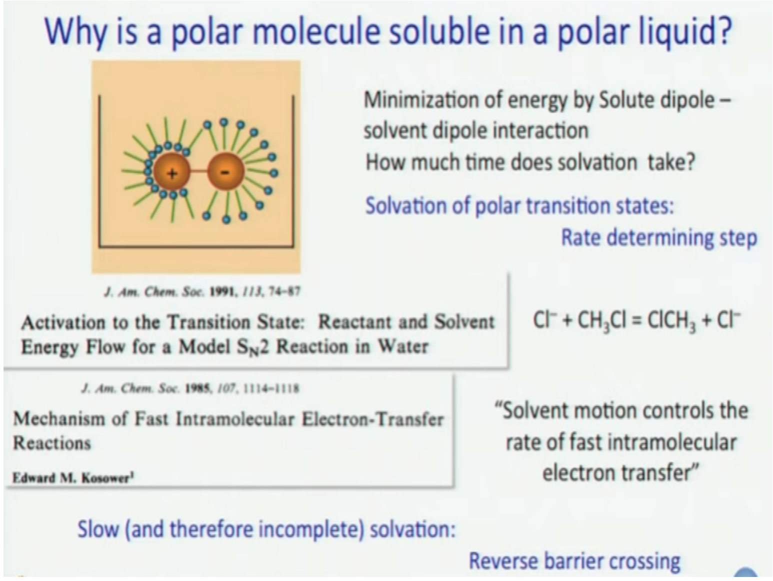
Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

Module No # 09
Lecture No # 48
Solvation Dynamics – Part 1

The last couple of modules we are talked about how one can study how the bond breaks so we talked about what is called snapshots of bond breaking. Today and also we have talked about an important excited state process twisted intra molecular charge transfer. Today we will discuss another process solvation dynamics and the reason why one is interested in solvation dynamics is this. Even in class 11 or so everybody is familiar with this diagram right so what this diagram tells us is.

(Refer Slide Time: 00:56)



Why is a polar molecule soluble in a polar liquid?

Minimization of energy by Solute dipole – solvent dipole interaction
How much time does solvation take?

Solvation of polar transition states:
Rate determining step

J. Am. Chem. Soc. 1991, 113, 74–87
Activation to the Transition State: Reactant and Solvent Energy Flow for a Model S_N2 Reaction in Water

$Cl^- + CH_3Cl = ClCH_3 + Cl^-$

J. Am. Chem. Soc. 1985, 107, 1114–1118
Mechanism of Fast Intramolecular Electron-Transfer Reactions
Edward M. Kosower[1]

"Solvent motion controls the rate of fast intramolecular electron transfer"

Slow (and therefore incomplete) solvation:
Reverse barrier crossing

Why is that solar molecule are soluble in polar liquids? Sometimes you talk about why ions are soluble in polar liquids? So the reason why polar molecule soluble in polar liquid is that the energy is minimized due to favorable solute dipole solvent dipole interaction this is something that everybody knows. Why is it that nonpolar solutes are not soluble in polar liquids? Yes so generally we say hydro phobic right so some people say this term hydrophobic is not right.

Where it is not as if there is any repulsion between a this non-polar solutes and polar solvents it is just that if you put in terms of a little more general interactions the cohesive force of this solvent in that case is much more than the adhesive force between the solute and the solvent. It is just that the solute molecules like each other very much so they do not care about the solute molecule that is why they do not dissolve.

Because after all the same non-polar solvent solute does dissolve in non-polar solvents okay but we do not have to get into that for the moment. Here we are going to concern ourselves only with solution of polar solvents polar solutes in polar solvents. Now the question that one asks in solvation dynamics is how much time does it take for solvation to take place. And the reason why this question is interesting fundamentally is that solvation of polar transition states transition states are polar more often are not we have seen an example of such a polar transition state in case of say DMABN in the last module.

So solvation of these steps is often the rate determining step so if you know solvation dynamics in principle you should be able to tell how much time a reaction takes place. So this would be very important step this is a very important step in understanding reaction that takes place in solutions. So there is a lot of literature this one for example published in 1991 where it says that activation of transition state this has been studied for reactants and solvent energy flow for a model SN2 reaction in water.

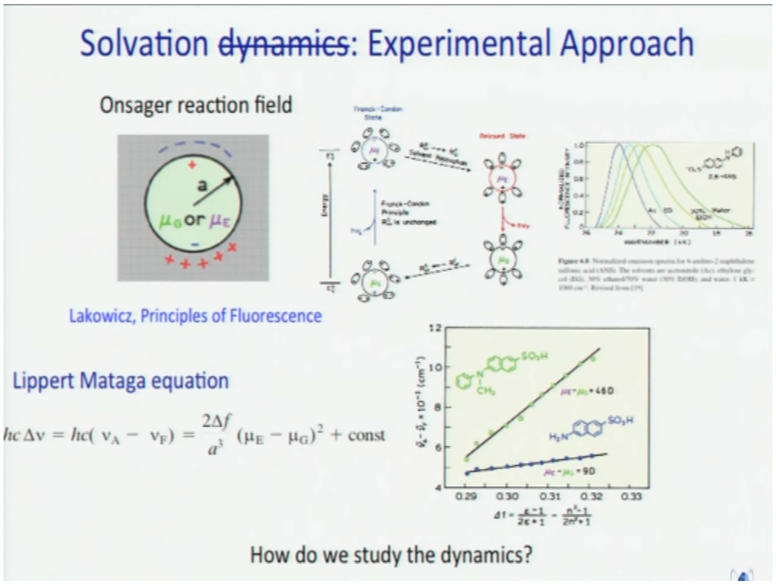
This reaction is chloride reacting with CH3Cl forming ClCH3+ chloride it might look trivial actually it is not. How do you know that chloride is going in that chloride is going out you can do it easily by using different isotopes of chlorine and the good thing about this is that what kind of potential well would this reaction have? Do I think of reactant energy of product it would be a symmetric double well potential right.

So it turns out that for this thing this kind of reaction the rate determining step is solvation another JACS paper published in 1985 by another solvent Kosower this was on mechanism of fast intra molecular electron transfer reaction. There he made a comment solvent motion controls the rate of fast intra molecular electron transfer. And then if solvation is slow if it is too slow then it may not be actually complete before that the reaction might takes place.

If there that is the case then you could have barrier crossing not only in the forward direction but also in the backward direction. So how fast solvation is often determines the dynamics of reactions involving polar intermediate polar transition states. So before we get into the question of how much time it takes a solvation and how we determine it experimentally let us remind ourselves of something that is very fundamental in this field not dynamics really but how do you get some quantitative measure of solvation experimentally.

Well of course experiment here starts with some theoretical model and the theoretical model one uses here is Onsager reaction field model this is discussed in detail in Lakowicz which is principle of fluorescence text book and it provides reference to this original paper for those who are interested. To put it very qualitatively the model is like this in this model the solvent is modeled as dielectric continuum a block with the same dielectric constant everywhere alright.

(Refer Slide Time: 05:43)



Solvation ~~dynamics~~: Experimental Approach

Onsager reaction field

Lakowicz, Principles of Fluorescence

Lippert Mataga equation

$$hc\Delta\nu = hc(\nu_A - \nu_F) = \frac{2\Delta f}{a^3}(\mu_E - \mu_G)^2 + \text{const}$$

How do we study the dynamics?

Now to consider this solute in this solution first of all we know once again from may be class 6 class 7 physical science we know that what are the properties of matter is that 2 different things cannot occupy the same space. So if you are going to put solute is inside the solvent you have to create space for it. So what Onsager did was that first of all to consider the solution he considered a spherical cavity the diameter of which is exactly the molecular diameter of the solute.

So you have this dielectric continuum some dielectric constant epsilon and you have cavity in it what is the meaning of cavity epsilon you can consider it to be 0 there is nothing in it cavity means vacuum. And the size of the cavity is that the molecule can just fit in that cavity so that is how solvent is modeled. The solute is model once again without considering the chemical structure. So if you see this is the physical model right if you look at other physical models.

If you think of thinks like borne charging is another process that takes place that is considered for solvation. In all this physical models there is no molecular structure thus if you consider molecular structure you have to use quantum mechanics so this are models that actually formulated using classical mechanics and it does all most all the work. So in this case the solute is model as a dipole moment which fits exactly inside this cavity that we have created okay.

So see if I take water and if it take some aprotic solvent which as a same dipole moment they would be modeled in the similar fashion right dipole moment of that same diameter provided the diameter of the molecules are also same. So what you would miss out on in this model is specific intra molecular interaction like hydrogen bonding alright. So that is something that this model cannot accommodate this model would work only when the interaction is purely electrostatic okay.

Now when is say purely electrostatic when am I saying that? I am saying that because all the interaction that arises henceforth is because of the presence of this dipole moment inside the cavity. Until now what have we said epsilon is same everywhere now the moment you put this dipole moment inside the cavity what will happen? Let us say the dipole moment is placed in such a way you see this minus sign here can you see? Minus sign inside the spherical cavity let us say that is the negative end of the dipole this plus sign let us say there is a positive end of the dipole.

That is how the dipole is aligned let us say what will happen this plus charge here is going to polarize the dielectric in its nearest vicinity so that the dielectric now develops some minus sign here. The minus sign of the solute dipole on this side is going to polarize the dielectric around it so that dielectric in immediate vicinity as a plus sign. So what we generate even without considering molecular structure is micro heterogeneity in the solution.

Micro heterogeneity around the solute molecule solute dipole let us say alright. So now what is the situation you have a solute dipole and this solute dipole is contained in a cavity one side of which is minus one side is plus. So one side minus one side plus what does that remind you off? One side minus one side plus what do you create that way? Capacitor yes you create an electric field right plus and minus of course a field will be created now this fields is created as a result or as a reaction to the introduction of the solute molecule in the cavity is it right?

So this is called Onsager reaction field I am skipping the entire mathematics here I am trying to build the physical justification mathematics you read Lakowicz book you will understand it is not very difficult. But sometimes what happens is just do the math we lose the we do not even think of physical insight that is more important. So what you have here is you have Onsager reaction field produce as a result of introduction of this solute dipole into this solvent which is a structure less continuum alright.

Now the dipole is subjected to this reaction field right so what will happen? And the good thing is that dipole is nicely aligned with the reaction field also because the reaction field is produced as the results of the dipole. So minus side of the reaction field is near the plus side of the dipole moment and dipole and the plus side of the electric field is near the minus side of the solute dipole. So what kind of interaction will you have? You will only have stabilization.

If we had a fixed field let us say I have 2 plates and I apply an electric field their one plate is positively charge one plate is negatively charged. Inside that I forcibly turned the dipolar around then you can have repulsive interaction as well not in this case. In this case interaction is intrinsically a an attractive stabilizing interaction. Because the field is produced as a result of the field is produced in the reaction to the solute dipole and so this solute dipole is nicely align to it okay.

So this field is going to stabilize the dipole right you are going to have stabilization as a result of interaction of this dipole with the reaction field okay. So this is what the story is now think of a situation where I have a molecule whose ground state is more or less non polar excited state is polar can you think of any such molecule? Ground state is non-polar excited state is polar dipolar.

So in charge transfer takes place of course one side of the molecule will become positively charged one side will be negatively discharge. So DMABN could be an example on nilered is an example ANS TNS all this things could be an examples. So when that happens according to Onsager reaction field this would be the situation now we bring in the structure of this solvent dipoles here we still will not considering molecule structure.

But we are at least recognizing the fact that this solvent molecules are dipolar in nature so in the ground state the solvent dipoles are oriented in whatever way they are. Because ground state dipole moment of the solute is well let us say less not 0 may be less. Here it is said I think Mu G is the dipole moment of the ground state in the excited state you have a different dipole moment Mu E in this case let us say Mu is greater than Mu G now what will happen?

You have stabilization due to Onsager reaction field if you go through the reaction you will see that this picture is only to recognize the molecular in nature the derivation is completely based on dipole and field no molecular structure at all. But since we know that solutes dipole moment we can think that this dipole moment will reorient so that you have on the minus side of the solute dipole you have solvent molecules pointing the plus sides and on the other side you have solvent molecules pointing the minus side.

And that causes the stabilization okay so this is the molecular picture Onsager reaction field is the gross physical derivation. So then what happens to the corresponding ground state should it have here in this diagram it shows that the ground state of this solvated species as a higher energy compared to the ground state of the un-solvated species why is that so? Ground state means the dipole moment is gone dipole moment back to Mu G.

So why is that this arrangement has a higher energy than this arrangement because yes you are right in this case the it was this structure because it is not only solute solvent interaction. So if you read say Bockris Reddy’s book on electrochemistry part 1 you will see that while considering solvation solution of a polar solute in polar solvent you consider not only the solute solvent interaction but also solute solvent-solvent interaction because let us not forget that solute solvent molecules are present in very large number.

What is the concentration of water in water? 55 molar so millions of solvent molecules compared to 1 solvent molecule. So solvent-solvent interaction also contributes very strongly to the energy of this solution. So here the thing is in the excited state you go from this unorganized solvent situation to organize solvent situation or what is called as solvent work situation because of strongly favorable solute solvent interaction.

However is the dipole moment is restored from the high value of Mu E to the low value of Mu G then that favorable solute solvent interaction is gone and when that is gone what is lacking in this structure is the favorable solvent-solvent interaction that is present here. So this is more unstable than this so you can draw in energy cycle like this so what will happen if you look at absorption spectrum and emission spectrum you record absorption spectrum and you record emission spectrum.

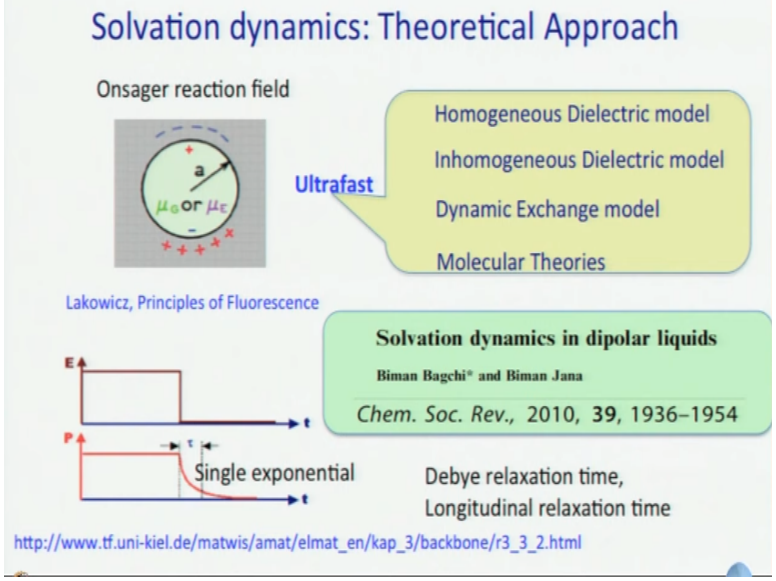
If the if you go to a more polar solvent then stabilization will be greater so stoke shift between absorption and emission is going to be larger right. So here stoke shift provides a way of telling how polar the solvent is. And of course it will work only when Mu E is greater than Mu G so this is some data using ANS and you can see how emission spectra are getting red shifted and if you go through this Onsager reaction field model derivation you will arrive at something that is equally well known that is Lippert Mataga equation.

And Lippert Mataga equation is something like this where it says hc delta Nu means Nu A – Nu F where usually these are written in transfer wave number the stroke shift in wave number = 2 delta f / a cube Mu E - Mu G whole square + some constant what is Mu E – Mu G? The difference in this dipole moment created upon excitation the dipole well the difference between the dipole moment created upon excitation and dipole moment of the ground state. What is delta f? Delta f is this we are referred to delta f in one of the earlier modules.

Epsilon -1 / 2 epsilon +1 –n square -1 / 2 n square +1 this is the measure of what is called orientation polarizability of the solute solvent. So the idea is that if you make this plot of Nu A- Nu F stroke shift against delta f then you are going to get a slope which is proportional to square of Mu E – Mu G. So greater the charge separation in the excited state steeper will be the curve alright and here we have an example of ANS versus TNS you see that in this case delta Mu turns out to be in 9 debye in this case delta Mu turns out to be 46 debye.

So of course this has a much more polar excited state compared to ground state this will be a better marker of polarity compared to this okay. So what we have presented so far is the effect of solvation of steady state spectrum we have not talked about dynamics yet. So the question is how do we study the dynamics of the excited state going from unsolvated one to a solvated one right that is what we want to discuss.

(Refer Slide Time: 19:28)



Solvation dynamics: Theoretical Approach

Onsager reaction field

Ultrafast

Homogeneous Dielectric model

Inhomogeneous Dielectric model

Dynamic Exchange model

Molecular Theories

Lakowicz, Principles of Fluorescence

Solvation dynamics in dipolar liquids

Biman Bagchi* and Biman Jana

Chem. Soc. Rev., 2010, 39, 1936–1954

Single exponential

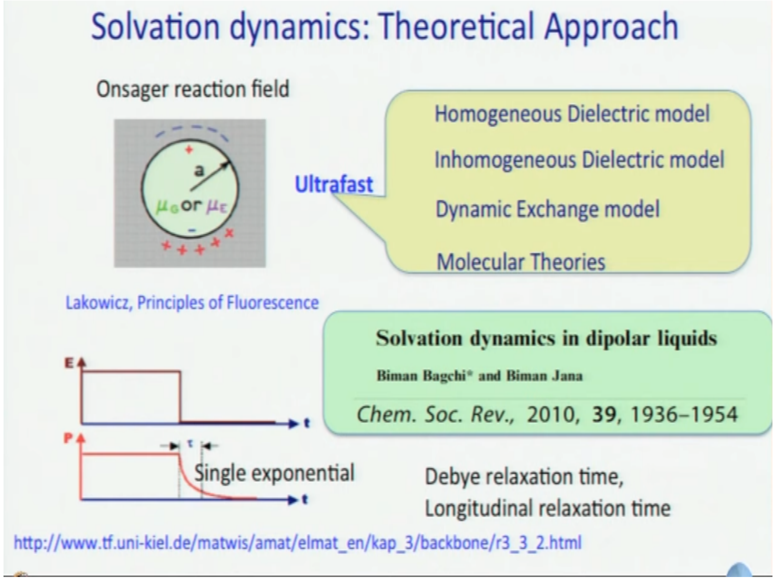
Debye relaxation time,
Longitudinal relaxation time

http://www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_3/backbone/r3_3_2.html

Now in this case theory preceded experiment and lots of theoretical approach is homogeneous dielectric model, inhomogeneous dielectric model, dynamic exchange model and molecular theories. You can see that in the order that they have written you are actually going from coarser theory to a finite theory to start with a model where the dielectric is homogenous as we have said already Onsager model.

Then you have to consider that dielectric may not be homogenous is after all once again if you go back and read some basic physical chemistry text book like Bockris and Reddy's electrochemistry book what is said is that see in the immediate vicinity of an ionic solute what is dielectric constant of bulk water, 80 or something right. what is the dielectric constant of water around say sodium ion? Much less it is about 5 because the natural order orientation of the water dipole molecules is destructed in the immediate vicinity of sodium they are solute solvent interaction takes place.

(Refer Slide Time: 20:51)



Solvation dynamics: Theoretical Approach

Onsager reaction field

Ultrafast

- Homogeneous Dielectric model
- Inhomogeneous Dielectric model
- Dynamic Exchange model
- Molecular Theories

Lakowicz, Principles of Fluorescence

Solvation dynamics in dipolar liquids

Biman Bagchi* and Biman Jana

Chem. Soc. Rev., 2010, **39**, 1936–1954

Single exponential

Debye relaxation time,
Longitudinal relaxation time

http://www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_3/backbone/r3_3_2.html

So just around the soluted is 5 in the bulk it is 80 so it is impossible that there is a step jump from 5 to 80. So it goes in steps so first solvation shell second solvation shell third solvation shell that way you have a gradual change from 5 to 80 well when I say gradual it is not really gradual it is quiet steep. But inhomogeneity of dielectric is an important factor that as to be accounted for and that has been done in theoretical approaches.

Then when you consider the molecular well even before that the third thing that you have to consider and we are going to harp upon this little later as well if dynamic exchange, see this is not a static picture. You have a solvent bulk model fine you have some of the solvent dipoles oriented nicely around the solute dipole but it is not a as if that this solvent dipole that is their present in the first solvation shell is going to there forever. It is not an if solvent dipole that are not bound by the solute are going to be there forever there is an exchange between the 2 and as it turns out that this exchange between bound and free dipole solvent dipoles actually has an important role to play in the dynamics.

Because when you talk about dynamics what do you have to do? You have to write a lot of differential equation right what do, we do in kinetics first order process, second order process what happens when we talk about some complex process. If there are several steps you have to write differential equation for each and every step right. Here since dynamic exchange is the reality one needs to account for it while building the model and finally you have to consider the solvent molecules as solvent molecules not just dipoles.

The problem with that is that how many solvent molecules do we have? Avogadro’s number let us say. If you are going to consider all of them to have some particular structure and you are going to use quantum mechanics for that is not going to work right. So very often what is used mostly here is statistical mechanical models statistical mechanical models with explicit solvent structures okay.

So this is how the theory has evolved and you can get a an overview of this different kinds of theories from this very informative review by professor Biman Bagchi and now professor Biman Jana solvation dynamics in dipolar liquids published in 2010 there are many other review as well. Now one thing that has been referred to constantly while talking about solvation dynamics or otherwise is dielectric relaxation.

Dielectric relaxation measurement are actually important here because the longitudinal relaxation time in simple liquids the solvation time. So lot of dielectric relation experiments have also been done in this context but that again gives the bulk picture dielectric relaxation measurement does not have the capability of going nearest solute and looking at it for that one has to use spectroscopy. So this module was an introduction to the process of solvation itself. In the next module we are going to discuss how one can use ultrafast spectroscopy to study the dynamics of solvation.