Ultrafast Processes in Chemistry

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Module No # 11
Lecture No # 52
Excited State Double Proton Transfer of 7 – Azaindole Dimer 1

Today we trying to discuss one of the most intriguing debates that went on for about 10 years from 1997 98 to about 2008 in the field of excited state process excited state dynamics. The reason why this is very close to my heart is that it is started when I was a PHD student when I was working in protons transfer. So and we could see that something interesting is breaking out and the 2 groups involved one were of Tahie Tahara who was in institute of molecular science Japan at that time later on it moved to RIKEN and the other group was Ahmed Zewail's group.

And this is started in about 1995 96 97 when all of us could clearly see that Ahmed Zewail is going to get the Nobel prize. So a potential noble loreate and on the other hand we have 33 year old Japanese researcher led group somebody who had that time did not was not confident in speaking English never went out of Japan. So that was almost battle of David and Goliath were and at the risk of giving a spoiler in the story in bible Goliath won that is what often happens in life as well.

But it is not really an issue of winning and losing this debate actually teaches us several interesting things maybe we will come to that at the end of this discussion. This discussing expected to span 2 modules before getting into this debate of 7 Azaindole Dimer let me first present something else that also comes from the group of Tahie Tahara more or less in late nineties. So all of us know Kasha's rule and all of know that the reason why this emission spectrum to be mirror image of absorption spectrum is when you draw Jablonski diagram this is what we always draw.

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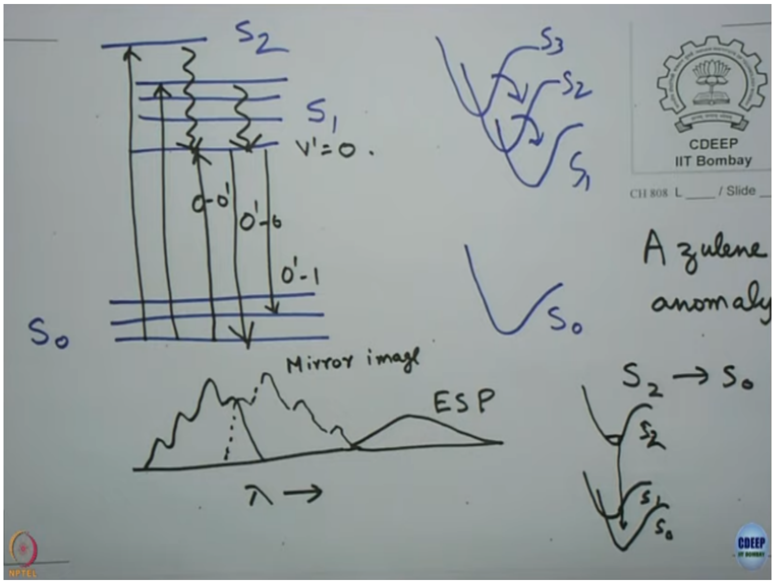

This is S0 let us say this is S2 then this can be many more of course and let us say this is S1 different vibrational states of S1 what we have learnt is that you excite no matter where you can excite to S2 you can excite to higher vibrational level of S1 there is always ultrafast vibrational relaxation to V dashed equal to 0. The lowest vibrational state of S = 1 and that is where the emission takes place from.

So this is the 0 dashed 0 transition you can have things like 0 dashed to 1 transition you can have something like 0 dashed to 2 and so on and so forth. And while excitation while exciting you can excite 00 dashed and you can excite to higher level as well. So we are very familiar with this kind of a picture where this is the absorption spectrum energy decreases this way so wavelength increases this way and this is the emission spectrum and we as we have said earlier we what to expect to see for well-behaved molecule.

Of course the entire business that we have is about molecules that are not well behaved because if all fluorescence spectra or at mirror images of absorption spectrum then this not much you can do about it anyway. So when we have excited state processes we get this red shifted band somewhere here so this is the mirror image spectrum and this is the spectrum from that arises from the excited state process I just write ESP.

Now the reason why you do not get emission from S2 usually is that if I draw not like this but in a different way if I draw potential energy surfaces then generally this is the case this is S0 this is

S1 this is S2 this is S3 and so on and so forth. Of course relative position of minima can be different what we are we want to highlight more is that there is a energy gap between S0 and S1 and generally S1, S2 S3 this 3 not only close in energy but generally this is crossing of the potential energy surfaces that crossing can be adiabatic non-adiabatic that is a different question.

So since energy gap is small it is very easy for non-radiative processes to happen among all this excited SN states and S1 is lowest energy state there is an big energy gaps so according to energy gap law V dashed = 0 of S1 that is where the molecule can reside for a while and that is when fluorescence get a chance this is a very premise of Kasha's rule and we have already seen how Kasha's rule can be violated deep excited state processes are formed are there then get red shift spectra.

Now we go to the other end of the story is it possible in any way to get emission from S2 or S3 and there is a very famous example most of us might know and that is Azulene so that used to be referred to for a long time for Azulene anomaly. In Azulene the major fluorescence is from S2 to S0 why that is because for Azulene I will just draw it here the energy diagram is like this is S0 S1 actually has an overlap with S0 and there is a big S1 S2 gap this is the conventional picture that has been known for 50 60 years.

So that is why if you excite to S1 non radiative process is takeover if you excite to S2 then only you can get some emission. So Azulene has an emission band that is at higher energy than the lowest energy absorption band because lowest energy absorption band of course it is S0 to S1 emission in this case S2 to S0 okay so this is something that is known classically. Now Tahara's group had tried to ask the question what happens in very short times is it that S2 is really not fluorescent no fluorescence takes place or is it that the life time is so small that you do not see the fluorescence in this steady state spectrum.

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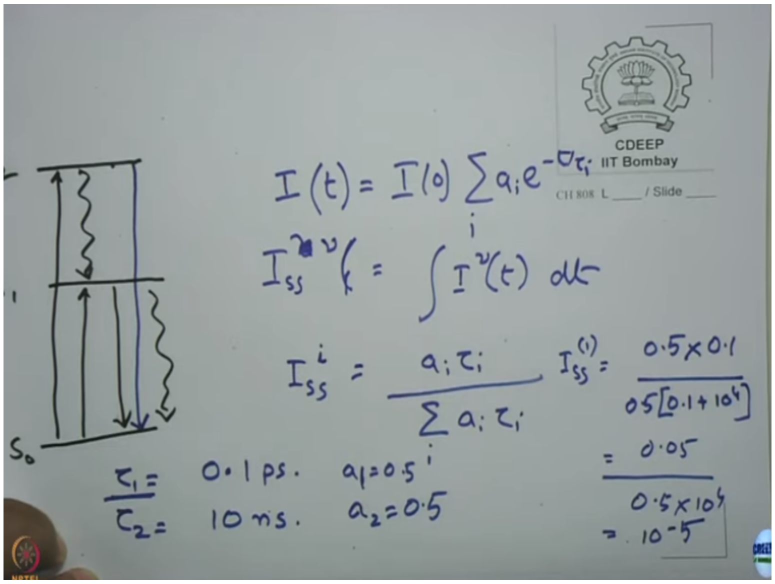

$$I(t) = I(0) \sum_i a_i e^{-t/\tau_i}$$

$$I_{ss}^{\nu}(\lambda) = \int I^{\nu}(t)\, dt$$

$$I_{ss}^{i} = \frac{a_i \tau_i}{\sum_i a_i \tau_i} \qquad I_{ss}^{(1)} = \frac{0.5 \times 0.1}{0.5[0.1 + 10^4]} = \frac{0.05}{0.5 \times 10^4} = 10^{-5}$$

$\tau_1 =$ 0.1 ps. $a_1 = 0.5$

$\tau_2 =$ 10 ns. $a_2 = 0.5$

So the question is this is it possible and now I will draw only 3 lines make things simple S0 S1 S2. So excite to S1 you get fluorescence and you get some non-radiatve process understood excite to S2 what is believed is this non-radiative process takes over okay and there can be some non-radiative process between S2 and S0 as well. But suppose for the sake of argument we say that there is emission for S2 from S2 as well.

First of all where will that emission come higher energy or lower energy compared to the S1 emission naturally higher energy. Now the problem is this we discussed this multi exponential model of fitting fluorescence decays right. This is the most popular model were you fit like this I of time T = I at time 0 sum over I ai e to the power –Ti / Tau i and steady state intensity and now I will write lambda also at some particular lambda or better write frequency there is a conversion factor between frequency and lambda at some frequency is equal to integral of I Nu at t dt.

So this turns out to be sum over ai Tau i and then what we know is that if there are several components then the contribution to steady state intensity of the Ith component is given by ai Tau i divided by sum over i ai Tau i I believe this all this we have discussed. Now see suppose I have 2 exponential decay bi-exponential decay Tau 1 is something like 0.1 picosecond and I will exaggerate just to bring out the fact tau 2 let us say is 10 nanosecond okay.

And let us say they contribute 50 50 ai is 0.5 sorry a1 is 0.5 and a2 is also 0.5 what will the contribution of this tau 1 species associated with Tau 1 what will be contribution to steady state intensity 0.5 multiplied by so I can write like this Iss of 1 will be 0.5 multiplied by 0.1 if I write it in picosecond divided by 0.5 multiplied by 0.1 + 10 nanosecond means how much? 10000 picoseconds right.

So 10 to the power 4 so what will you do you are going to neglect this 0.1 with respect to 10 to the power 4 naturally. So in the numerator you have 0.05 in the denominator you have 0.5 into the 10 to the power 4 what is the answer? 10 to the power -5 it is really very small so point is if you have emission from a higher energy state that is short lived then you will not see it statistic is that point made where will it be seeing? Is there any way of seeing it? There is a way of seeing it and the only way of seeing it by using ultrafast dynamics we have discussed already.

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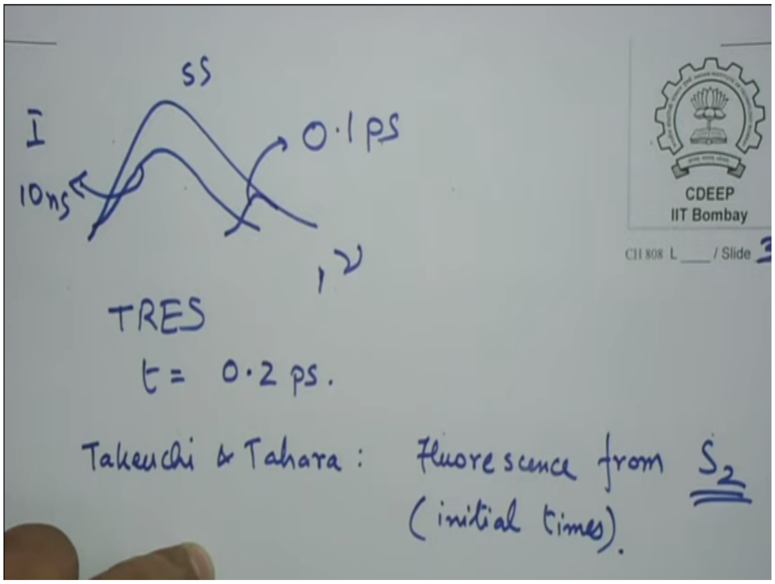

TRES

$t = 0.2$ ps.

Takeuchi & Tahara : Fluorescence from $\underline{\underline{S_2}}$

(initial times).

Let us say this is your emission spectrum steady state this is steady state X axis let us write frequency let us be consisted then I should have perhaps becomes draw into the other way anyway Y axis is intensity. Let us say I have 2 components like 1 like this is the 0.1 picosecond component and this is the 10 nanosecond component. Suppose I look at this steady this the time resolved emissions spectrum which you have discussed earlier.

And suppose you look at spectrum at time t = something like 0.2 picosecond will you agree with me that spectrum at initial times very short time after excitation will be dominated by this species that has a lifetime of 0.1 picosecond. So that is one way in which you can actually see a spectrum that is elusive in steady state right. So this is what mainly Takeuchi and Tahara done prior to this debate actually.

So what they had done is they had taken some molecules and they had demonstrated that you can actually see the S2 spectrum I encourage you to find those papers and read them right in our presentation we are not going to talk about them but what Takeuchi and Tahara had done before the 7 Azaindole debate broke out was that they could actually demonstrate that you can see fluorescence from the S2 state at very small times after excitation okay.

That is the background we need before we can get into the discussion so we are not saying Kasha's rule is wrong we are not saying that Jablonski diagram we had drawn is wrong always saying is that you can hold strictly when you only you do steady states spectroscopy. When you do time resolve spectroscopy then you can actually see things that are relaxing in fast time scale and therefore are not observe in steady state spectroscopy.

Similarly if we go down to further attosecond which is now the state of the art then you can see things that we assume even now in femtosecond time scale to be instantaneous. Almost nothing is instantaneous is anymore okay. So the take home message from this is you can actually see fluorescence from a higher energy excited state if you look at small times post excitation. Now we get back to the debate and see how this concept turned out to be critical in this discussion okay.

So we will talk about excited state dynamics non polar solvents manifested by excited state double proton transfer by 7 Azaindole dimer mainly we will discuss these papers there are many more I am going to show you we are actually presenting almost only one side of the debate we are not presenting the other side so I encourage you to read everything it is a endorsing debate. Now I must thanks professor Tahei Tahara for sharing this slides with me that first of all you almost if not here see it from the author's perspective and it also save my lot of time I did not have to prepare the slide as myself.

So 7 Azaindole dimer is widely popular model for DNA base pairs because if you just look at the dimer it will remind you of how ATGC are there in the DNA okay. So you have 2 kinds of nitrogen's here 1 in a 5 membered ring, 1 in a 6 membered ring you have 2 kinds of nitrogen and the hydrogen is covalently bonded to the nitrogen in the 5 membered ring in both the cases okay.

So this is where I use to get confused that why is it going from nitrogen to nitrogen please be very clear about that the 2 nitrogen not equivalent one is 5 membered ring and one is 6 membered ring there acidity and basicity are different.

So in ground state the proton is covalently bonded to this 5 membered ring nitrogen and hydrogen bonded to the 6 membered ring nitrogen of the neighbor of the partner and that is 2 as in the other as well. What is the symmetry of this system? What is the point group? Do we have the point of inversion point no? Point of inversion yes or no? Actually we do dimer I am talking about the dimer not the monomer point of invasion is there actually but that hardly matter when we are trying to determine the point group unless nothing else is there do we have a principle access of symmetry in the dimer.

We have a C2 access right perpendicular to the plane do we have a horizontal plane right so that makes it C2H do we have perpendicular C2 access one is there no nothing is there. There is no perpendicular C2 access actually because you cannot draw C2 access in maybe you are thinking of this nitrogen that nitrogen right. That may be true if you have a C2 access to this 2 nitrogen's but then these carbons will not find a partner.

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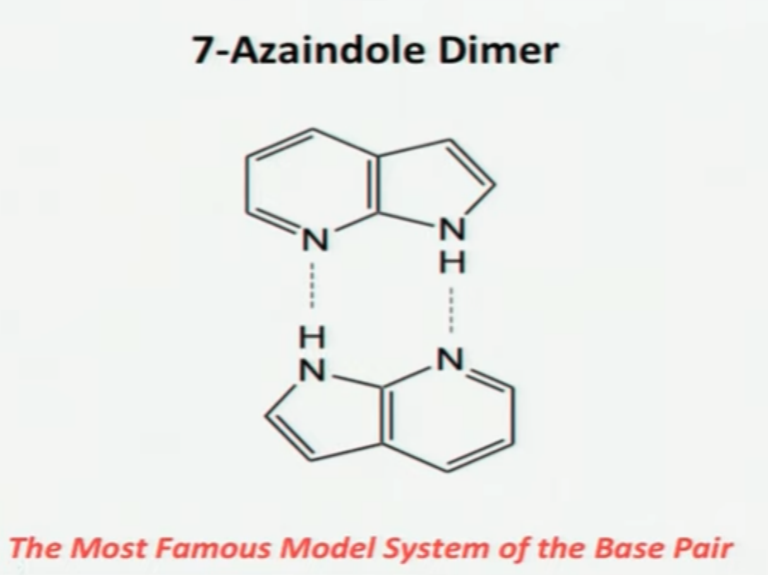

7-Azaindole Dimer

The Most Famous Model System of the Base Pair

And for those you might be wondering what we are talking about in case you need we are talking about symmetry of the molecule and we have a prior NPTEL course on symmetry in chemistry those lectures are freely available on YouTube in case you need help you can refer to that okay.

So this as C2H symmetry we will mention to we will refer to this C2H symmetry in passing a little later.

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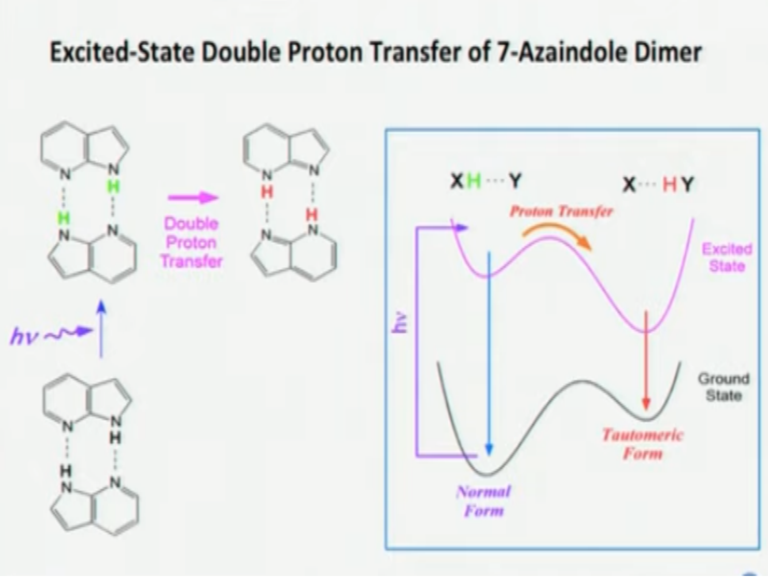

Excited-State Double Proton Transfer of 7-Azaindole Dimer

So this is something that was known for a long time almost as long as the 3-hydroxyflavone case that we discussed earlier. That you have this dimer you excite it and then when you excite remember organic acids because stronger as its in excited state this NH is an organic acid this nitrogen in the 5 membered ring in an organic base this is becomes stronger bases and therefore there is a double proton transfer.

This was known very well I am going to show you a spectra it was manifested amply in the spectrum and the energy surfaces were also worked out. And the energy surfaces is qualitatively same as that what we had for 3-hydroxyflavone asymmetric double well potentials in ground and excited state with the reversed asymmetric between them okay. The state that is more stable in the ground state the well let us say the form that is more stable in the ground state is less stable in the excited state that is why proton transfer takes place in the excited state.

And since 2 protons are getting transferred it is called excited state inter molecular double proton transfer. In our lab we have done some study on another molecule which we call BPOH2 there we have excited state intra molecular double proton transfer.

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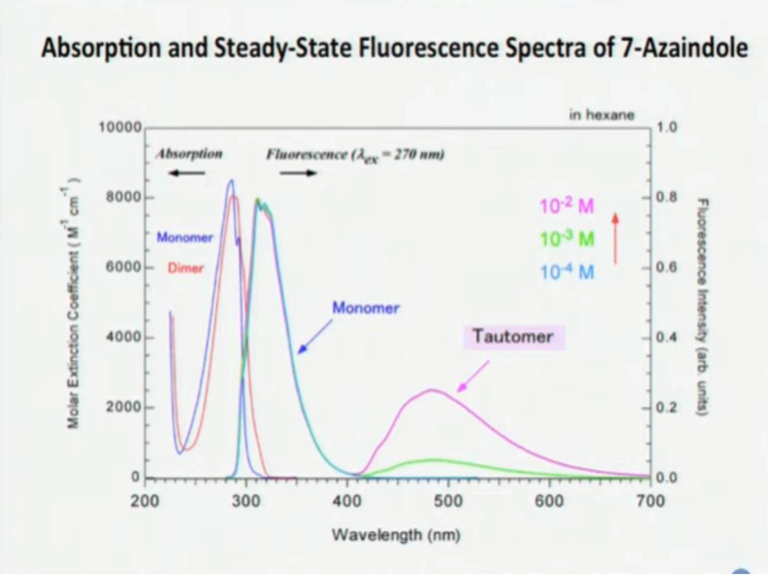

And it is manifested in the steady state spectra as I told you like this okay these are the absorption and emission spectra at different concentration of 7 Azaindole. Do not think that dimer are formed very low concentration they are not in fact even for 10 to the power -4 molar concentrations which is pretty high for fluorescence we do not get dimers okay. In absorption you see there is a little bit of change this one the blue one is monomer and other one which color is it green or red?

Red the red one is for dimer so as concentration increases from 10 to the power -4 molar to 10 to the power -2 molar the absorption changes little bit there is little bit of red shift and the structure also changes. But you get more drastic changes in the emission spectra this is the monomer emission spectrum between 300 and 400 nanometer and you say it is more or less mirror image of the absorption spectra okay.

And this spectra are all I think normalize to this peak as concentration increases what you see is in this 400 nanometer to 700 nanometer region at 10 to the power -4 molar there is hardly anything actually something is there but you will see it only when you write when you draw a semi-log plot. And as the concentration increase as you look for C2 access later it is not there as concentration increases the stoke shifted band characteristic of excited state process keeps on increasing that is why the primary assignment of this to the excited state process happening in dimer was done alright.

So this is something that was known and even reaching there actually was not easy the reason why this debate started in 1998 and not in 1978 is that people have to characterize people have to say with confidence that this is a dimer. So several kinds of studies have to be done must spectroscopy so on and so forth they had to confident that excited state double proton state is taking place and there is lot of studies where already there before the debate broke out. So what was the debate? That is what we will take in the next module.