Ultrafast Processes in Chemistry
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Module No # 09
Lecture No # 47 Part -1
Twisted Intramolecular Charge Transfer

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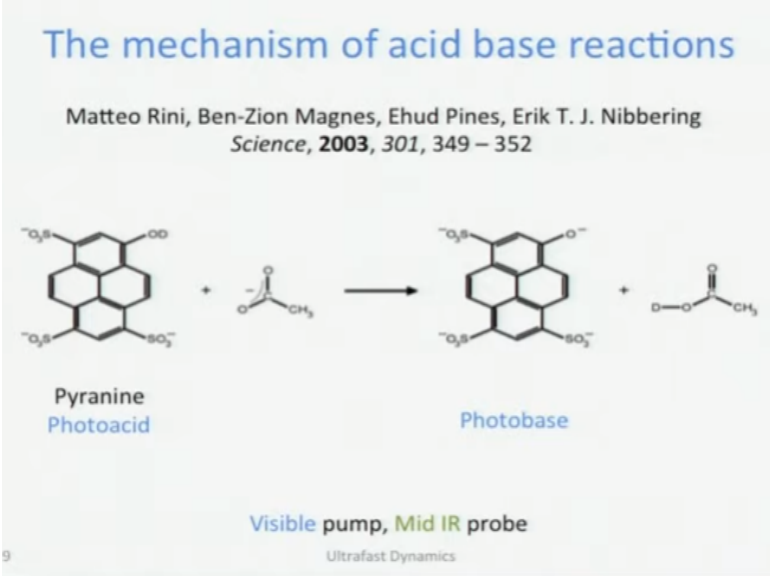

The mechanism of acid base reactions

Matteo Rini, Ben-Zion Magnes, Ehud Pines, Erik T. J. Nibbering
Science, **2003**, *301*, 349 – 352

Pyranine
Photoacid

Photobase

Visible pump, Mid IR probe

Right so in the previous module we have seen how the dynamics of the fastest possible process breaking of a bond was determined in Ahmed Zewail's group and we have also seen how they could show you not only give you a time constant but actually tell you how the process is taking place making and breaking on and on until it breaks and goes away. Now what will do is will jump cut to a couple up decades later and present to you glimpses of a couple of pieces of work from Erik Nibbering group in Maxbond institute.

And this is my favorite I like it very much one reason is that we I read it in real time the moment it is published and also Nibbering had come and heard him present this work. So this is elegant so what has been done is this okay all of us have studied acid base reactions in school and college right. And what is written invariably in chemistry textbook is that acid based reaction is very fast and the mechanisms is unknown mechanism cannot be established because this is so fast right.

Now what we are going to discuss in the next 10 15 minutes is how the mechanism of this supposedly impossible to establish mechanism kind of reaction how then we can that mechanism was elucidated by pump probe spectroscopy once again I will not discuss the whole story i will just present to you the logic and then you should read this 2 science papers once you know a little bit about pump probe spectroscopy those papers are not very difficult to understand alright.

So what we did is again in the beginning of the course we have presented the concept of photo acidity we have said that organic acids become stronger acids when they are excited organic bases becomes stronger base and we have explained why in the light of molecular orbital theory. So what Nibbering groups did is that the used is strong photo acid Pyranine or SPTS as it is called. So here you see and they used OD signal is easier to see in this experiment.

And they used a regular base that is acetate ion and the idea is that they would excite Pyranine it would lose D+ ion to form the what they called the photobase and this acetate ion would get deuterated to give you deuterated acetic acid okay. This is the reaction and how do you follow it? By using pump probe spectroscopy but here the pump is visible 400 nanometer or something because that is where Pyranine absorbs any way the probe is IR.

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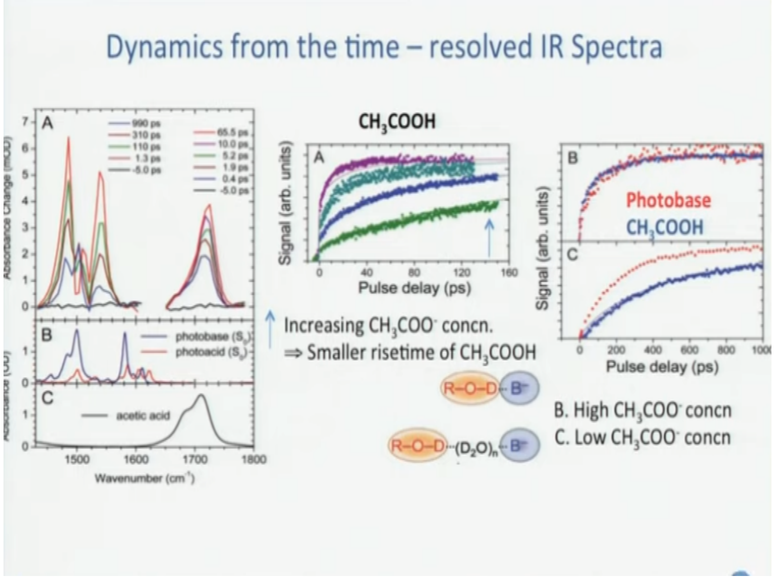

Dynamics from the time – resolved IR Spectra

CH_3COOH

Increasing CH_3COO^- concn.
⇒ Smaller risetime of CH_3COOH

B. High CH_3COO^- concn
C. Low CH_3COO^- concn

Probe is not your visible because the good thing is if you use IR there is lot of data do not look at everything just show at where ever the arrow points just see wherever the arrow points this here is the IR spectrum of acetic acid and it is a little different from the IR spectrum we are used to see because Y axis is absorbance and not transmittance. So the idea this is your acetic acid absorption in IR of course OD will come deuterated acetic acid and this is the absorption of the photo base and photo acid remember what photo base and photo acid is?

Photo acid is Pyranine deuteriated Pyranine photo base is the deuterium removed right the anion corresponding anion of Pyranine. These are the IR spectra of those now the idea is when to start with ground state what do you have you have the photo acid and you have no acetic acid so when you excite by an ultrafast pulse if you use the frequency of characteristic absorption frequency of deuteriated acetic acid then you should see a transient absorption signal right.

Point to note is that this transient absorption signal arises due to absorption of a ground state and not an excited state okay. And techniques like this often used in other experiment like recombination of axial ligands of heme proteins. So it transient absorption does not necessarily have to be of an excited state okay it is forming as a result of excitation of the photo acid that is right. But what you are looking at as ground state absorption spectrum of acetic acid and this is actually the most useful range of frequencies as you see that the transient absorptions spectrum change significantly.

You can also work with this range and Nibbering group is actually done that but there is significant overlap between the absorptions of photo acid and photo base so you might understand that analysis of this part of the transient absorption signal is a little more complicated I read the paper they are actually done it but this is very easy to follow. So what you should see in this second panel is how the absorption of acetic acid changes as a function of time post excitation of Pyranine photo acid okay.

Is there problem understood? What do you expect to see? You expect to see a raise time so they look at the rise time what they saw is that first of all rise time is there secondly you see a smaller rise time if you increase the concentration of acetate ion why. Because if you have higher concentration acetate ion then the moment this deuterium ion is liberated I do know whether it is a good idea use what is like moment when you are talking about ultrafast phenomena but I think you understand what I am trying to say?

When the D+ ion is liberated as a result of photo excitation of pyranine it find an acetate ion faster that is what I mean if the concentration is more that is why the rise time is shorter as you increase the CH3COO minus concentration. And also they compared the evolution time evolution all the signals for photo base and CH3COOH. So at high CH3COO minus concentration you can see the dynamics are more or less the same see photo base is also produced as a result of excitation right.

Because you start with the photo acid when the D+ goes out from pyranine 2 things are produced first is photo based is produced right away and then that liberated D+ is taken up by acetate ion and then acetic acid is produced the question is are the dynamics same for this 2 process? The rise in the population of photo base and rise in the population of acetic acid are they same or different? What do you expect? If it is a simple mechanism involving something like this where you have contact ion pairs HOD and B- then when D+ is liberated what do you get well ROD.

So you get RO- and you get DB let us say so dynamics of formation of RO- and dynamics of formation of DB should be the same? Understand what I am saying? So rise in population of the anion of pyranine and rise in population of acetic acid should be the same if they are just 2 ions in contact and it happens is instantly that is what you get for high concentration of acetate ion. However when you work at low concentration acetate ion this is what happens this is the dynamics of photo base and this is the dynamics of your acetic acid actually I should have written CH3COOD here because it is D+.

So which one is first of all they are not the same which one is faster which one is slower formation of photo base is faster right and formation of acetic acid is slower what does that mean? It takes some time for D+2 get liberated right and time taken for that is reflected in the time taken for population of the photo based to build okay. After that if the proton is doing something else gets engage somewhere else then the time of formation of acetic acid will be longer understand what I am saying?

So I pass on a message to you if I speak to you the time taken for me to get read of the message and the time taken for you to get the message is the same. But suppose I do not tell you I tell somebody else that person somebody else that person tells somebody else then I have delivered the message but sometime would go before you get it that is what is reflected in this kind of a difference in population dynamics of the photo base and CH3COOH okay.

And then of course this is a very qualitative way of putting it but it is very important because it gives you the idea. The idea you get is that at high CH3COO- concentration this is the situation at low CH3COO- concentration when you have a chain of solvents in between the proton donor and proton acceptor then it takes a little longer. Okay this is the qualitative picture to get the quantitative picture what they are that is why they have not 1 but 2 science papers out of this.

They did a thorough analysis of the data and establish quantitatively how much time it takes for the proton to get lost from the photo acid how much time it takes for it to get associated with water.
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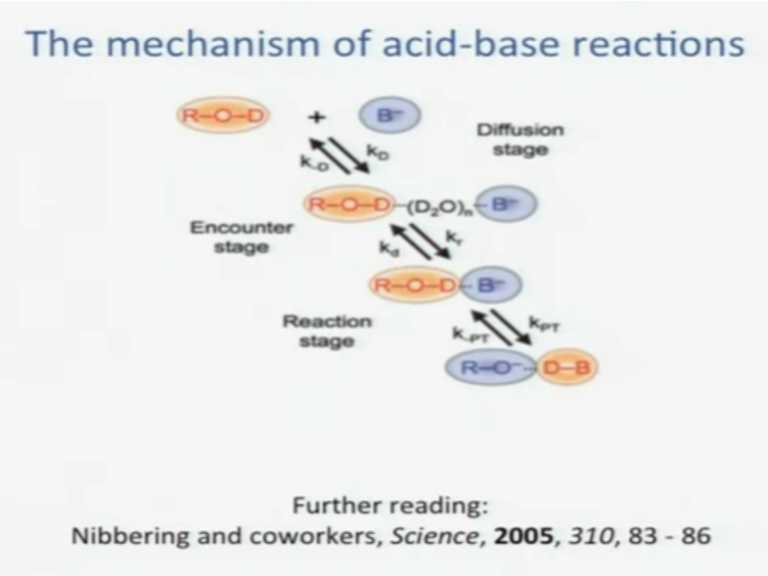

The mechanism of acid-base reactions

Further reading:
Nibbering and coworkers, *Science*, **2005**, *310*, 83 - 86

And then after a thorough analysis they came up with this picture looks very simple when you look at it and in fact almost looks intuitive so what they said is ROD + B- first there is a diffusion stage. In diffusion stage you have a lot of water molecules just separated so they come a little closer and they have this you can call it water polymer between the proton donor and the proton acceptor. This is called the encounter stage where this polymer is eliminated and you form the contact ion pair.

And then you have the reaction stage where the proton actually gets transferred so what you see in front of your eyes is the reaction mechanism of acid based reaction something that has been for a long time to be beyond our capabilities. So for the last 13 14 years this has not been beyond our capabilities we know exactly what the mechanism is and what is not written is here is that you see all the rate constants all the values of this rate constants are exactly normal okay that is the power of the ultrafast spectroscopy not only do you get to know how a bond is broken we also get to unravel mechanisms of reactions that no other technique.

So this is a fantastic piece of work from relatively recent times after all we have been showing a papers 1972 to 1965 so on and so forth which is still recent compared to what we usually do in class rooms we often talk about the things that were already known by 1900. But what you see now is the paper was published in 2005 science fairly recent I hope to get back to the work of Nibbering once again we need to talk about energy transfer between vibrational modes of water.

But before that let me see if you can introduce another excited state process which is perhaps the most widely debated excited state process of all times and that goes by the name of twisted intra molecular charge transfer.

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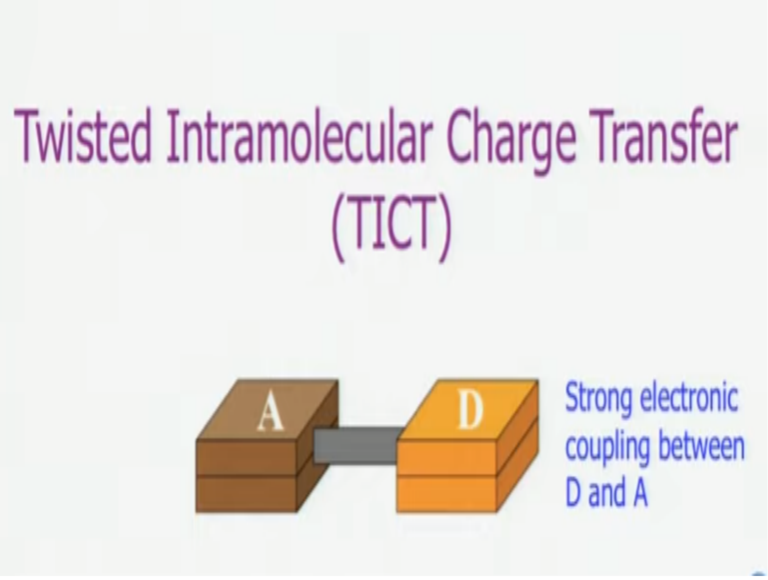

Twisted Intramolecular Charge Transfer (TICT)

Strong electronic coupling between D and A

And there have been bitter fights over decades over whether that first T in TICT should be there or not be there okay. So to cut a long story short and I will show you the example suppose you have a coplanar molecule in which you have this donor moiety and the acceptor moiety right they are bonded to each other and they are coplanar. Coplanarity is essential or at least so it was thought because when they are coplanar 2 rings then their pi-electrons talk to each other right. If they are perpendicular then the communication is lost so the idea was that you have this donor and acceptor coplanar excite by light.

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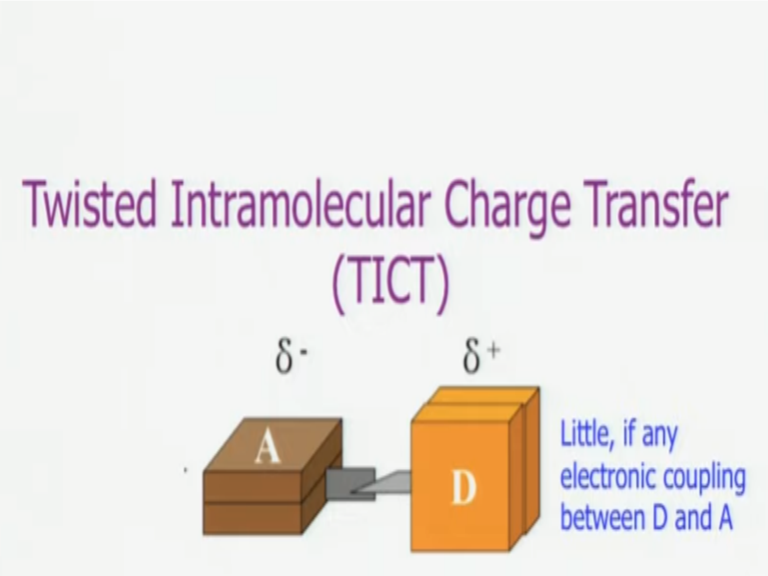

Twisted Intramolecular Charge Transfer (TICT)

Little, if any electronic coupling between D and A

Then the electron transfer takes place and then if that is associated with the twist then what will happen you have delta minus on one side delta plus on one side and since this delta plus and delta minus fragments are perpendicular to each other that electronic communication is lost so you cannot have back electron transfer. The reason why interest grew in this kind of systems was because people wanted to develop things like disensitized solar cell.

What is a meaning of a battery or a cell? If you have a plus end or minus end right essentially that is what makes a cell so here the idea was that light energy would be converted potentially into electrical energy because you have producing a molecule one end of which is plus and one end of which is minus now how you are going to connect the 2 ends of the molecule that is the different issue all together in any case we are not going there.

But then what it as it turned out that more than making a solar cell out of this of very rich field of photo physics are unraval by this kind of molecule. The most celebrated perhaps molecule of this class goes by the name DMABN dimethyl aminobenzonitrile even now people work on it.

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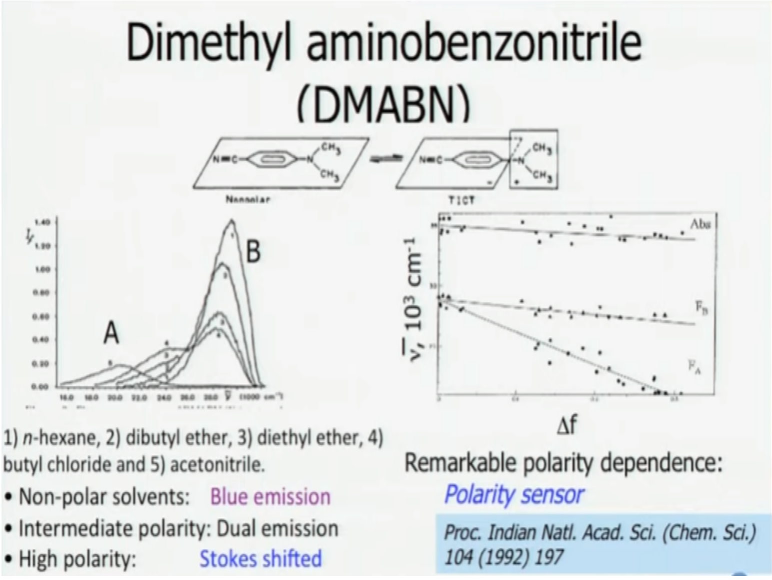

Dimethyl aminobenzonitrile (DMABN)

1) *n*-hexane, 2) dibutyl ether, 3) diethyl ether, 4) butyl chloride and 5) acetonitrile.

- Non-polar solvents: Blue emission
- Intermediate polarity: Dual emission
- High polarity: Stokes shifted

Remarkable polarity dependence: *Polarity sensor*

Proc. Indian Natl. Acad. Sci. (Chem. Sci.) 104 (1992) 197

I do not know how many 1000 papers have been published on the photo physics of DMABN and its brothers and sisters and cousins but even now people find use for it. So DMABN you can see what the structure is and for a chemist if I say dimethyl aminobenzonitrile that should be enough you can see that this donor moiety and acceptor moiety and idea was that after charge transfer they become perpendicular to each other.

The fact that charge transfer takes place it is not very difficult to understand because if you look at the fluorescence spectra and here when you look at the fluorescence spectrum be careful this paper is not very recent. Well I am showing you 1992 paper but that is sort of a review this is after 2 decades of work okay so this data is not really from this paper. Data is from some 1970's paper so they use to draw things differently at that time as you can see X axis in Mu bar in centimeter inverse I do not know if you can read and this side is high energy spectrum high energy side.

This is the low energy side is it right? Yes it is this is 16 on the left side this is 24000 or something 16000, 24000 so what you see is you have 2 kinds of bands spectra reported in several solvents NXN is non-polar and there is only one band the B band so called B band which is higher energy. And if you go all the way to acetonitrile then you get only A band a stoke shifted band and remember what we said the stoke shift is one of the signatures of excited state process happening.

So something is happening post excitation in this molecule and it is charge transfer because we will see why we think it is charged transfer. Right what you see here is not exactly Lippert plot but it is the maximum of spectrum fluorescence spectrum centimeter inverse plotted against a polarity parameter this polarity parameter is obtained from Lippert Mataga equation which we will talk about very briefly in the next module.

So what you see is this look at absorption this is the graph for change of absorption maximum in centimeter inverse with polarity not much. This is the second one is the variation of the emission maximum of the B band the higher energy band with change in polarity well you do not see it in very high polar molecule polar solvents or it is very feeble but as long as you see it there is not much of a variation.

But when you look at A emission there is distinct emission on delta F more delta F is polarity parameter greater value of delta F means the solvent is more polar will see what it is little later. So for a more polar molecule we see a greater red shift of the A band what does it mean? That mean A band the stoke shifted is associated with the polar emissive state right and that corroborates very nicely with this kind of a picture that the higher energy state corresponds to this where charge transfer as not taken place.

Lower energy excited state corresponds to this by charge transfer has taken place but why do you think there is twist? In the data that we have shown so far we might have been able to establish that the stoke shifted band is associated with the polar excited state who has said that there is a twist? Lot of calculation said first of all you are not going to show you all that.

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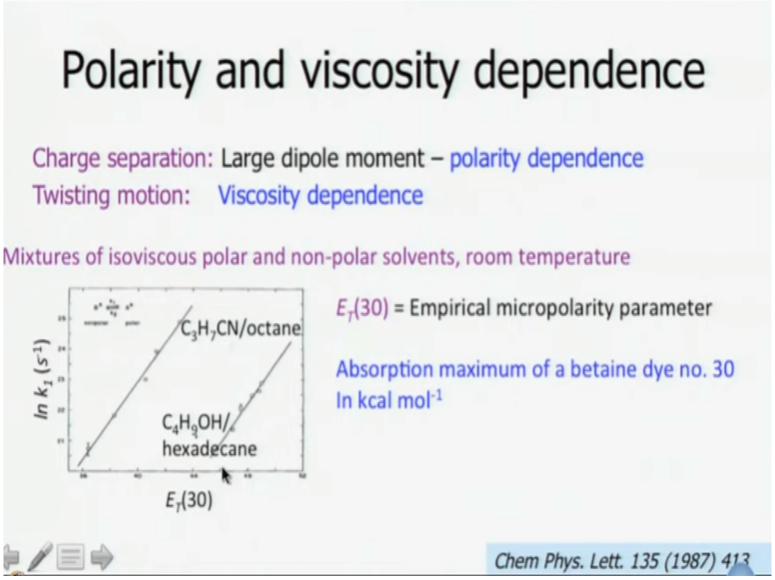

Polarity and viscosity dependence

Charge separation: Large dipole moment – polarity dependence
Twisting motion: Viscosity dependence

Mixtures of isoviscous polar and non-polar solvents, room temperature

$E_T(30)$ = Empirical micropolarity parameter

Absorption maximum of a betaine dye no. 30
In kcal mol^{-1}

Chem Phys. Lett. 135 (1987) 413

But will present another piece of work extremely elegant piece of work this time from Isenthals group Colombia university department of chemistry Kenneth Isenthal so what we said is this that we think that it is associated with the twist with the theory calculation and some other preliminary steady state fluorescence spectra if there is a twist actually then the photo physics would depend not only on the polarity but also on the viscosity.

Because whenever there is a segmental motion that has to take place overcoming the viscosity of the medium so for more viscous mediums the process would get slowing down so before this work in 1987 there was plenty of work of usual Lippert Mataga team all that of the DMABN. So the reason why I am very fond of this work and actually everybody should read this paper. Chemical physics letters so the paper it is not very big and not very difficult to understand either.

This is a must read paper for anyone who wants to work with photo physics of molecules especially because it is instructive it teaches you tools in one paper that can be very useful if you are going to work with the molecules. So beauty of this work is that Isenthal and suddenly cannot remember the name of the then student who worked on this they said that well what about viscosity dependance?

If you want to talk about polarity dependence of the rate constant associated with this then we should also take into account the role of viscosity that might be there. So what they did is they did 2 things first experiment is the result of which you see here is due to mixture of isoviscous polar and non-polar solvents at room temperature. So what happen when you take mixture of isoviscous polar and non-polar solvent?

2 pairs are shown here one is C3H7CN Nitrile and they actually did s series of nitrile and octane and the reason why they choose these 2 as you see none of these are commonly used solvent right. Whoever works with octane whoever works with C3H7CN of all things but they chose this pair because this pair as the same Viscosity more or less same but octane of course it is non-polar nitrile is polar.

And another representative mixture is C4H9OH butane and hexadecane again you might think that sometimes you might have done experiments with butane have butanol also sorry no butane but hexadecane of all things the reason why they were chosen once again is that they have same viscosity and then the first solvent mixture is the mixture of a non-polar solvent and a polar aprotic solvent. Second one is a mixture of a non-polar solvent and a polar aprotic solvent.

So not only do you get to understand the role of polarity and viscosity but also the role of protocity. So an, everything is done in room temperature X axis Et 30 is an empirical micropolarity parameter, introduce by Reichard. Reichard as a book on properties of solvents where Et30 is discussed very nicely essentially what Reichard group did was they looked at Reichard what we often pronounce his name but I think the correct pronunciation is Reichard but I am not good at general pronunciation anyway.

So they work with a library of molecules which with exhibit solventochromism and they found out that the absorption maximum of this betaine dye number 30 is basically a roll number right. When you work with a large library of molecules for here you works with molecule 72 all the time who is going to mention the IUPAC name? All of us spent so much time in school learning IUPAC in name we hardly never used them. Because we work with molecules that are IUPAC name to write it not a name it is like a name address lot of things okay.

So absorption maximum of betaine dye number 30 in their inventory okay if somebody else might have called dye number 82 I do not know but they called this dye number 30 then they work in the series of betaine dye they found that dye number 30 has this absorption maximum which is nicely dependent on polarity. So what they said is this why they call it micropolarity and they say that see organization of solvent around a solute is very different from the organization of bulk solvent especially for polar solvents and polar solutes.

So the polarity that we measure by measuring di-electric constant need not necessarily be the polarity experience by the solute. In fact sometimes the polarity is much lower right around a solute polarity of what water epsilon of what about 5 or a bulk polarity everybody knows very high value. So they said that when you talk about photo physics when we talk about property of a solvent solute you should talk about not epsilon not dielectric constant but some kind of a polarity parameter that is seen by this solute.

See when you do spectroscopy you use fluorescent probe or something they are myopic they do not see far away. They see the first solvation step maybe second solvation step beyond that nothing. So they introduce this and they said that this is a better polarity parameter when you are talking about photo physics of solutes. So that is that they used and they found that in the plotted against 30 you get this 2 different lines one for the nitrile nonpolar solvent mixture.

The other for your alcohol hexadecane mixture okay good thing about this plots is that there is not effect of viscosity in any of the plots okay. The plots are not the same right that could be because this mixture has a different viscosity then this mixture it could also be because here we have a protic solvent here do not that we will elucidate later on. But then what is done here is that if you forget about viscosity polarity dependence is clearly there.

So this is a superior piece of result then what is showed you a little earlier simple Lippert plot because viscosity is taken care of. Another way of handling situations like this is to do multi parametric analysis what is called Kamlet Taft analysis that is also very useful in understanding complex situations.