exaggerated. So, it will be very similar. So, what we see here is that in the polar solvent usually the absorption line chips are red shifted, because as you can see that energy gap between the two electronic state ground state and the excited electronic state is very very its actually going smaller whereas, in the non-polar solvent it will be as if it is almost equivalent to the gas phase energy gap.

So, we can say that in the pores often what happens the electronically excited state which had a large dipole orientation are rearranged large dipole due to charge redistribution. So, that state actually gets stabilized. But this stabilization the way we have drawn it is not actually instantaneous because nothing is instantaneous the stabilization is happening due to the reorientation of the movement of the solvent and that movement has some timescale. So, this happens on the order of a few 10s of femtosecond, those are the first test timescales of solvation to some few 100s of nanoseconds or even more timescales. So, it actually varies and a wide range of a wide range of timescales. So, this effect is known as salvation which we are going to study right now.

This is an example where the solvent molecules are dynamically controlling the energy levels of the molecules. Now, as often shown in many textbook that this picture which you have shown on the left hand side what are the affected relative effects of say polar solvent and a non-polar solvent in stabilizing and electronically excited state this picture is a very static picture and so, but the role of the solvent you have to always remember that is very very dynamic. So, that is why I call it as a dynamic effect of solvents.

Another effect which this effect is basically as we said is called polar salvation and another effect of dynamic effect of solvents is in electron transfer. So, both of which we will study. So, first let us talk about the polar salvation dynamics which you I have already kind of schematically shown here.

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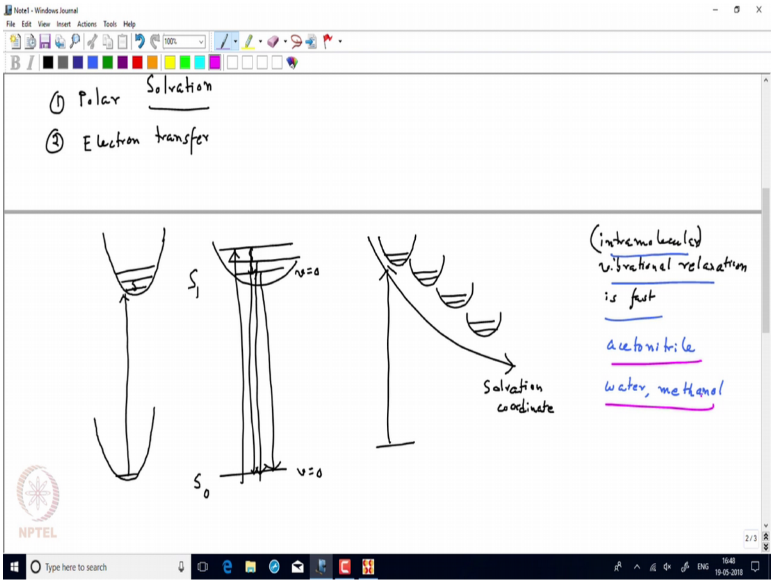

① Polar Solvation

② Electron transfer

(intramolecular) vibrational relaxation is fast

acetonitrile

water, methanol

Now, think about it like we have an electronical excited state and we showed that there is a potential for the electronically excited state, which actually will be a little bit shifted towards right because of the reason that we said that the excited electronic state is always; because of the fact that we know that in the electronically excited state the electronic configuration is a like homo minus 1 and homo plus 1. So, in the sense that we have a change in the bond order the bond order actually decreases and or the bond length increases. So, the equilibrium one position shifts that we already discussed. Now, this picture is very much intramolecular in the sense all the energy levels we are showing is actually the energy levels which come pertains to the molecule itself.

However, in the presence of a solvent what will happen the electronic state itself will as we showed earlier will actually get stabilized with respect to time. As the solvents are reorganizing I am around this newly created dipole or newly created just redistribution. So, we can think that there is apart from this intra molecular coordinate there is also a salvation coordinate, something like we can think that, ok. So, there is an intermolecular coordinate, but overall there is also an coordinate which you can think about being the salvation coordinate.

So, the reaction coordinate here is the salvation coordinate. Now, usually we do not actually show these both these pictures like small wells harmonic potential well kind of a picture of potential where we are showing the intermolecular relaxation and the salvation. Now, usually it is assumed that whenever you excite the molecule the vibrational relaxation which happens within the molecule which is the intramolecular process that is very fast. So, here the assumption we are making is that vibrational relaxation which is intramolecular of course, intra molecular vibrational relaxation is fast. And how fast it is? It is it actually completes within one pico seconds or a few 100s of femtosecond timescale.

So, again this is an assumption now this assumption will be valid for a polar solvents like say acetone nitrol. But for poor solvents like water and methanol we started with an example of water, but water is a very complicated solvent to study and for those solvents like water and methanol the salvation timescale actually is almost comparable to the fast timescale of vibrational relaxation. So, you have to be very careful there because there is a first component of salvation which actually more or less equivalent to the fast vibrational relaxation time scale. But otherwise there is a it is a fairly good assumption to think that this intra molecular vibrational energy redistribution is fast compared to salvation.

Now, why we are making this assumption? Now, think about it. So, suppose we are exciting this molecule. Now, you can think about a detection which is basically the fluorescence from the molecule which comes from the excited state now already we told that for there is a rule, if you remember that we talked about a rule which is known as a Kirchoff's rule and which says that this vibrational relaxation is complete before actually emission takes place. And we assume that all the emission the radiative emission starts from the v equal to 0 state of the excited vibrational excited electronic state which is the S 1 state and remember it all started from the v equal to 0 straight from the ground state that is a fairly good assumption.

Now, this Kirchoff's rule has a violation because in indeed what you see here is that as the vibrational relaxation happens you also see emission from the excited state. So, what you will see here, you will see an emission from all these states and this emission as you can see here is that this fluorescence emission, initially for this emission. Let us actually draw it once again just to make sure that the drawing is clear. So, let us draw the energy level diagram of the molecule once again.

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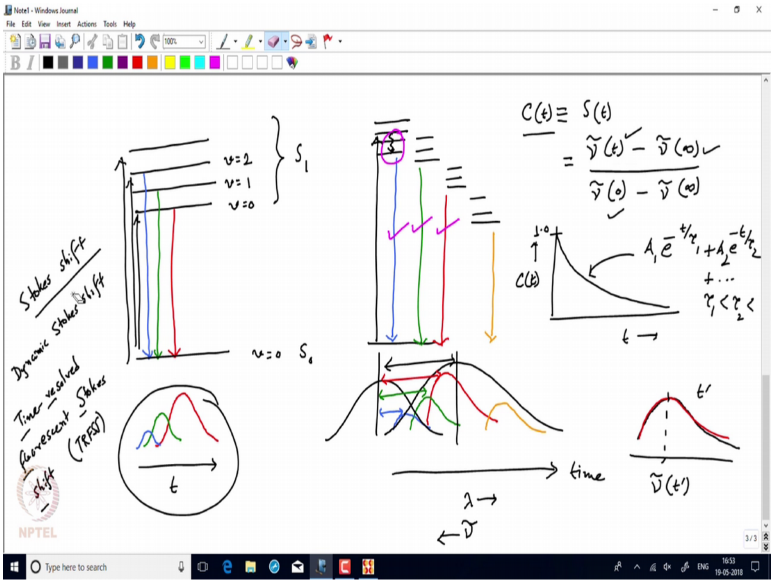

And remember that all the excitation started from v equal to 0 in the ground electronic state which we denoted at S 0 and then it goes to all these levels and that is the absorption. I am not showing the absorption right now because we already discussed how the absorption spectrum look looks like.

Now, we are saying that if there is any exception to Kirchoff’s rule how this fluorescence spectrum will look like. So, suppose I have all these energy levels in the all these levels actually corresponds to S 1 state, and suppose we are having fluorescence originating from all these levels say from v equal to 2, v equal to 2 as well as v equal to 0.

Now, as I have shown here the there will be of course, a blue region of the fluorescence we are actually we see the fluorescence coming from the excited state. But those fluorescence will be of much weaker fluorescence because in general a Kirchoff’s rule is a violated of course, because it says that it comes from the v equal to 0 state. But still predominantly the fluorescence actually originates from the v equal to 0 state in the excited electronic state.

So, in the fluorescence spectrum we will see a large contribution from the, this state which actually is v equal to 0 state in the excited electronic state, along with some small contribution of fluorescence coming from all other states. So, the interesting thing here is that all these fluorescence which are coming from different energy level has a time evolution. Because we know that with respect to time the electronic states get stabilized or the vibrational state gets stabilized and we get up shift in the fluorescence.

Now, the way I have shown it is basically a vibrational effect a intramolecular effect. So, there will be a shift in that due to the intermolicular vibrational relaxation, if we actually want to see or want to time result of fluorescence. And then we will see also a shift in the in the fluorescence spectrum which is purely intermolecular. Now, we are not considering that effect what we are considering is actually salvation effect in the sense that this change in the fluorescence due to the vibrational relaxation that we are going to ignore. Because the reason we are putting forward here is that this effect or this shift in the spectrum fluorescence spectrum is too fast to capture and the contributions are also very little. So, a major contribution is coming from the salvation effect where actually there is of course, a vibrational relaxation that will happen and which will be much faster compared to after the excitations.

But along with that, so this quickly actually comes from that v equal to 0 state and then the entire molecule like electronic states are actually relaxing. So, these are the vibrational energy levels. So, all we are doing are or we are saying in salvation is the emission from predominantly that v equal to 0 state over time. And now we are not talking about any intramolecular effect. So, this is very important thing to know about that we ignored the effect of intramolecular shift in the salvation and in the similar argument we will see there will be a spectral evolution the fluorescence spectrum will evolve with respect to time.

So, as you see the fluorescence spectrum will actually shift with respect to time, and we will have a predominant contribution of fluorescence coming from the v equal to 0 state until at a later time where molecule has realized, and an intermediate time scale will also see the fluorescence coming from the v equal to 0 state, but at a much earlier time and at a very very early time, we will see also the blue edge of the fluorescence. So, thus we see that the fluorescence spectrum which if we take a steady state fluorescence spectrum it will be something like this and we see that the small parts of the fluorescence actually comes at a very early time that blue edge of the fluorescence, and the red edge actually comes at a very later time and that is what we study or want to study in polar salvation because we also have a radiate fluorescent something like that.

So, all we want to do is to time resolve this entire thing and detect how this fluorescence spectrum are evolving. And what I have not told so far is that you can actually construct something known as a correlation function which is known as a salvation correlation function we cannot talk about detail about the solution correlation function. So, the solution correlation function says that if I take the spectrum at say infinite time. Now, what is a infinite time spectrum? When actually the steady state has reached completely the more the salvation is complete at that time if I take the spectrum, so you will see that. So, this is this basically corresponds to the I mean after some assumption the steady state spectrum.

So, if I call the center of the spectrum now I am writing nu here, nu is the frequency unit and the way I have drawn it is basically in the scale of lambda, in the sense that the wavelength actually increases. But in other sense the nu are more specifically the nu part the wave number actually decreases. So, because the if you see that the wave number is actually increase in the blue side and with respect to time the wavelength increases, but the wave number of the frequencies are actually decreasing. So, we see blue to red.

Now, if we tell that nu infinity is the infinite time floor the spectrum or, but again it is not exactly the spectrum it is basically the central position of the spectrum. Now, what do you see here? From the spectral shift we can actually say or we can actually define some I mean parameter which will actually quantify how fast or how slow the salvation is. For example, suppose if I take acetone hydrol and if I take some other solvent like glycerol how the salvation will take part and then what you measure is basically what are the spectral position at different time.

Now, what is spectral position? Now, spectral position by that we mean that suppose at some time you construct the fluorescence spectrum and you find there is some spectrum at some particular time. And then you what you do here is that you fit that spectrum with some known function usually we fit it with a log normal function and then you call the center of your spectrum. Let us say it is it was taken at time t prime and then we call it as the spectrum at nu prime.

So, the center of that spectrum we are calling as a spectral position at that particular time. Now, if you know that spectral position then we can quantify something which is known as a salvation correlation function. So, which is known as which you write it usually as c of t which is identical to the spectral correlation function which we are writing right now under some assumption I am not going into the details and that basically tells you we have to take the correlation function at any time is basically the spectral position at that time minus you have to take the spectral position at infinite time.

What is infinite time? In finite time means actually when the salvation is over the entire electronic state has fully relaxed and that time spectrum usually we assume it to be the steady state spectrum and divided by I mean it is not exactly again the steady state spectrum. So, there is a then, so the spectral salvation correlation time is defined as the spectrum or the spectral position again at time t minus spectral position at infinite time and this infinite time corresponds to at the time when the molecule has fully relaxed divided by and we always want to normalize it.

Now, how do you normalize it? So, usually this if we plot the salvation correlation time with respect to the time. Then you will see an multi exponential decay in the salvation correlation time and if we want to normalize it making that time 0 it is normalized. So, you have to divide it by the corresponding 0 time definition. So, it will be divided by time 0 and divided by minus time infinity.

So, as you can see that with respect to time the nu of t that actually evolves and all you need to know is nu of 0, and nu of infinity. Now, nu of infinity you can actually get from your experiment, nu of t you are measuring during the experiment; now nu of v 0 measurement there are many like arguments how to measure the time 0 of salvation usually it is assumed that fine, you take the gas phase spectrum, but gas flow spectrum you cannot take you take the molecular spectrum in a non-polar solvent. Because we already showed that in the non-polar solvent the shift will be almost similar as a gas phase and in the non-polar solvent there is no salvation effect. So, all the shift is coming from vibrational relaxation.

So, you account for only the vibrational relaxation shift already which is intermolecular which you cannot remove, and then you see on top of that how much shift is happening. So, this shift which we have marked here that shift will be same as if I do this experiment in gas phase or in non-polar solvent because that is a very intramolecular effect. And then we see how much it is shifting with respect to time assuming that this vibrational shift happened much before that salvation occur. And again this will be true only for solvents like acetonitrile and many other solvents, but not for water or methanol where actually the salvation might have a very very fast component. Now, this when you feed it to a multi exponential and calculate the average time constant from that, so this time constant actually refers to the overall salvation time scale.

Now, this multi exponential thing comes from that corresponds to different motions of the solvent around it. For example, there could be very fast motion around the solvent of the solvent. So, that suppose as I wrote as I drew earlier that I initially there is a situation where the dipole has been created because the solute has been excited and the solvent around it did not have enough time to reorganize themselves and they find that immediately after the excitation there is a huge unfavorable interaction.

So, water this water molecule will try to do is that this water mark will try to abruptly moved; so, that the hydrogen in the delta positive end points toward the delta negative end of this dipole. So, that there is some solve stabilization of the excited electronic state of the solute and that effect will be very fast. These are called inertial effect and those timescale of salvation will be very very fast. But then there will be overall slow motion where a water molecule actually moves and then reorient sits a hydrogen end to the negative end and vice versa.

So, those motions will be a translational diffusion motion type and those are will be diffusion control and since diffusion has a longer time scale those time scales will be reflected in or in the salvation correlation function, but as a longer time scale. So, what I am saying here is that the this entire curve we can actually write it as like several time constant e to the power minus a t by tau 1 plus A 2 e to the power minus t by tau 2 and suppose that tau 1 is smaller than tau 2 and so on.

So, in this case this tau 1, tau 2, tau 3 and all these timescales actually corresponds to a particular solvent motions, like tau 1 may corresponds to the inertial motion, tau 2 may correspond to the longer motion longer timescale motion which are say diffusion mediated. So, once we construct the salvation correlation function from this spectral shift which is basically how the fluorescence emission itself is shifting over time we can actually get an idea of these how what are the salvation effects and this correlation function basically quantifies the dynamics of salvation.

Now, one thing I want to point out here is that we have not talked here how you measure the fluorescence spectrum at different time. And secondly, already we talked about this term which is known as stokes shift and you know that stoke shift is basically the shift between the absorption spectrum and the emission spectrum that Gabrielle stoke was observed. And usually it is used for both in the context of fluorescent stokes shift as well as robust stoke shift, but we are talking about fluorescence only here. So, this stoke shift itself as we see evolves with time because there was an absorption which we did not show here prior to the emission there are absorption to all these states here, and then we had we can actually draw it here, so when these when the absorption happens.

So, due to absorption there is a there is an absorption spectrum and due to emission there is a fluorescence spectrum and this is the, stokes shift. But what we are saying right now is that the stokes shift itself evolves with time because there is an absorption and you see that there is a shift due to early time fluorescence then eventually there will be a shift due to the late time fluorescence.

So, we are actually measuring the dynamic stoke shift here or sometimes it is known as time resolved fluorescence stoke shift measurements because it is the, it is not a Raman stoke shift, so fluorescent stoke shift experiment. So, it is called TRFSS, and all these I mean that terms are self explanatory, and or sometimes it is known as the dynamic stoke shift. As opposed to the static stoke shift where you basically talk about the stoke shift which is just between the overall absorption spectrum and the steady state fluorescence spectrum. So, your steady state fluorescence spectrum actually is a time averaged spectrum of all this fluorescence spectrum that come at that originate at different time.

So, we will conclude our discussion on polar salvation dynamics here. And now we will switch to the second topic which is the electron transfer reactions and there also we will see the solvent actually dynamically how it influences the rates of electron transfer that was explained by Rudy Marcus.