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

Module No # 10
Lecture No # 51
Excited State Proton Transfer: Introduction

Ok now in the next couple of modules I want to talk about one of the most favorite process favorite excited state process is personal favorites for me. Partially because half of my PhD thesis was on this and we have done lot of work on this process and this process is excited state proton transfer. We have already talked a little bit about that but I realized that we have presented in a bit and pieces over several modules.

So at the risk of repeating something that we have discussed already we are going to do a very brief recap at the beginning and then in this module we will only provide an introduction. Second part of real ESPT there is no ultrafast dynamics theory. In fact we are going to present an ancient paper for from 40 years ago because it is still relevant it is still tells you how one can approach a problem of understanding photo physics.

In the next module I want to present debate that rage for 10 years about the exact mechanism of excited state proton transfer intermolecular proton transfer in 7 Azaindole dimer. So this is something that I must of said in one of the module earlier.

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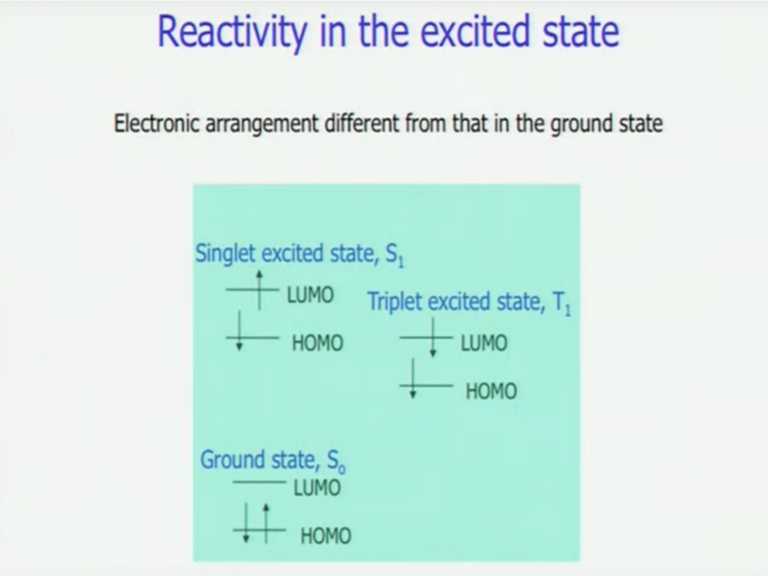

Reactivity in the excited state

Electronic arrangement different from that in the ground state

Singlet excited state, S_1

Triplet excited state, T_1

Ground state, S_0

The reactivity in excited state is different from that of ground state. And that is because the chemist we know that the electronic configuration is different and it is electronic configuration that determines the reactivity. So if you look at the ground state this is the electron configuration HOMO to LUMO 0. This is well in first approximation the electron configuration of this S1 state I see first approximation because I have just drawn arrows I have not written this spin wave function alpha beta minus beta alpha.

And then this is the triplet state where you once again have 1 electronic in HOMO and 1 in LUMO but spin wave functions are different. This is how the first approximation you draw it. So all this states are different reactivity and this is as you have said earlier this slice of the harsh of excited state processes because since excited state electron configuration is different reactivity is also different. So many reactions or chemical processes that do not take place in the ground state and takes place when the molecules is excited. So we generally do things better when we were excited molecules do the same usually they work better when they are excited.

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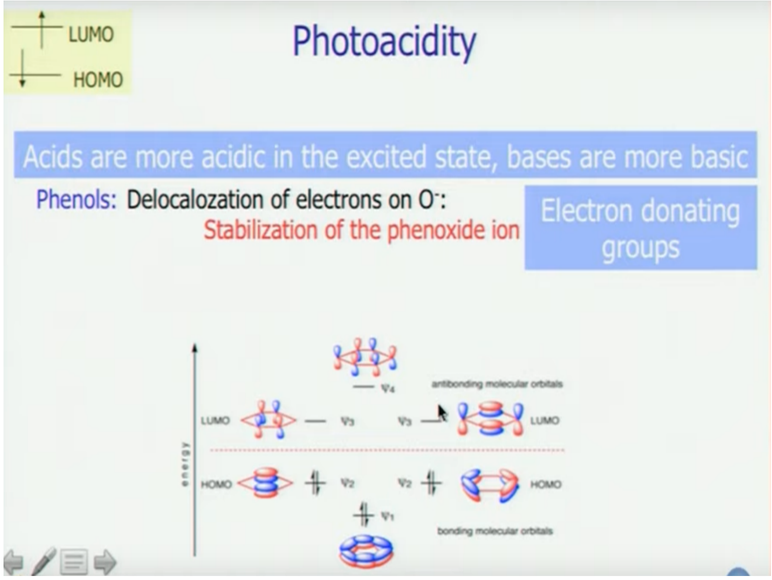

LUMO

HOMO

Photoacidity

Acids are more acidic in the excited state, bases are more basic

Phenols: Delocalozation of electrons on O⁻:

Stabilization of the phenoxide ion

Electron donating groups

And as we said earlier photoacidity is something that arises from there organic acids more excited acid acidic in the excited state organic bases are more basic. And the example we took of the phenol everybody knows that phenols are acidic because if phenoxide ion that is produced as a result of deprotonation is stabilize because of de localization of the electron cloud on oxygen over the ring.

And if you think of this from the MO picture this is what it is. Let us think of simple phenol the molecular orbital energy diagram of energy benzene is like this. So the 3 bonding orbitals are all occupied. When the electron cloud from the oxygen has to get delocalized over the ring. Then the electron clouds have to be accommodated in one of the higher energy antibonding orbitals. And that is what happens that is an important role anti-bonding orbitals play.

Sometimes while studying MO theory we think their antibonding orbitals are useless they are not. They have important roles to play SN2 reactions for example make use of antibonding orbitals. Here we see another example of user anti-bonding orbitals. And all of us might would have studied this carbonyl complexes where again anti-bonding orbitals which are heavily displaced towards carbon atom are used to accommodate electron cloud coming back from the central metal atom and that is what give size to this synergistic effect.

So here the electron cloud is accommodated in well ground state in the antibonding orbital that is phenol is acidic. However if you perform a pi-pi* excitation for example then a vacancy is created in lower line bonding Pi orbitals. And now the incoming electron cloud can be accommodated in lower energy MO's bonding MO's rather than anti-bonding MOs. The consequent stabilization is a driving force for enhance acidity in the excited state.

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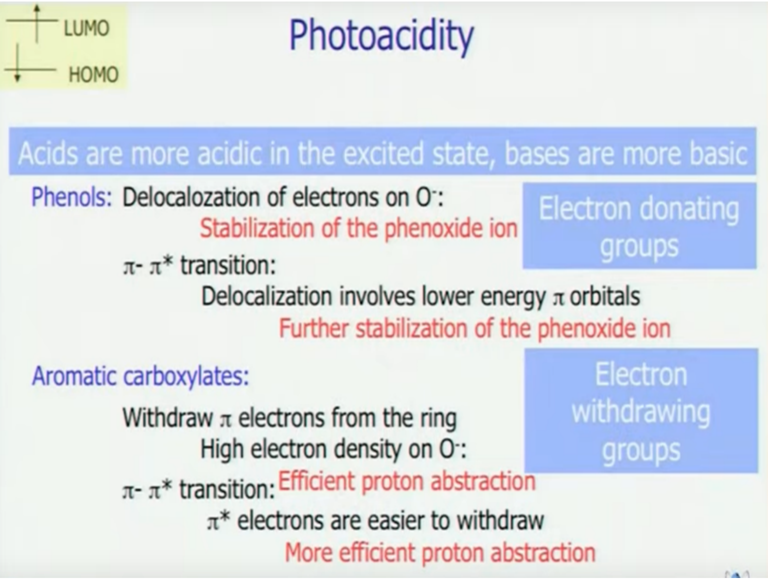

Photoacidity

Acids are more acidic in the excited state, bases are more basic

Phenols: Delocalozation of electrons on O^-:
Stabilization of the phenoxide ion
π- π^* transition:
Delocalization involves lower energy π orbitals
Further stabilization of the phenoxide ion

Electron donating groups

Aromatic carboxylates:
Withdraw π electrons from the ring
High electron density on O^-:
π- π^* transition: Efficient proton abstraction
π^* electrons are easier to withdraw
More efficient proton abstraction

Electron withdrawing groups

And once again if you take example I have in the well this same things happens for anions

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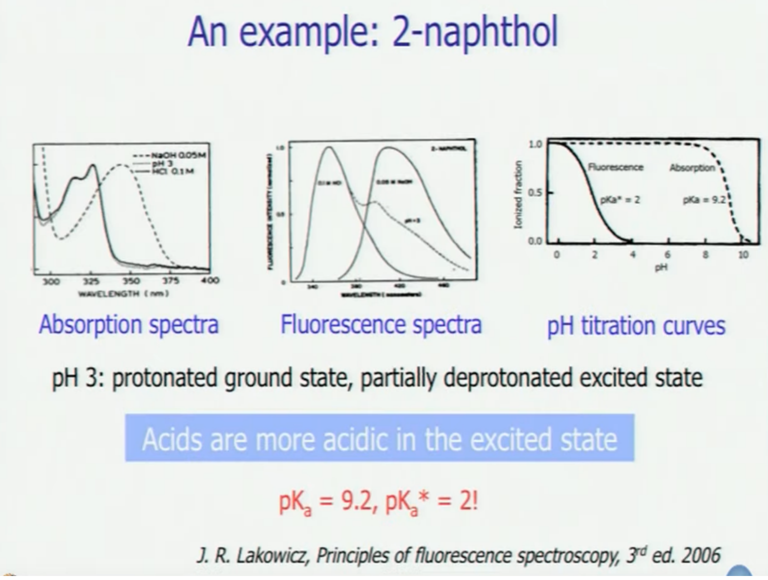

An example: 2-naphthol

Absorption spectra

Fluorescence spectra

pH titration curves

pH 3: protonated ground state, partially deprotonated excited state

Acids are more acidic in the excited state

$pK_a = 9.2$, $pK_a^* = 2$!

J. R. Lakowicz, Principles of fluorescence spectroscopy, 3rd ed. 2006

To demonstrate this the favorite example I have all this is taken from your Lakowicz book is that of beta naphthol one can generate titration curves using absorption spectrum to get the ground state pKa or from the fluorescence spectrum to get excited state pKa it turns out that pKa for beta naphthol in ground state is 9.2. Whereas in excited state is 2. So shift in pK by 7 units is huge amount.

So you are talking about a change in 7 orders of magnitude of proton concentration in which the molecule beta naphthol can give of proton. So if you take a beta naphthol in a neutral solution ph 7.4 it is it is not going to lose a proton it is going to made in protonated state. But you excited with light of appropriate wavelength then you can actually release the proton making beta naphthol or photo acid.

So this has several applications one thing that has been done to trigger many biological processes is a Ph jump. So use a photo acid in water you excite proton is lost so as a result of excitation proton concentration goes up. And if you do this excitation using pulse light then proton concentration goes up all of a sudden ok. So if you have an acid catalyze reaction then that is your time 0 the time of excitation.

That is when the acidity is switched on like dipolar switched on in solvation dynamics and the reaction starts. So you can start following the kinetics of this reaction so you can follow very fast acid catalyzed or basic catalyze reaction using this method of photo excitation using photo acids if you just catalyzed.

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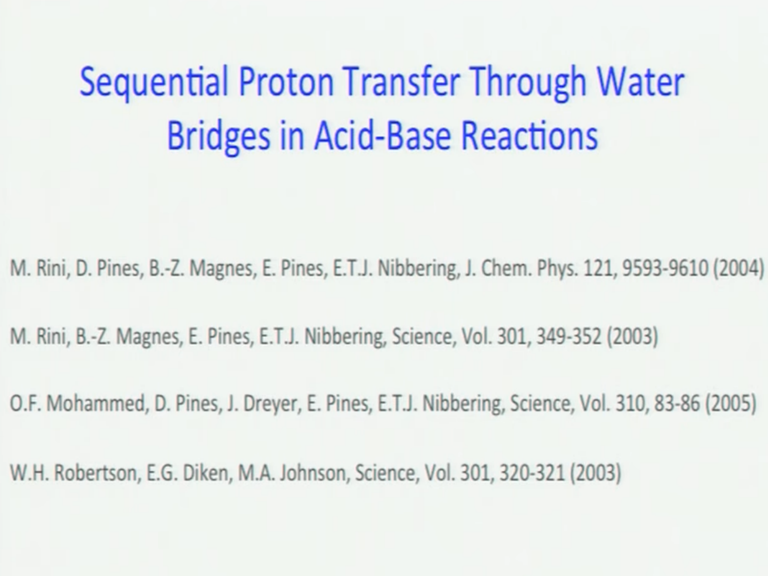

Sequential Proton Transfer Through Water Bridges in Acid-Base Reactions

M. Rini, D. Pines, B.-Z. Magnes, E. Pines, E.T.J. Nibbering, J. Chem. Phys. 121, 9593-9610 (2004)

M. Rini, B.-Z. Magnes, E. Pines, E.T.J. Nibbering, Science, Vol. 301, 349-352 (2003)

O.F. Mohammed, D. Pines, J. Dreyer, E. Pines, E.T.J. Nibbering, Science, Vol. 310, 83-86 (2005)

W.H. Robertson, E.G. Diken, M.A. Johnson, Science, Vol. 301, 320-321 (2003)

And one experiment that has been done very elegant experiment using a photo acid we have discussed already is the mechanism of sequential proton transfer through water bridges in acid base reaction. I did not give all the reference last time. So let me make up now if you are interested in learning about this these are the paper that you can study. You can see J Chem Phys science.

So the reason why so many papers have been published in science this is that it is very fundamental question. So if you can provide an answer to a question that has stayed on for a long time then it is highly interesting. And that is what mainly in Nibberings group and to some extend Johnson group had done.

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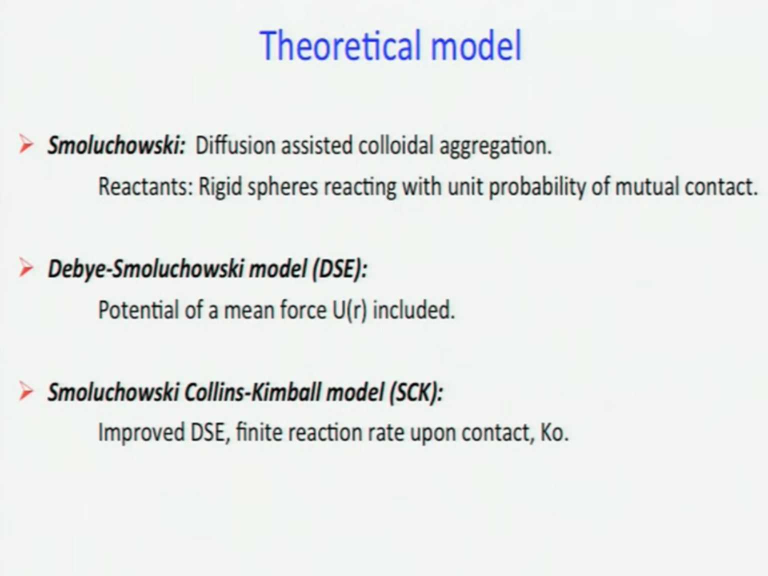

Theoretical model

- ***Smoluchowski:*** Diffusion assisted colloidal aggregation.
  Reactants: Rigid spheres reacting with unit probability of mutual contact.
- ***Debye-Smoluchowski model (DSE):***
  Potential of a mean force U(r) included.
- ***Smoluchowski Collins-Kimball model (SCK):***
  Improved DSE, finite reaction rate upon contact, Ko.

And this is something again I did not say last time and then I felt that this discussion is incomplete if I do not at least mention them. So in all kinds of experiments actually it is important to know theory understand theory be aware of what has been done by theoretical chemist otherwise it is not possible to make much of progress. There are so to do experiments one cannot be afraid of reading papers of computational chemistry or molecule dynamic simulation so on and so forth.

We are going to do a good theory you cannot be afraid of reading experimental paper. It is actually a synergetic go hand in hand. So in theoretical model that is what is that are very important here you see all of them have a name of one person and that is Smoluchowski. Smoluchowski you might have read Smoluchowski name in some of the context but his worked was one mainly in liquid phase.

So to understand how proton get transferred in hydrogen bond network as you talking about hydrogen bonded network there is connection with what we did in the last module there also it was high energy get transferred in hydrogen bonded network. So here Smoluchowski model was for diffusion assisted colloidal aggregation. Then in the next step is Debye Smoluchowski model dealt with this potential of mean force method to adjust a same problem.

And Smoluchowski Collins Kimball model of course names I am taking are all stalwarts, I think everybody has heard this names. Anybody who has done MSc physical chemistry would definitely have at least heard this name. If not I have studied their work so there has been a continuous improvement in theoretical studies in this context.

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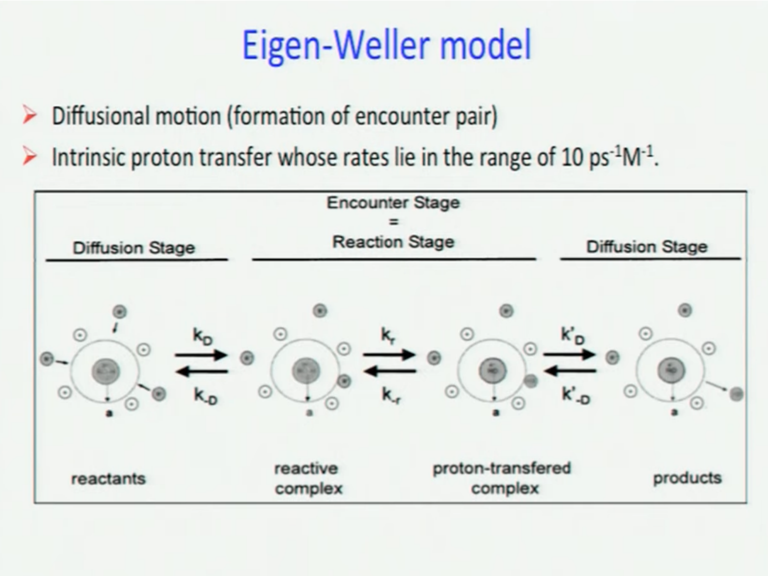

Eigen-Weller model

- Diffusional motion (formation of encounter pair)
- Intrinsic proton transfer whose rates lie in the range of 10 $ps^{-1}M^{-1}$.

And very celebrated model that existed already is this Eigen Weller model. So you see that experimental results of Nibberings that I showed you earlier and I am going to show you in few minutes I once again that did not fall from the sky because they already knew that this Eigen Weller model existed. Remember I had talked about encounter stage all that, all that was actually predicted theoretical. So again there is a diffusion stage in which you have this is the acid this is the base and the diffusion stage the acid and base has come together and form the reactive complex.

And then the encounter stage or the reaction stage this reversible reaction takes place which involved protonation deprotonation. And in the third stage the proton transferred species have to diffuse apart ok. If this stops the encounter stage then what will happen then some proton will be transferred some will not be transferred. So finally it do not really get that acid based reaction to that extent. So it is the diffusion in and diffusion out they are naturally going to be very important in this entire process.

So this is Eigen Weller model we are showing you only this schematic but of course they will develop the model that is very detailed lot of work into that. And the most important extract from there that we can take is that the intrinsic proton transfer here that is our 10 picosecond per picosecond per molar. Ok the very first one that is why you need ultrafast. So to study this ultrafast UV pump IR probe and IR pump and IR probe both have been done ok. To the best I gave you a impression that only UV pump IR probe is done that is not actually the case the both are actually done.

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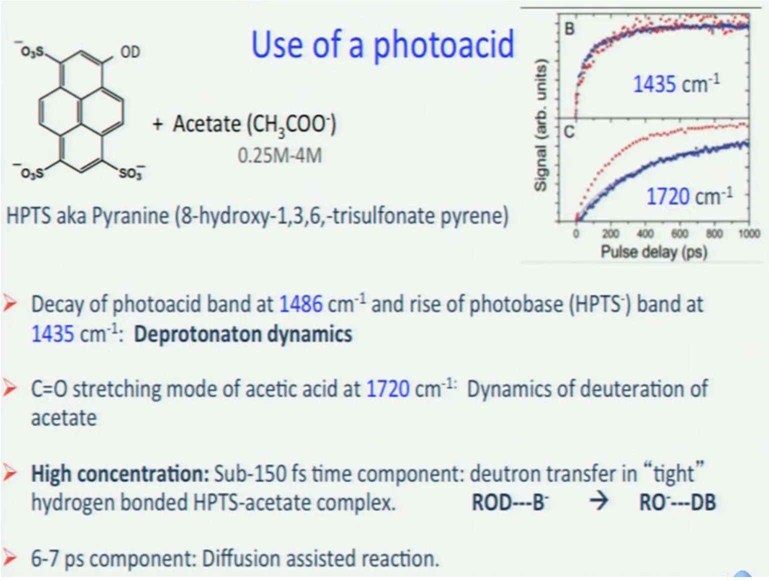

Use of a photoacid

+ Acetate (CH_3COO^-)
0.25M-4M

HPTS aka Pyranine (8-hydroxy-1,3,6,-trisulfonate pyrene)

- Decay of photoacid band at 1486 cm^{-1} and rise of photobase (HPTS$^-$) band at 1435 cm^{-1}: **Deprotonaton dynamics**
- C=O stretching mode of acetic acid at 1720 cm$^{-1:}$ Dynamics of deuteration of acetate
- **High concentration:** Sub-150 fs time component: deutron transfer in “tight” hydrogen bonded HPTS-acetate complex. **ROD---B$^-$ → RO$^-$---DB**
- 6-7 ps component: Diffusion assisted reaction.

Ok and the acid photoacid that we use I will go little fast on this part because we have presented this already was is this Pyranine the decay of the photoacid band is 1486 centimeter inverse rise of the photobase is the it is the anion corresponding anion after the loss of proton. That is that 1435 centimeter inverse. We follow this you get to know the deprotonation dynamics. CO stretching mode of acetic acid is at 1720 centimeter inverse. So the base that is used is acetate right.

So when acetate becomes acetic acid then this 720 1720 centimeter inverse stretch should show a rise time. That gives to the dynamics of protonation of acetate. Here it is written deuteration because they are actually used a deuterated photoacid because then the signals are easier to see. So as we said earlier in a high concentration we see that this dynamics are same at low concentration they are different that is where this diffusion comes in.

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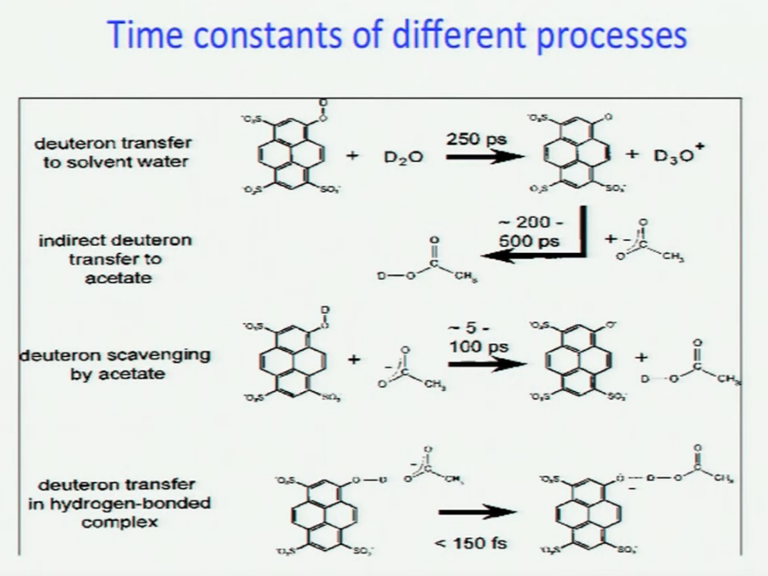

Time constants of different processes

deuteron transfer to solvent water

indirect deuteron transfer to acetate

deuteron scavenging by acetate

deuteron transfer in hydrogen-bonded complex

I have already shown you this data and this one is a little more detailed than what we shown earlier. There here the numbers are actually mention by analyzing the data they could work out all the time constants.

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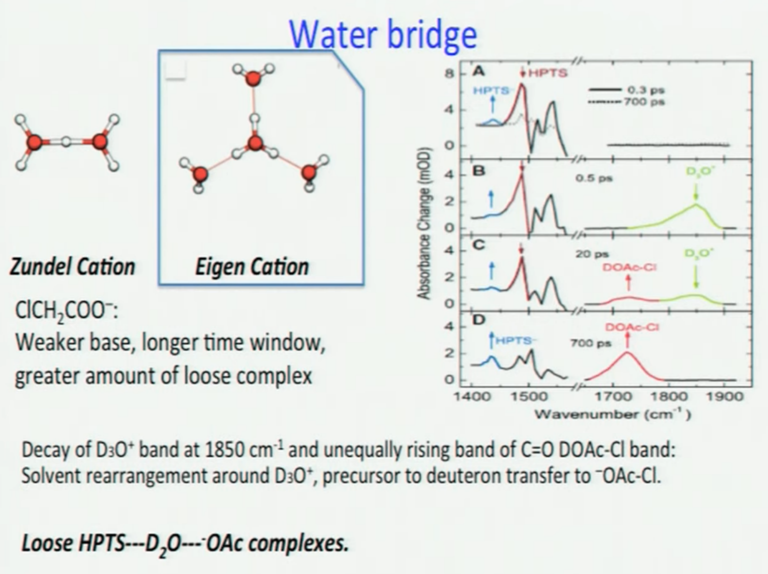

Water bridge

Zundel Cation

Eigen Cation

$ClCH_2COO^-$:
Weaker base, longer time window, greater amount of loose complex

Decay of D_3O^+ band at 1850 cm^{-1} and unequally rising band of C=O DOAc-Cl band: Solvent rearrangement around D_3O^+, precursor to deuteron transfer to $^-$OAc-Cl.

Loose HPTS---D_2O---$^-$OAc complexes.

And then what they found is that when you found talk about water bridge and this is an important this is another reason why I wanted to show you this explicitly once at least. There is there has been a lot of work on what kind of associated states protons exist in water. And even now people do contest these things. But it is lastly believed what we talked about always is H3O+ right. But why will it stop at H3O+ after all look at this first one this is oxygen, hydrogen that is H3O+.

That can get hydrogen bonded to another water molecule right. So this kind of cation where H3O+ is hydrogen bonded to a molecule to another water molecule that is called Zundel cation. And the second one where each you can see the central moiety here is H3O+. Where H3O+ is hydrogen bonded to not 1 but 3 water molecules that is called the Eigen cation as you perhaps understand these 2 ions would have different IR frequencies.

The stretches would have different IR frequencies. So by looking very carefully at the IR spectra what you see is that you get this D3O+ signal going down you get something rising here. So, careful analysis reveals that this Eigen cation can be detected actually. So when you formed that encounter stage you do get an Eigen cation.

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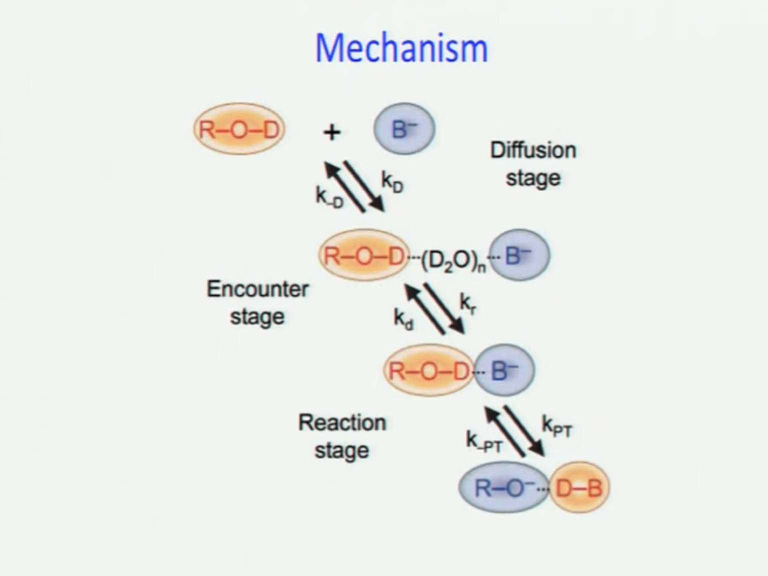

Mechanism

And hence this mechanism was illustrated ok. So that is the revision that I wanted to do quickly.

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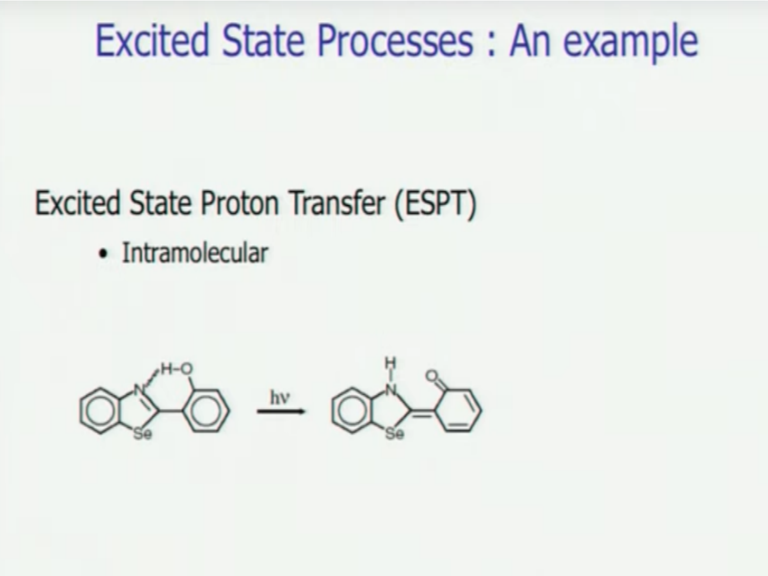

Excited State Processes : An example

Excited State Proton Transfer (ESPT)

- Intramolecular

Now let us move on to the introduction of excited state proton transfer. So the thing is this suppose we said that upon photo excitation organic acids become more acidic organic basic become more basic. Now suppose in a molecule we have an organic acid as well as an organic basic. We have phenolic OH and we have a nitrogen imidazole nitrogen or something. Then what will happen this is the situation this is the organic acid group this is organic base group and this is hydrogen bonding.

The shine light there is proton transfer. And this proton transfer takes place within molecule itself. That case it is called excited state intra molecular proton transfer and this is an example of molecule where excited state intra molecular proton transfer takes place. Now if you have 2 molecules coming close together you can intra molecular transfer as well.

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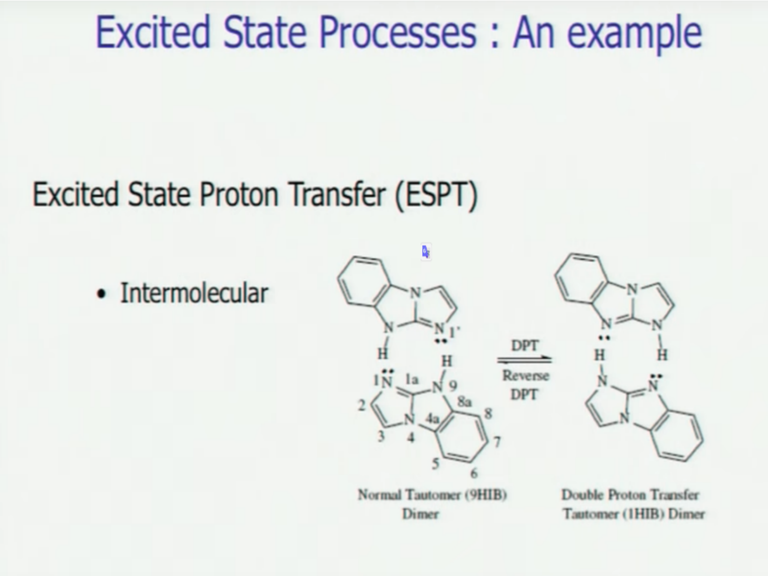

Excited State Processes : An example

Excited State Proton Transfer (ESPT)

- Intermolecular

And for intermolecular proton transfer the kind of molecule that have been studied very extensively this is not really 7 Azaindole dimer. I will discuss 7 Azaindole next day very close. So does this remind you have something this kind of a structure where you have 2 molecules that are hydrogen bonded to each other and from a pair of molecules? Generally they remind us of hydrogen bonded base pairs of DNA.

So the claim to fame of 7 Azaindole primarily is that it is supposed to be a good model of hydrogen bonded base parity GC of DNAs. So we will come back to the actual 7 Azaindole problem the next day.

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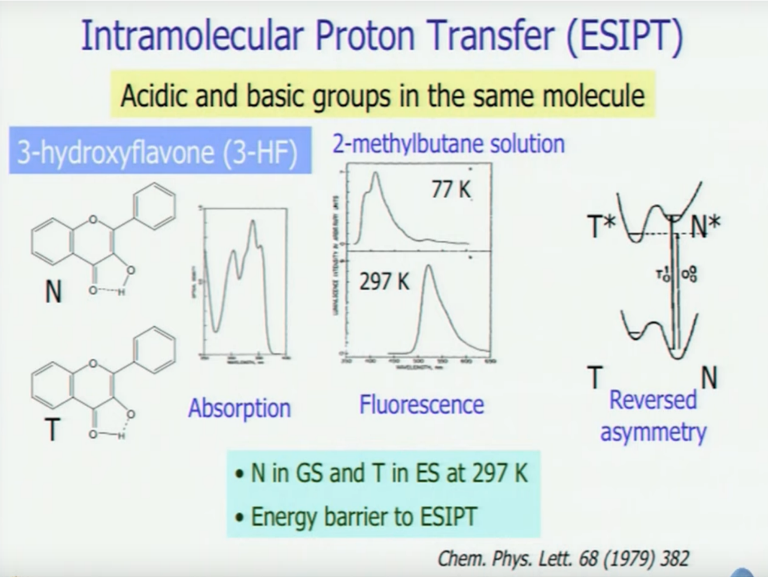

Intramolecular Proton Transfer (ESIPT)

Acidic and basic groups in the same molecule

3-hydroxyflavone (3-HF)

2-methylbutane solution

- N in GS and T in ES at 297 K
- Energy barrier to ESIPT

Chem. Phys. Lett. 68 (1979) 382

But now let me present to you this piece of paper which I am very fond of as you can see it was published in 1979 long ago 40 years ago and this is actually remarkable paper. Kasha is a legendary kasha Michael Kasha of fluorescence spectroscopy Sengupta became a professor in a Pradeep Kumar Sengupta become a professor in saha institute of nuclear physics. He retired about 10 years ago 9 years ago. And you can understand in 1979 so we they did not really have the instrument that we have today. So what I am going to present in the next few minutes is actually all steady state data.

No ultrafast no time resolved even because it is important to understand the steady state spectra before we can going into time resolved data. So see the reason why the people got interested in 3 hydroxyflavone is a product and all is that look at the absorption spectrum well you can only look at it we cannot read at the X axis unfortunately but I will just tell you this absorption is in UV this colorless compound.

But emission is in the green 297 kelvin room temperature emission is in the green. So you have a molecule that you excited at UV high energy and it emits in the green which is considerably lower energy why? As we have studied earlier one of the most prominent signature of excited state processes is stoke shift and here we definitely have a stoke shift. And the one that what is not shown here is that the excitation spectrum matches the absorption spectrum.

So stoke shift is not due to presence of some impurity. Why does this happen? To explain this and that is the time when ESPT was being discussed for the first time to the works of Feler and all. What they looked at the structure this is the structure ground state that is established. And you can see there is a phenolic OH and there is a carbonyl, group oxygen. So one might expect that upon excitation this proton goes from this oxygen to this oxygen and from this ground state normal form it forms a tautomeric forms in the excited state.

We will have more to say about the energy diagram shortly. But if this is the model then the next piece of data already in front of you is this. The experiment that was done is you look at the spectrum at low temperature nitrogen liquid nitrogen temperature it is 77 kelvin. And then immediately you see a blue shift it is hardly anything that resembles the room temperature emission spectrum the entire emission moves to blue.

And now look at this spectrum unfortunately they might not have had and of course they did not have computers that we have like today's normalization and all where not done. But look at this look at this spectrum forget about the first part look at this bands and look at this band structure. Do not they look alike mirror images? So at liquid nitrogen the spectrum that you see is for the local excited state at liquid nitrogen temperature.

So if this is the ground state the emission at 77 kelvin is due to the corresponding locally excited state N star. And in the, at room temperature this stoke shifted one is due to the proton transfer tautomeric state ok. Of course, it is only logical to ask who has told you it is proton transfer and that is address shortly some excited state processes right. So we can say that this is emission from the Franc Conden state this is the emission from the nascent state that is the one that is formed by excited state process.

So what would the energy diagram look like? From the absorption spectrum here there is no signature of the ground state corresponding to this green emission excited state. So the energy of the N form has to be significantly lower than energy of T form right. So you get what is called a double well potential. What happens in excited state? In excited state you see at room temperature emission is exclusively from T star. That means in excited state T star must have low energy in than N star. So again you have a double well potential let me so what I am saying is this

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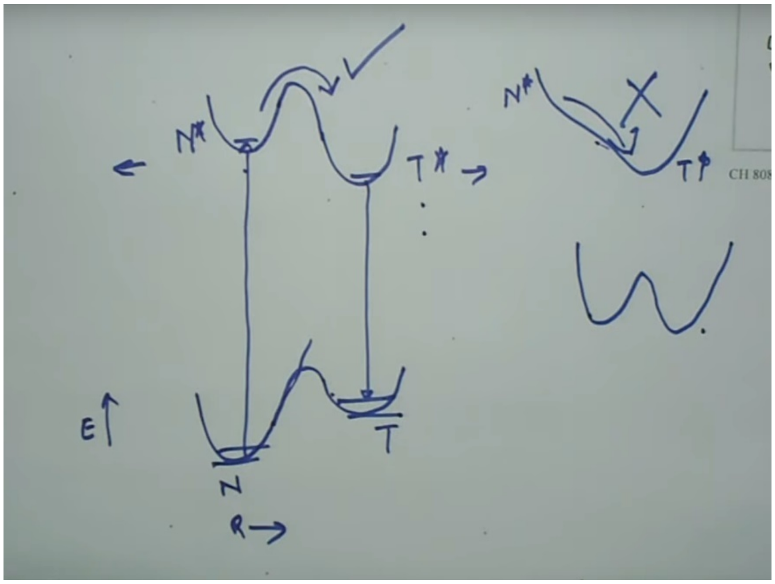

In ground state this is the energy of N let us say x axis so this is the energy y axis x axis is a reaction coordinate you can write R this is N and energy of T must be higher right. So this is double well and let us see ok will back to that in the excited state however this would be energy surface for N star. Energy surface for T must be lower in energy right. So this energy gap is naturally much higher than this energy gap.

So there is why T star fluoresces in green N star fluoresces in blue alright. Now to complete the picture I will draw this reaction barriers. How do you get the barriers because there is some curve crossing and mixing of this 2. How do I know if there is a barrier I could have drawn a diagram with this is N star this is T star. Why I am saying this is not the case and this is the case because there is a temperature effect.

If the barrier is sufficiently high then what will happen? At low temperature the molecule cannot cross and you will see emission exclusively from N star that is what is happening. If there is no barrier then even at 77 kelvin you should see some T star emission. So the effect of temperature that is present there that will tells us that this is an activated process. So this is how the energy diagram turned out to be ok.

So what do you have this is one well double well potential here also double well potential. Double well potential can be two of 2 types. If the energy minima are same then it is called symmetric double well potential. If they are not same then you called them asymmetric double well potential ok. And here you see this is the diagram that was drawn. So you have asymmetric double well potentials ground as well as excited state.

And when you go from ground well to excited state the asymmetry is reversed asymmetry is there. So this is the schematic that was drawn and later on plenty of calculations have been done to prove that this is correct. Now we come back to the question who has said that this is proton transfer and not something else. To do that, experiments were done in methanol and Deuterated methanol.

So in which proton transfer and if the proton here of course there is a catch we will come to that so if a proton transfer and the reaction coordinate is the proton transfer coordinate that is the important part then you should see this primary kinetic effect primary kinetic isotopy effect right.

So you should see more of proton transfer in methanol than in Deuterated methanol because deuterated is heavier that is what happens.

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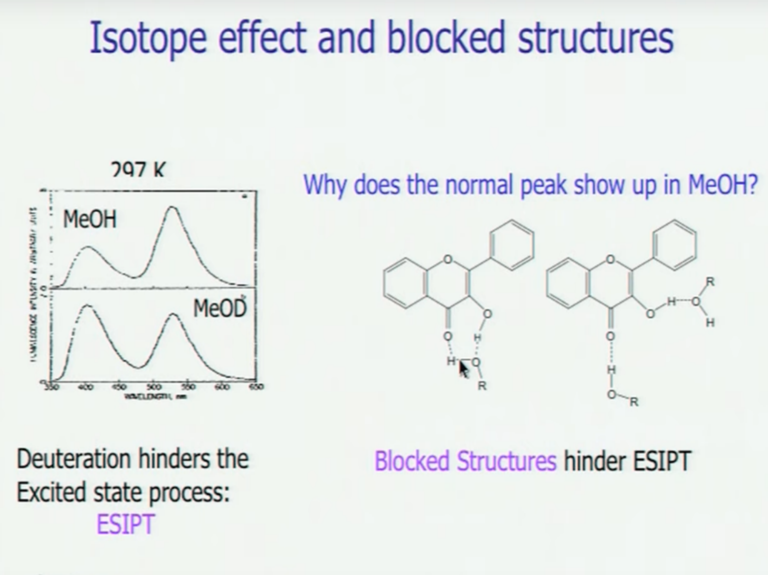

Isotope effect and blocked structures

Why does the normal peak show up in MeOH?

Deuteration hinders the Excited state process: ESIPT

Blocked Structures hinder ESIPT

This are the emission spectra by the way this is 2 methylbutane something very close to our 3 methyl pentane. Non polar and this is methanol and MeOD. Why this particular solvent because you are going down to 77 kelvin you cannot work with water you cannot work with aceto nitryl because you need a solvent that forms glass. It will remain transparent and does not become hazy at low temperature.

So methanol ethanol, methanol ethanol mixtures, 2 methylbutane, 3 methyl pentane is that some solvent that forms glasses. And depending on you experiments you might want a polar glass or non-polar glass. So earlier it was polar non polar now it is polar. So in here you see the ratio of N to TP N star to T star band is more in methanol than in deuterated methanol right. That is why we get an indication that it is proton transfer in the excited state and proton transfer is the reaction coordinate.

Why I am saying this because later on has been shown that for many proton reaction you do not see kinetic isotropy effect. That is because this is not the reaction coordinate because the lowest process determines the rate of the reaction. So suppose the molecule is such that this is your OH group and this is your proton accepting group okay. There in some kind of an orientation where they have not close and it requires a conformational relaxation to bring the OH group close to the proton accepting group then this conformational relaxation becomes the reaction coordinate ok.

So at that time you do not see any effect of protonation because how much time it takes for this to take place that is what it determines the rate. Compare to that this proton transfer is so fast then you do not see an isotropy effect. Fortunately, in this case the molecule is planar right no question of any relaxation that is required. So proton transfer is the reaction co ordinate and you see primary kinetic isotropy effect ok.

Of course we are showing you only the one of the earliest works in this molecule there have been many later on. Ok so proton transfer is established but this spectrum bring up a new question. Remember what is the spectrum is like in non-polar solvent room temperature single band right green emission. What is the spectrum like this are all room temperature spectra? Here in methanol or deuterated methanol you see 2 bands instead of 1.

So normal peak normal band which is not there in non-polar solvent why does it show up in protic solvent and well this is another reason why I like this paper so much because introduces you to many important factors in proton transfer. Well what happens in hydrogen bonding solvents is that you can of course you will get hydrogen banding with your solvents all around. So you get this kind of blocked structures.

Block structure means your OH proton even though it is also believed that if there is an internal inter molecule hydrogen bond it is the possibility of that then inter molecule hydrogen bond will not be formed by they may not hold in liquids due to sheer number of solvent in molecule present around a solid molecule. So this kind of structure so just look at this if there is hydrogen bonding in this carbonyl oxygen and Nibbering alcohol molecule then what will happen? It will be difficult for it to take to hydrogen bond with another proton and accepted. So block structures hinder ESIPT that is something that is normal

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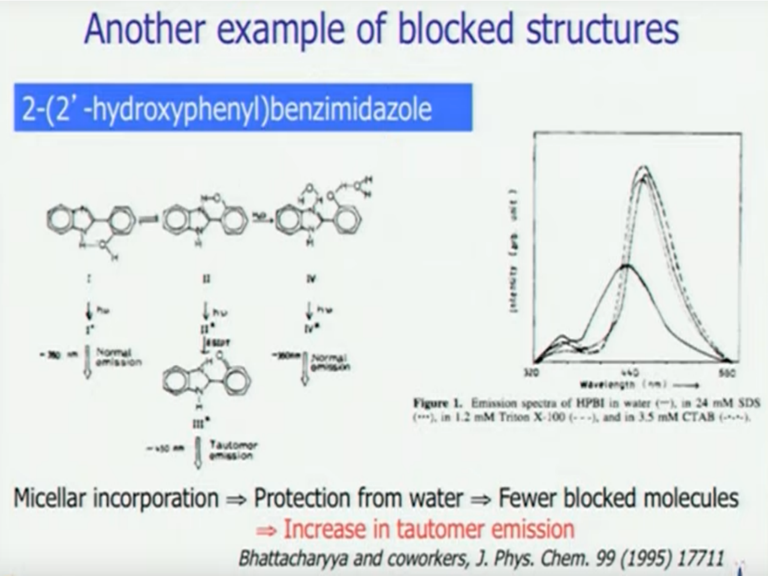

Another example of blocked structures

2-(2’ -hydroxyphenyl)benzimidazole

Figure 1. Emission spectra of HPBI in water (—), in 24 mM SDS (···), in 1.2 mM Triton X-100 (- - -), and in 3.5 mM CTAB (-·-·-).

Micellar incorporation ⇒ Protection from water ⇒ Fewer blocked molecules

⇒ Increase in tautomer emission

Bhattacharyya and coworkers, J. Phys. Chem. 99 (1995) 17711

And this is an example of block structures again I am very fond of this paper because this is my first published paper molecule is HPBI. This small band that you see is due to the normal form this is due to tautomeric form. Here what happens is this molecule exist in different tautomer’s. So you always get 2 bands here all what happens is here when the molecule is incorporated in micelle you see there is a rise in tautomer that is because it is protected from water and you have fewer blocks structures tautomer emission is enhanced. But do not think that hydrogen bonding is always the Villian sometimes it can be hero as well.

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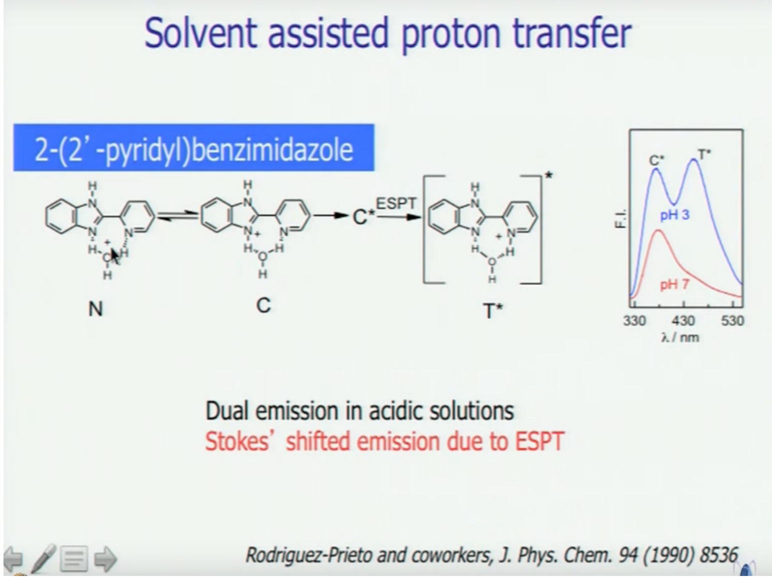

Solvent assisted proton transfer

2-(2’ -pyridyl)benzimidazole

Dual emission in acidic solutions

Stokes’ shifted emission due to ESPT

Rodriguez-Prieto and coworkers, J. Phys. Chem. 94 (1990) 8536

There are plenty of examples this molecule has been studied extensively by this group of Rodriguez Preito and then we have done some work of this in confine media lot of work or this family the pyridyl benzimidazole. Here the geometry of the molecule is such that you need a H3O+ bridge for the proton transfer to take place. So if you do not have this hydrogen inter molecule hydrogen bonding with solvent then there is no ESIPT.

So it can work both ways right. To conclude we have introduced this concept of excited state proton transfer intra molecular and inter molecular. And we have discussed some of this salient factor that have a role to play in its dynamics. So next day we are going to talk about this celebrated debate of inter molecular excited state inter molecular double proton transfer. ESIDPT in 7 Azaindole dimers will that is going to teach us how careful one has to be while analyzing ultrafast dynamics data.

So here we have an example of a nobel laureate going wrong. And it also takes us to another important concept in fluorescence spectroscopy we always go by Kasha rule and we think Kasha rule is always correct. Maybe as a prelude to the 7 Azaindole problem we will discuss to what extent Kasha rule is correct when you look at time revolution of emission spectrum okay That is what we are doing in the next module.