Ultrafast Processes in Chemistry
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Module No # 10
Lecture No # 53
Excited State Double Proton Transfer of 7 – Azaindole Dimer 2

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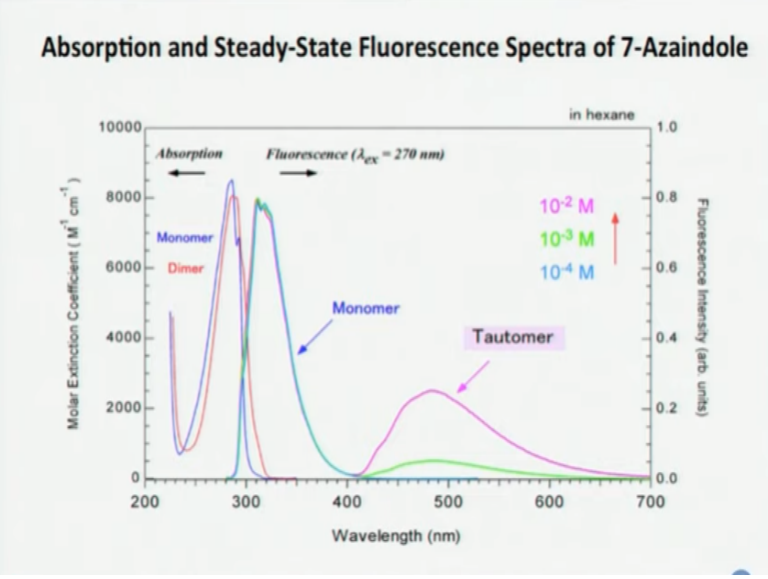

Okay we are back and this is where we left in the last module the absorption and emission spectrum of 7 Azaindole in hexane, n-hexane it is difficult to get this kind of a result in protic solvent because as we discussed in the case of 3-hydroxyflavone in some other case is you would get block structures that are formed the hexane is a better solvent and I am only showing you will not even the tip of the iceberg tip of the tip.

The hundreds of the papers on this where people have done temperature variation quantum chemical calculations different kinds of experiments and it was more or less agreed already by mid 1995 that double proton transfers takes place here. And 7 Azaindole dimer has been studied by people who are not spectroscopy also because it is DNA base pair model so that biomimetic aspect is also there so lot of studies were there for our purpose what we need is?

Upon increasing concentration from 10 to the power -4 to 10 to the power -2 molar small change in absorption is seen but what is most significant is that this monomer emission goes down and

you do not see going down here because it is normalized here. And Tautomer emission becomes very prominent between 400 to 700 nanometer emission maximum somewhere at 480 490 nanometer this tautomer emission becomes prominent in a at higher concentrations right.

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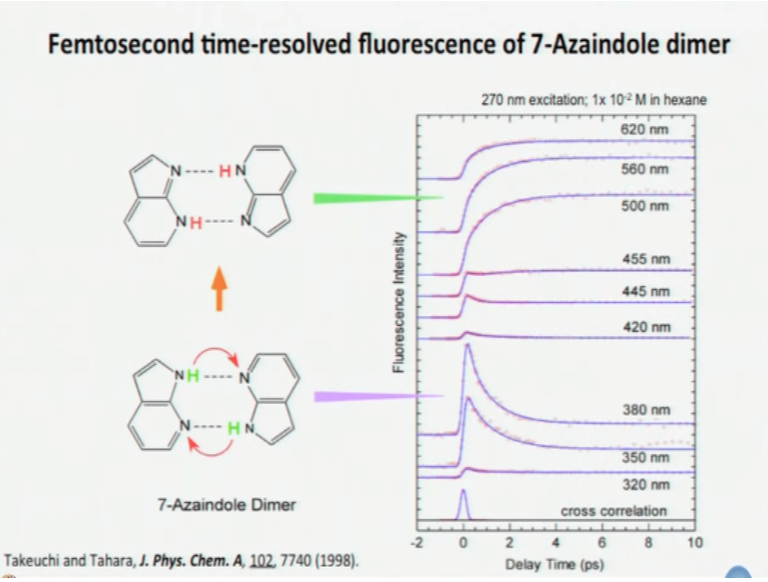

And this is the starting point of our time resolved spectroscopic discussion and this data that you see here is from this 1998 J Phys Chem A paper by Takeuchi and Tahara. So what they started with is this starting point was very well non ambitious and I will show another paper that which was published by as Zewail group before this 1995 so the some background so what they thought was this that alright this excited state double proton transfer takes place we know that this non proton transferred species the locally excited state has emission in 320 to say 400 nanometer region.

And beyond 400 nanometer it is predominantly the proton transfer species and there is another attractive feature look at this spectrum this locally excited state emission gets over by 400 nanometer and that is where the proton transfer species spectrum begins. So good thing here is that here is almost no overlap since this almost no overlap the data are simpler if there is overlap between the 2 then they would be a significant region where you get signal from this as well as that actually it is there as you will see but it is not very much okay.

So if that is the case then as we know then in the region of the non-proton transfer locally excited state Dimeric excited state you expect a fast decay. And in the region of emission of the proton

transfer dimer you expect to see a rise okay this is the expectation and that is what they saw so let us go through the data a little carefully so 320 and this are not normalize by the way that is why you see difference in heights.

At 320 nanometer of course that is the blue end of the spectrum the intensity is really small so you see a decay. It becomes more and more prominent as you go 350 nanometer 380 nanometer when you go to 420 nanometer once again intensity is small and you understand that if you remember the spectrum 420 nanometer is somewhere here. So just before and just after 400 nanometer intensity is small but you have made the cross over already from the locally excited dimer to proton transfer dimer.

And here you see it looks like there is that fast decay still there but there is something very long live and that becomes prominent at 440 nanometer, 445 nanometer at 455 nanometer look at the data very closely what are the features that you see and look for the feature that are subtle what do you see? I will give you the easiest you see a long life time right but there are 2 other features what are the 2 other features? Initial time that fast decay still there that means some monomer emission is still there even though you do not see it really in this steady state it is still there.

Do you see the hint of a rise? Do you see that there is a hint of a rise here? Of course the moment you go from 455 to 500 it is rise all the way followed by a long life time but the reason why I am spending so much time on this is that this is what you see a fast decay followed by a rise when you see emission when you are in the region of emission spectrum where you have both. Generally our expectation is rise is for the destination state right the proton transfer state.

But since the non-proton transfer the locally excited state also makes a contribution to fluorescence at this wave length this is are 2 independent things almost I mean this goes from there fine but you do see the decay there as well so you can get data like this so in our J Chem Phys paper of 2010 I think in another system 2 - 2 dash pyridylbenzaimidazole absorb something like this in our conversion.

This is all of conversion data for us no need to say so after 455 nanometer so this is something that you might get if you do an experiment you should not ignore it. If you go more towards the and you can see that there is deliberately put in a gap 455 and 500 actually they are recorded decays at

many wave lengths in between also but the gap is so you see it nicely that there is a rise. So what is this first decay? Decay of the locally excited state what is the rise due to? The rise is due to the formation of your proton transfer state.

And this decay on blue at blue end and rise at red end emission spectrum is something that you expect that work out this kinetic of this 2 states model where 1 state depletes and as a result of that other state probes you get a simple bi-exponential function where one of the where the formation of second species is associated with a negative amplitude and decay of course as positive amplitude fine.

So qualitatively nothing very surprising but when the decay was fitted and this is where fitting becomes very important as we have said several times earlier you can fit almost everything to a bi-exponential decay that may be appropriate may not be appropriate in this case they could fit the blue end decay to 2 components, 0.2 picosecond and 1.1 picosecond. So there to be confident so whenever you go to bi-exponential fitting there are still plenty of conservative people and for good reason who would start doubting your fit that is how do you know it is not bi-exponential?

How do you know that it is really bi-exponential? Because over parameterization always gives a better fit so one needs to be very careful one needs to have a model in mind and one needs to be able to interpret the data correctly so 0.2 picosecond, 1.1 picosecond. Here Takeuchi and Tahara has helped from their prior work that we discussed in the previous module their already established that the time required for S2 to S1 conversion is something like to 100 200 picosecond like 100 200 femtosecond. So they were confident they was already had this kind of data in other systems the rise was fitted to single Tau.

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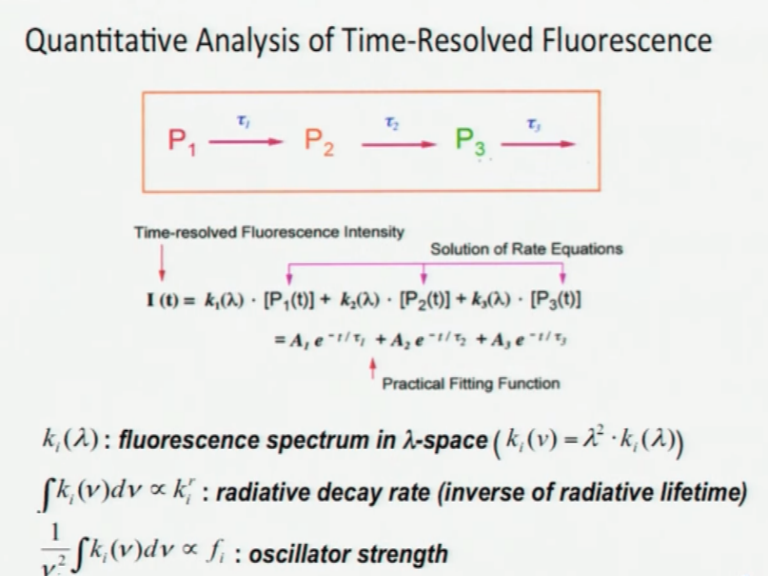

So what they did is for this kind of sequential process where you excite and then you have a first precursor, precursor 1 which makes way for precursor 2 with time constant Tau 1 then precursor 2 gives rise to P3 with time constant Tau 2 which as a life time of Tau 3 you have expression of fluorescence decay like this which is not unknown to us in this course I at time t after excitation is equal to k1 of lambda multiplied by P1 of t + k2 of lambda multiplied of P2 of t + k3 of lambda multiplied by P3 of t which simplifies into our well know tri-exponential fit A1e to the power –t / tau 1 + A2e to the power -1 / tau 2 + A3 e to the power –t / tau 3.

The reason why we are showing this line even to emphasize the fact many times it is not enough to just fit your data and work with the amplitudes you might want to do a simulation of the data when I say simulation I do now mean MD simulation simple kinetic simulation small code that you can write using Matlab you might want to actually work out the kinetics and you might want to get this function P1 of tP2 so on and so forth eventually it will be like this.

So I recommend that you go through the work of Rodricks they have done a very efficient very thorough foster cycle analysis of the time resolve data of proton transfer in benzimadazole source well pyridylbenzimadazole source. Foster cycle is something not discussed in this course but it is there in Lakowicz book among other resource quite easy to understand. Generally when you have things like this it is good if you can foster cycle analysis in case of proton transfer and get greater insight out of your amplitudes in lifetimes that is what Takeuchi and Tahara done.

What is k1 of lambda? That is the fluorescence intensity in lambda space and of course when you go from lambda to Nu you have to multiply by this fact lambda square. If you integrate k1 of Nu over all frequencies then that gives you an idea of radiative decay rate is the inverse of radiative life time. So remember in basic courses of spectroscopy we talk about Einstein kinetic treatment of stimulated and spontaneous emission.

So hence we get Einstein's A coefficient and coefficient and B coefficient Einstein A coefficient is associated it is basically a rate constant associated with a spontaneous decay. Inverse of that is the radiative lifetime that we are of talking about. And you can get the oscillator strength you might remember is something that tells you how well how strong the transition is so oscillator strength is has simple mathematical relationship with other parameters like the experimentally determine epsilon molar absorption coefficient of molar extinction coefficient.

And transition moment integral which is theoretical quantity so oscillator strength is a more classical concept and you can find it from this data by integrating K1 over all frequencies and dividing by 1 / Nu square. So this is something that you can get from the emission and the premise of this discussion of getting oscillator strength from the emission when you excite and emission become B1 = B2 right. From there you can actually relate it to absorption as well and we are going to say.

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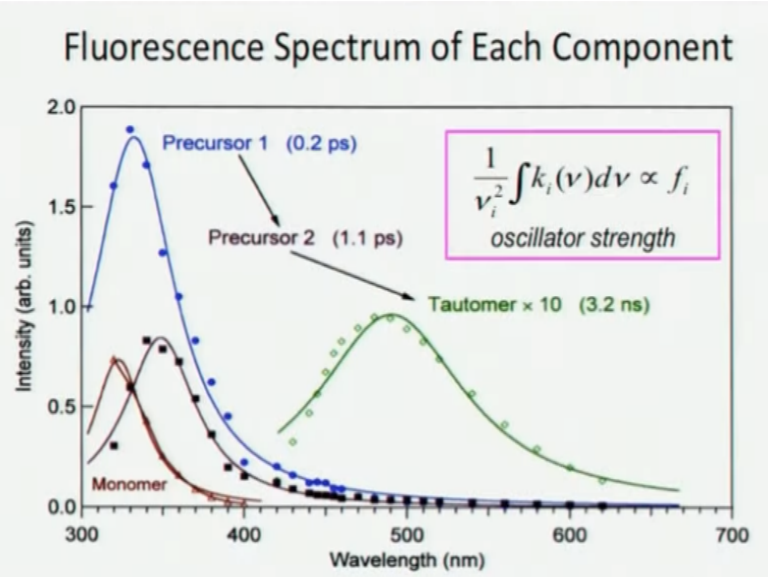

So hence doing all this from the time resolve data Takeuchi and Tahara could construct the fluorescence spectrum of all the components. So this is the fluorescence of monomer not very difficult to find because it is there in the steady state this is the fluorescence of tautomer again not difficult to find because it is there in the steady state. So that helps your time resolve data analysis also.

Then in addition to monomer and tautomer they identified 2 precursors, precursor 1 and precursor 2. Precursor 1 is at smaller wave lengths and therefore higher frequence higher energies precursor 2 is at lower longer wavelengths therefore lower energies. And they established that the 0.2 picosecond time constant is the time associated with precursor 1 to precursor 2 transformation.

1.1 Picosecond is the time associated with not only the decay of Precursor 2 but also the rise of tautomer emission. And here in starts the debate so what they are saying essentially is that we have some precursor to start with from which no proton transfer takes place no tautomer is formed from there you get another precursor which is associated with slightly longer time 1.1 picosecond and from there you get tautomer okay. So it is I will tell you why this was the one of the starting points of the debate but well this we have said already we also determined oscillator strength.

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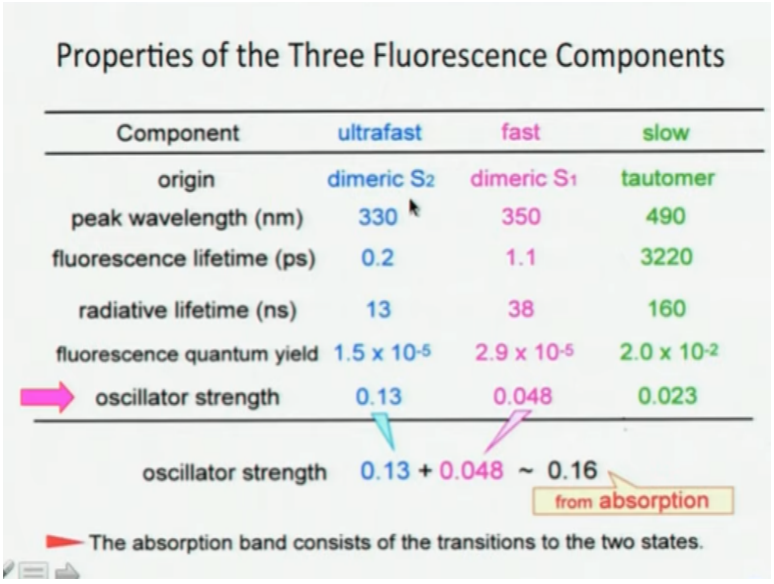

And to summarize that data that they had this is neglect the first line for the moment even though I have shown it you already know the answer there this 3 components right 0.2 picosecond, 1.1 picosecond and 3 nanosecond or so. Peak wavelengths are for the first one 330 nanometer for the

fast decay this species as peak wavelength emission wavelength of 350 nanometer this one this tautomer emission 490 nanometer.

Fluorescence lifetime turns out to be 0.2 picosecond, 1.1 picosecond, 3.2 nanosecond and radiative lifetime turns out to be 13 nanosecond, 38 nanosecond, 160 nanosecond okay. What is radiative lifetime? 1/kr remember what is life time? Life time is 1/kr + knr 1/ kr is 13 nanosecond 1/kr + knr is 0.2 picosecond what does that mean? Means there is some very efficient non-radiative process going on here that is why you do not get so much because 13 nanosecond radiative lifetime is not actually bad it is quite good.

But due to this non-radiative process it does not get a chance so remember I refer to this Einstein kinetic treatment little while ago one thing that is not included in that treatment is non-radiative process. An Einstein treatment you get to learn that spontaneous emission is a reality and it is always there we also get to learn that the rate constant of excitation is equal to rate constant of stimulated emission.

This are the 2 important things that we leant from the treatment rather simple treatment but what is still not done there is non-radiative rate constant which is of utmost importance when you discuss ultrafast process okay. So this is very good piece of data also to sensitizers to the fact that non-radiative processes can bring about a sea change. If you can somehow stop the non-radiative process then this switches will have life time of 13 nanosecond.

Suppose is no non-radiative process at all lifetime will go up from less than picosecond to 13 nanosecond and you will see a huge increase in fluorescence. You do not see it because of the non-radiative process okay and associated quantum means you know how to calculate them Ai tau i divided by sum over i tau . For the ultrafast component it is 1.5 into 10 to the power -5 really very small fast component 2.9 into 10 to the power -5 marginally better.

Slow component 2 into 10 to the power -2 now 2 into 10 to the power -2 may not seem attractive for somebody who is looking for a brightly fluorescence molecule but then compared to 10 to the power -5 10 to the power -2 is 1000 times. Alright now the oscillator strengths calculated from the fluorescence spectra well not fluorescence spectra fluorescence data turn out to be 0.13 for ultrafast 0.048 for fast and 0.023 for the slow component.

And then if you add this 2 0.13 + 0.048 that turns out to be 0.16 which closely matches the oscillator's strength that you determinates experimentally from the absorption spectra. Remember what I said little while ago oscillator strength generally when you oscillator strength you think of absorption spectrum. From their there is a straight forward determination from epsilon that turns out to be 0.16 and when you sort of back calculate from the fluorescence data it turns out that almost the entire oscillator strength is accounted for by excitation to this species associated with ultrafast and fast components.

So that means ultrafast and fast components together make up sort of a 2 fold excited state ensemble to which excitation is taking place. Remember excitation that we do here is by ultrafast pulse is not monochromatic so if you have 2 states that are closely aligned to each other then you might end up exciting both together okay. So this is the state of affairs here up to here that oscillator strength is accounted for by excitation to not 1 but 2 species.

And what are the species now the first line that was written in the table the ultrafast one will associated is as assigned to dimeric S2 state the first decay associated with the dimeric S1 state why did they think this should be assignment? Because they had prior knowledge that there in other compounds they had shown that you actually can look at the emission spectrum originating in S2.

If you look at ultrafast time scales without that they could have achieved this alright so this was the assignment that was done and the main contention here is that excitation is taking place to not 1 but 2 excited states one is S1 one is S2 what are this 2 closely lying states what is the do we have some additional evidence to support what has been set so far will take that up in the next module.