Ultrafast Processes in Chemistry
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Module No # 10
Lecture No # 54
Excited State Double Proton Transfer of 7 – Azaindole Dimer 3

Right so this is where we are the we are actually discussing only one paper so far in the last couple of modules that 1998 J Phys Chem A of paper Takeuchi and Tahara. So we are doing that because we want to introduce a problem slowly and then later on we will just flashed the paper and you will see how the quality of the papers and number of the papers change over time and then it is up to you to read them.

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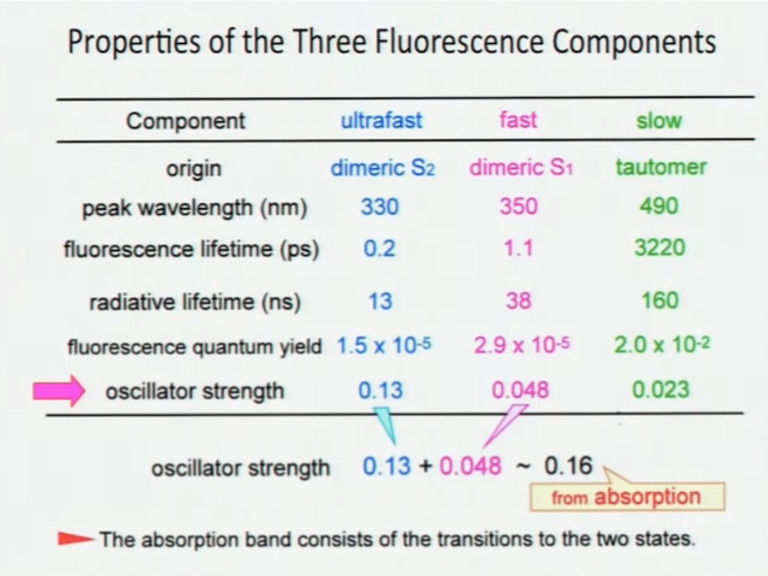

Properties of the Three Fluorescence Components

Component	ultrafast	fast	slow
origin	dimeric S_2	dimeric S_1	tautomer
peak wavelength (nm)	330	350	490
fluorescence lifetime (ps)	0.2	1.1	3220
radiative lifetime (ns)	13	38	160
fluorescence quantum yield	1.5×10^{-5}	2.9×10^{-5}	2.0×10^{-2}
➡ oscillator strength	0.13	0.048	0.023

oscillator strength $0.13 + 0.048 \sim 0.16$ from absorption

The absorption band consists of the transitions to the two states.

So the facts of the matter is that the excitation is taking place to not 1 but to 2 states. And again when you said that this is not talking in the air that was some existing literature about some very well-known Fluorophore ok. And the additional evidence that came here came in the form of fluorescence anisotropy.

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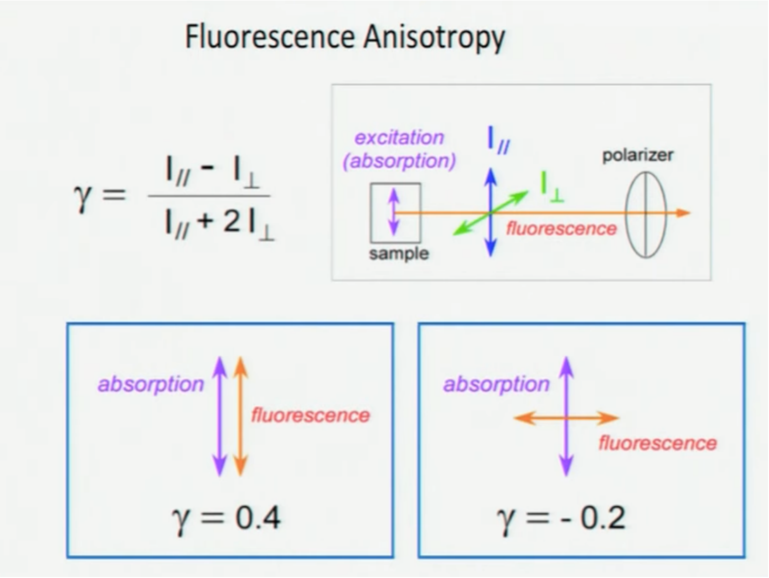

Fluorescence Anisotropy

$$\gamma = \frac{I_{//} - I_{\perp}}{I_{//} + 2I_{\perp}}$$

You all know that we excite by polarized light and then look at parallel and perpendicular depolarized emission light. You can get fluorescence anisotropy parallel I parallel -I perpendicular / I parallel + 2 I perpendicular. And this fluorescence anisotropy where is it used most of the time what does it stands for? Rotation and relaxation right that is I mean if there are at least in last 30 years if there are n number of paper in fluorescence anisotropy perhaps 0.9 n or more would be of about rotational depolarization.

But one of the very if you go back to early times look at very early papers on fluorescence spectroscopy you will see fluorescence anisotropy has been put to use to address a more fundamental issue. Rotation is not only the thing that causes depolarization. Why does this question of polarization arise in spectroscopy?

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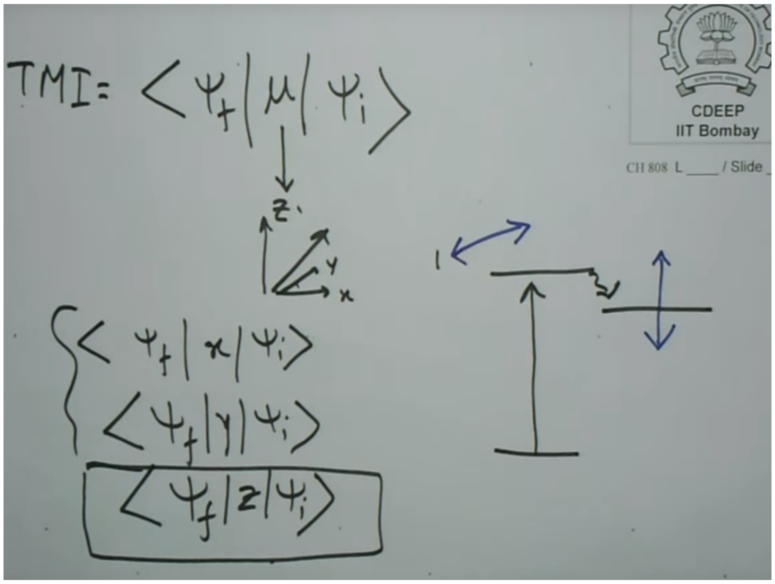

$$TMI = \langle \psi_f | \mu | \psi_i \rangle$$

$$\langle \psi_f | x | \psi_i \rangle$$

$$\langle \psi_f | y | \psi_i \rangle$$

$$\boxed{\langle \psi_f | z | \psi_i \rangle}$$

Because as we know the most important quantity in spectroscopy is this what is this quantity? Transition moment integral I like to call it TMI different people call it different thing Mu and all. What is Psi i? Psi i is the wave function of this state from which the transition origins initial i for initial. What is Psi f? Final wave function of the state to which the transition takes place we are not even saying absorption or emission and this Mu is basically the dipole moment.

So dipole moment is a vector and can be resolved into x, y and z components. So a transition as we know takes place only when this transition moment integral is non zero. And when you say this transition moment integral is nonzero what we mean is one of these 3 integral Psi f x Psi i or Psi f y Psi i or Psi f z Psi i. Of course, I should not say Psi f x Psi i it is integral Psi f star x Psi i d Tau one of this has to be non-zero essentially.

And many transition for many transitions only this transition is non zero while this maybe 0 or the other way around ok. In emission spectroscopy the idea is this you excite y z polar vertically polarized light and well excitation by vertically polarized light is better than horizontally polarized light if you going to detect in 90 degrees. So then the issue is the when emission takes place if emission takes place from the same state.

Since you have already done photo selection you have already excited by z polarized light the emitted light also have z polarization vertical polarization right. The thing is messed up apparently if you use horizontally polarized light because if this is the polarization of excitation light this is the direction of propagation. And when emission takes place from here the problem is generally you detect at 90 degrees.

If you detect in the same direction there is no problem. If you detect at 90 degree then this direction is the polarization is the direction of polarization of the light as well. And that messes up things completely both this as well as this are actually perpendicular. But coming back to the question in hand you expect the emission to be completely z polarized vertically polarized if the emission is from the excited state.

So one thing that can happen is that the molecule can tumble before can rotate before emission takes place. And then starting from this polarization you can get emission in different directions and that is where fluorescence anisotropy come in is of a great help will tell you whether rotational depolarization is taking place or not. However it takes some time for the molecules to rotate.

If you are talking about the time scales of less than picosecond the molecules will move this much. And not enough fluorescence depolarization will take place in that ultrashort time due to rotation. However suppose this is the situation where you excite and you excite to a state which has some kind of a polarization and then there is a rapid excited state process ultrafast excited state process that takes it to another state which has some polarization in transition dipole moment in some other direction.

So this is the direction of transition dipole moment of the local excited state this is the direction of the transition dipole moment of a state that is produced by some rapid excited state process. Then what will happen then also you will have some depolarization and this depolarization will take place in ultrafast time scale which is not accessible to rotation. So if you have a little slow depolarization then you can think that is due to rotation something like tens of picosecond and longer.

If you are talking about proteins and all it will become nanosecond. However if you have depolarization which is ultrafast 0.1 picosecond, 1 picosecond, 2 picosecond then it is not enough time for rotation that means you there is some rapid transformation from one state to the other ok right. And it is actually known that this phenomenon is take place in some kinds of molecules.

Will come back to that in a moment but now let me show you the data of Takeuchi and Tahara fluorescence anisotropy data.

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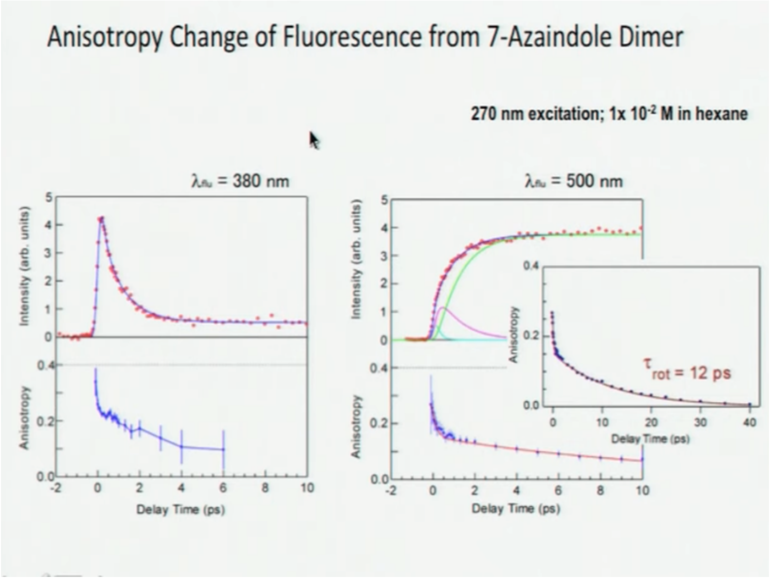

Anisotropy Change of Fluorescence from 7-Azaindole Dimer

270 nm excitation; 1x 10^{-2} M in hexane

This is the fluorescence decay excited at 380 nanometer. This is the rise followed by a long decay at Lambda m 380 nanometer sorry this is Lambda fluorescence 380 nanometer excitation is at 270 nanometer benzenoic band and this is the fast decay you see at 380 nanometer. This is the rise followed by a very slow decay that you see at 500 nanometer emission. Now here this is the time evolution of anisotropy you see the first component and here the time evolution of anisotropy is slower this associated with 12 picosecond right.

So when you look at 500 nanometer tautomer band the fluorescence depolarization take place is mainly due to rotation. However when you look at the locally excited state there is a very fast component ultrafast component will tell you how much it is that cannot be due to rotation.

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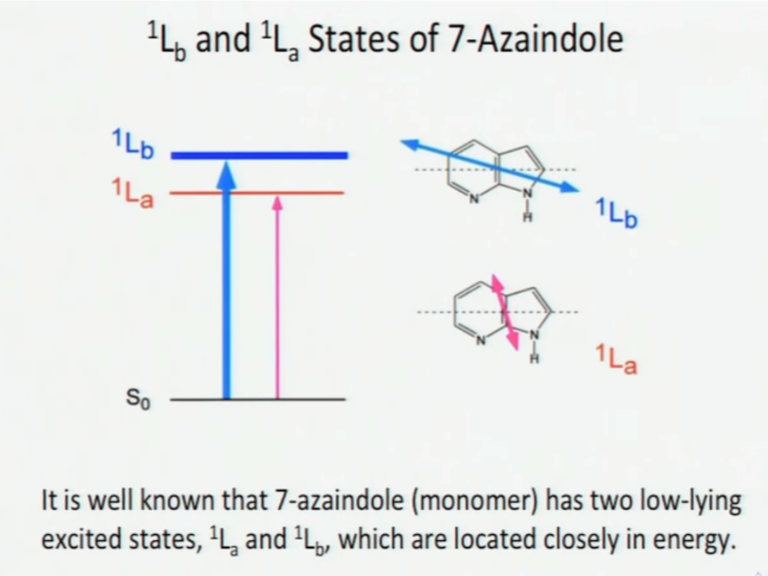

^1L_b and ^1L_a States of 7-Azaindole

It is well known that 7-azaindole (monomer) has two low-lying excited states, ^1L_a and ^1L_b, which are located closely in energy.

And the reason came from a classical knowledge of this kind of molecules. It is known that 7 Azaindole has 2 very close relying excited state singlet La and singlet Lb. And for once again the as a result of experiment as well as calculations it was well established by that time that singlet La has a transition moment transition dipole moment in this direction. Single Lb has the transition dipole moment in this direction.

Here we are talking about monomers do not forget ok. Excitation essentially is absorption does not change much. Does this remind you or something? You have 2 transition moments 1 almost perpendicular to the other not exactly perpendicular and one we have why we have drawn a longer arrow in one case and shorter arrow in the other case double headed arrow? Because this one passes through more atoms this one passes through fewer atoms.

So this is called the long axis the singlet Lb state is known to have transition moment in transition dipole moment along the long axis and singlet La is known to have transition dipole moment along short axis does that ring a bell? Long axis short axis those of us who have studied the spectroscopy of naphthalene would perhaps remember that for naphthalene there are very well defined long and short axis transitions at 90 degrees to each other perfect 90 degrees.

And now for 7 Azaindole and for triptophan it is well known that you have this again this short axis long axis business it is just that the axis are tilted. They are not exactly at right angles because the 2 rings are not at same. So this idea of long axis and short axis and this closer line excited state all this stands really from the symmetry discussion of naphthalene energetic from naphthalene ok that is the starting point.

So those who might be interested we have discussed this naphthalene case in detail in our symmetry NPTEL course symmetry in chemistry once again the lectures are freely available on youtube alright. So this was known. So what Takeuchi and Tahara said was a simple explanation Tahara's group specializes in providing simple explanation. In fact Tahara once told me that you should not think maters in a very complicated way and it is very typical manner he said I do not understand things that are complicated.

There has to be simple explanation for everything. Of course you say that to quantum chemist they will not agree but that is not too bad an approach. What they said is this we know very well that there is singlet Lb state which is a little higher lying state than singlet La. So singlet Lb would be S2 singlet La would be S1.

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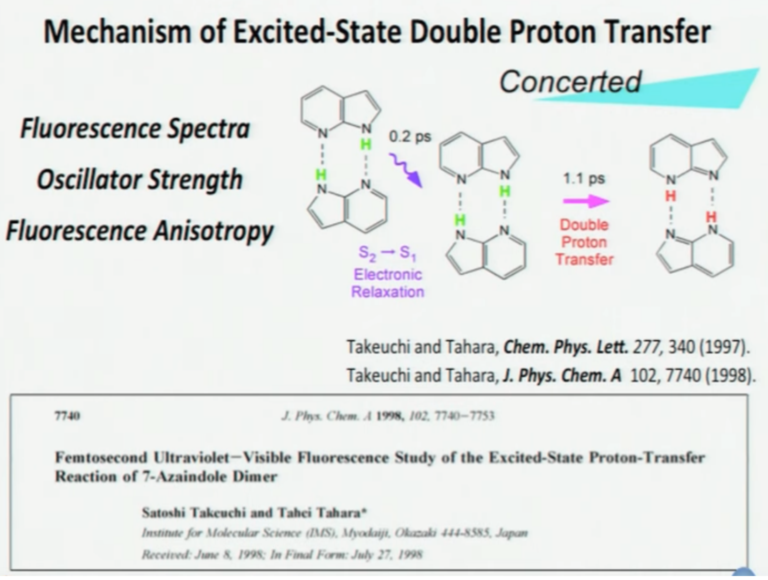

Mechanism of Excited-State Double Proton Transfer

Fluorescence Spectra

Oscillator Strength

Fluorescence Anisotropy

Takeuchi and Tahara, ***Chem. Phys. Lett.*** *277*, 340 (1997).
Takeuchi and Tahara, ***J. Phys. Chem. A*** 102, 7740 (1998).

7740 *J. Phys. Chem. A* **1998,** *102,* *7740−7753*

Femtosecond Ultraviolet−Visible Fluorescence Study of the Excited-State Proton-Transfer Reaction of 7-Azaindole Dimer

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Received: June 8, 1998; In Final Form: July 27, 1998

And from the time resolve spectroscopy experiment that is there their assignment was when you excite to this singlet Lb. That gets transformed to singlet La without the proton being transferred. So this is basically S2 to S1 vibrational cooling in 0.2 picosecond. And then the double proton transfer takes place from this electronically relaxed in S1 state singlet La state of the dimer or rather i should say dimer or singlet La states because after all the single the singlet La singlet Lb states are defined for the monomer not the dimer.

And here in started the trouble because their interpretation was that the ultrafast component 0.2 picosecond is associated with sort of vibrational cooling say S2 to S1 non radiative transformation and the proton transfer is consorted. Both the proton get transfer at the same time. Proton transfer is not sequential but concerted 1.1 picosecond is the time associated with transfer of both the protons together alright. Note the time, timeline is important here 1998 also note the page number 7740 J Phys Chem A ok.

And the reason why that was a beginning of some trouble was that already about 3 years ago and that is not the only paper by the way there was this 1997 CPL paper and well as I said one reason I am very excited about it is that I read all this paper in real time as a published goes that is when I was student. The reason why this spark of this debate is that 2 years prior to this CPL paper 1995 there were the paper published by Douhal Kim and Zewail in nature.

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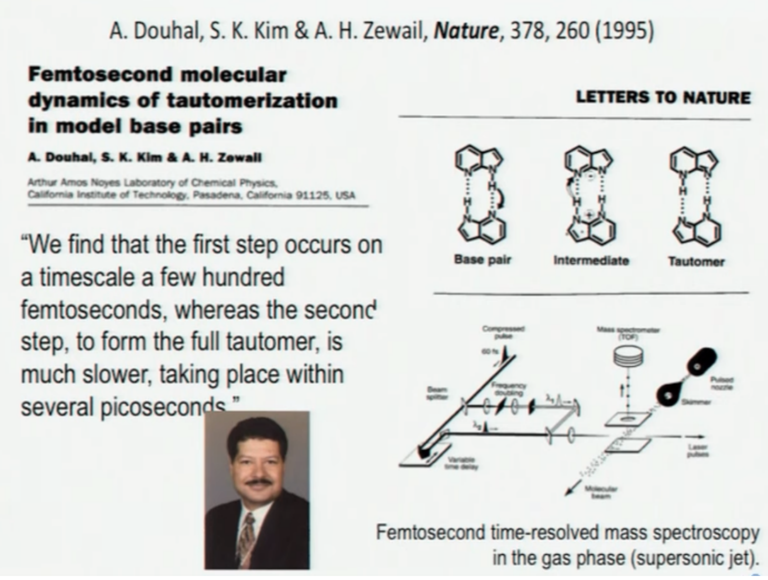

A. Douhal, S. K. Kim & A. H. Zewail, *Nature*, 378, 260 (1995)

Femtosecond molecular dynamics of tautomerization in model base pairs

A. Douhal, S. K. Kim & A. H. Zewail

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA

LETTERS TO NATURE

“We find that the first step occurs on a timescale a few hundred femtoseconds, whereas the second step, to form the full tautomer, is much slower, taking place within several picoseconds.”

Femtosecond time-resolved mass spectroscopy in the gas phase (supersonic jet).

Where they had studied the same 7 Azaindole dimer in gas phase using mass spectroscopy you can see the set up here it is very similar to the setup we have next to our lab in professor Naresh Patwari’s lab the only difference is that this is time resolved mass spectrometer ok same time of mass spectrometer but time resolved in femtosecond resolution. This is where there are lot of the Nobel prize winning work has been done. So there 1995 is 4 years before Zewail Nobel prize. When everybody knew that the Nobel prize is coming to this gentleman.

That time nature paper came where they said based on this mass spectroscopy data that they also work by the way the interesting thing is they got very similar time constant 0.2 time picosecond and 1.1 picosecond. Almost close to what Tahara group had got. But based on the mass data they said that the 0.2 picosecond component is associated with the transfer of 1 proton. 1.1 picosecond is associated with transfer of second proton.

So PK1 PK2 kind of thing and then you get the tautomer. So now the question was that Zewail group said the proton transform is sequential 2 step. Tahara's group said it is concerted and preceded by S2 to S1 cooling which one is correct?

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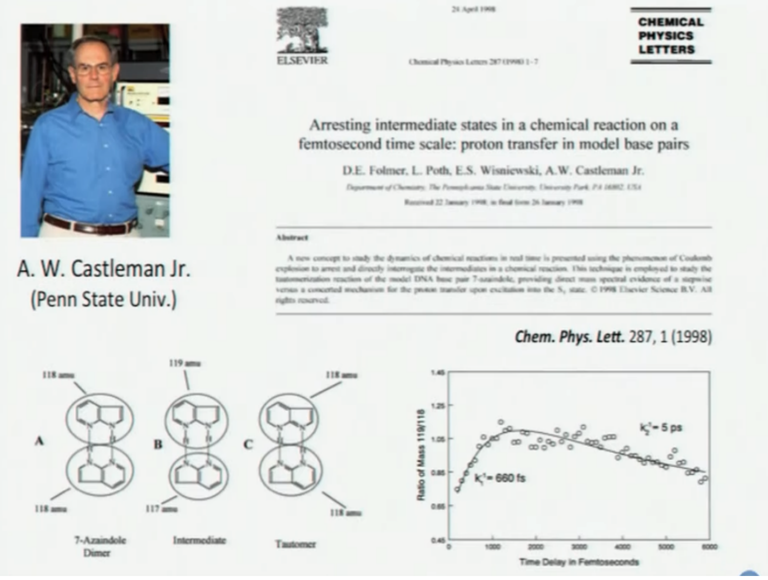

A. W. Castleman Jr.
(Penn State Univ.)

21 April 1998

ELSEVIER

Chemical Physics Letters 287 (1998) 1–7

CHEMICAL
PHYSICS
LETTERS

Arresting intermediate states in a chemical reaction on a femtosecond time scale: proton transfer in model base pairs

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Received 22 January 1998; in final form 26 January 1998

Abstract

A new concept to study the dynamics of chemical reactions in real time is presented using the phenomenon of Coulomb explosion to arrest and directly interrogate the intermediates in a chemical reaction. This technique is employed to study the tautomerization reaction of the model DNA base pair 7-azaindole, providing direct mass spectral evidence of a stepwise versus a concerted mechanism for the proton transfer upon excitation into the S_1 state. © 1998 Elsevier Science B.V. All rights reserved.

Chem. Phys. Lett. 287, 1 (1998)

More or less around the same time 1998 again Castleman is very well known name in this field. Castleman groups in Penn state did some experiment once again on mass spectroscopy and it is very easy to understand what they did and perhaps it is not very difficult to understand where the problem lies here. So what they said is this you take a monomer the mass is 118 amu if a proton gets transfer then the protonated species has a mass of 119 amu then the deprotonated species has a mass of 117 amu is as simple as that.

When both the proton get transferred transfer what is the mass? Again both of 118 so what they their argument was based on the fact that if I look at that 119 amu fragment how much of it is there in relation to 118 fragment they said this is the evidence of single proton transfer species ok. And this is what they got. Can you read the y axis? Can you read the x axis? Time delay in femtosecond very easy to understand can you read the y axis? Ratio of masses 119 to 118 and there they see arise and that is associated with 660 femtosecond.

So they said yes it is proton sequential. First one proton get transferred otherwise why are we getting 119 amu. So the problem of course with this experiment is that you are differentiating 118 and 119 with femtosecond resolution. So is the data really that good right that skepticism is going to come but this Castleman group said anyway.

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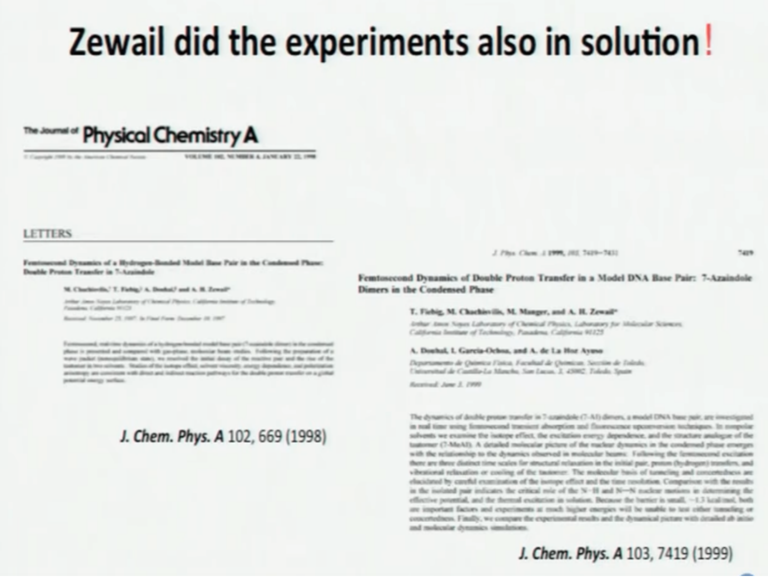

Zewail did the experiments also in solution!

The Journal of Physical Chemistry A

LETTERS

Femtosecond Dynamics of a Hydrogen-Bonded Model Base Pair in the Condensed Phase: Double Proton Transfer in 7-Azaindole

M. Chachisvilis, T. Fiebig, A. Douhal, and A. H. Zewail*

J. Chem. Phys. A 102, 669 (1998)

Femtosecond Dynamics of Double Proton Transfer in a Model DNA Base Pair: 7-Azaindole Dimers in the Condensed Phase

T. Fiebig, M. Chachisvilis, M. Manger, and A. H. Zewail*

A. Douhal, I. Garcia-Ochoa, and A. de La Hoz Ayuso

J. Chem. Phys. A 103, 7419 (1999)

But then do not think that this is are only the gas phase experiments that said that it is sequential. Zewail also did experiments in solutions Zewail's group and they did in different solvent. So this is these are the paper that I am not going to discuss in detail. But I strongly advice that you read this then only you understand the intricacy of this discussion several studies mostly by in one case when Douhal was in Zewail's lab the case when Douhal went back and their groups collaborated.

Every time same Douhal every time Ahmed H Zewail. Every time they said it is sequential. So this is the debate this is what it is all about. Is it concerted Tahara model is it stepwise Zewail model?

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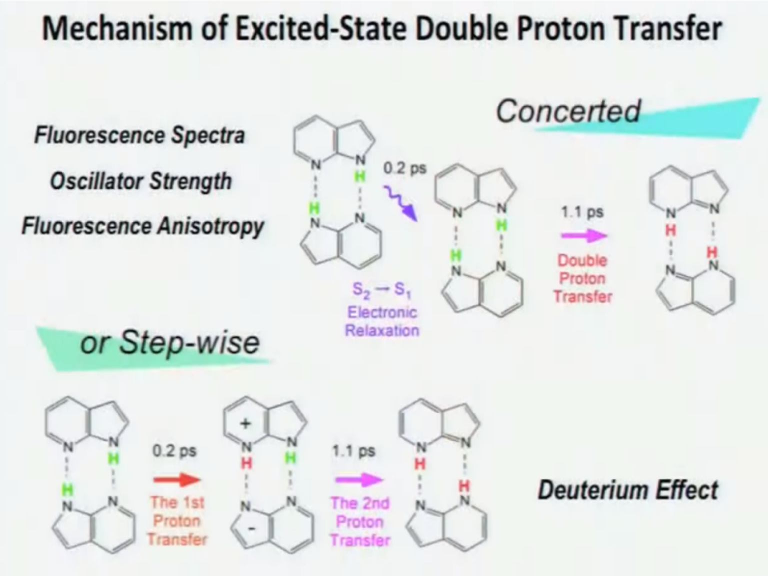

Mechanism of Excited-State Double Proton Transfer

Fluorescence Spectra

Oscillator Strength

Fluorescence Anisotropy

Deuterium Effect

And then well to somebody who of course you know in any field understand the importance of anything if you are interested. So to an outsider this might seem to be fool who cares if it is one at a time or both at a time or but is not frivolous. At the end as promised we will discuss all what we have learned and one evidence that it was not frivolous rather than very interesting thing in this community was that father figure one of the father figure of fluorescence when you say fluorescence this is the name comes into your mind Michael kasha actually got into this.

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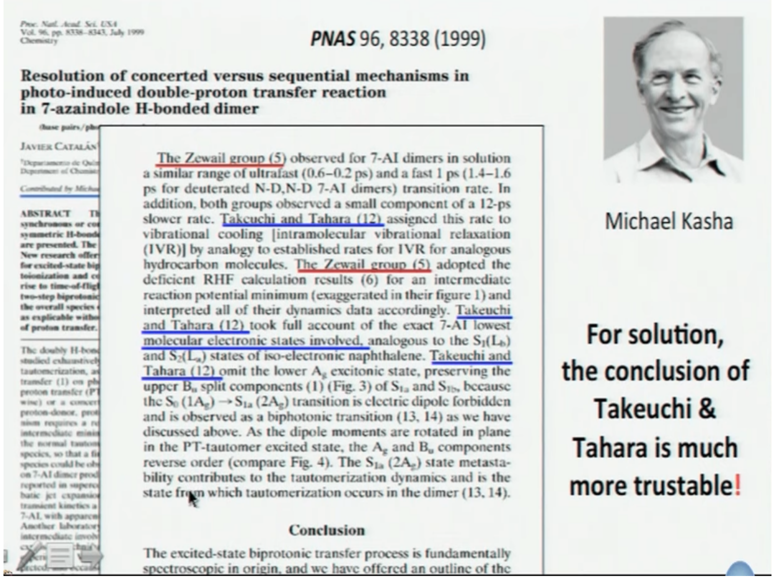

Proc. Natl. Acad. Sci. USA
Vol. 96, pp. 8338–8343, July 1999
Chemistry

PNAS 96, 8338 (1999)

Resolution of concerted versus sequential mechanisms in photo-induced double-proton transfer reaction in 7-azaindole H-bonded dimer

The Zewail group (5) observed for 7-AI dimers in solution a similar range of ultrafast (0.6–0.2 ps) and a fast 1 ps (1.4–1.6 ps for deuterated N-D,N-D 7-AI dimers) transition rate. In addition, both groups observed a small component of a 12-ps slower rate. Takeuchi and Tahara (12) assigned this rate to vibrational cooling [intramolecular vibrational relaxation (IVR)] by analogy to established rates for IVR for analogous hydrocarbon molecules. The Zewail group (5) adopted the deficient RHF calculation results (6) for an intermediate reaction potential minimum (exaggerated in their figure 1) and interpreted all of their dynamics data accordingly. Takeuchi and Tahara (12) took full account of the exact 7-AI lowest molecular electronic states involved, analogous to the $S_1(L_b)$ and $S_2(L_a)$ states of iso-electronic naphthalene. Takeuchi and Tahara (12) omit the lower A_g excitonic state, preserving the upper B_u split components (1) (Fig. 3) of S_{1a} and S_{1b}, because the $S_0\,(1A_g) \rightarrow S_{1a}\,(2A_g)$ transition is electric dipole forbidden and is observed as a biphotonic transition (13, 14) as we have discussed above. As the dipole moments are rotated in plane in the PT-tautomer excited state, the A_g and B_u components reverse order (compare Fig. 4). The $S_{1a}\,(2A_g)$ state metastability contributes to the tautomerization dynamics and is the state from which tautomerization occurs in the dimer (13, 14).

Conclusion

The excited-state biprotonic transfer process is fundamentally spectroscopic in origin, and we have offered an outline of the

Michael Kasha

For solution, the conclusion of Takeuchi & Tahara is much more trustable!

1999 Kasha's group published a paper and it is not only Kasha Catalan is also very major player. Catalan and Kasha and all they published a paper and this was published in PNAS as you can see. This PNAS paper it was essentially discussion of what these 2 groups had seen Zewail group and

Tahara group please read this paper. First of it is the work of a master well commentary of a master Kasha and what he said I will just show one part and I will read it what is said is that? Zewail group observed for 7 Azaindole dimers in solution a similar range of ultrafast and fast components for deuterated dimers.

So Zewail group also did the deuteration work. Takeuchi and Tahara assigned this rate to vibrational cooling by analogy to establish rates for IVR for analogous hydrocarbon molecules. So as you know every research is really linear combination of previous knowledge and something more. So you cannot really do anything in the air. So that is what Tahara had done. The Zewail group adapted the deficient RHF calculation results.

So one of the main strains of Zewail work purpose whenever you do any gas phase work you understand that you will have to do calculations quantum chemical calculation and quantum chemical calculations are very helpful but if you are not careful or if you are biased towards a particular result that you want to see you actually get to see the result you want to see. So for an RHF calculation results for an intermediate reaction potential minimum exaggerated in their figure 1 and interpreted all of their dynamics data accordingly.

Takeuchi and Tahara took full account of the exact 7 azaindole lowest molecular state energy states involved analogous to the S1 Lb and S2 La states of isoelectronic naphthalene. Takeuchi and Tahara omit the lower Ag electronic state preserving the upper Bu split components of S1u and S1b because the S0 singlet Ag to S1a doublet Ag transition is electric dipole forbidden and is observed as a biphotonic transition as we have discussed above.

As a dipole moment are rotated in plane in the PT tautomer excited state the Ag and Bu components reversed order there is a reversing of order that takes place. The S1u state metastability contributes to the tautomerization dynamics and is the state from which tautomerization occurs in the dimer. So Kasha actually said at that point itself that for solution he did not want to comment on the S phased results. For solution the conclusion of Takeuchi and Tahara is much more reliable. That is what Kasha has to say at that point.

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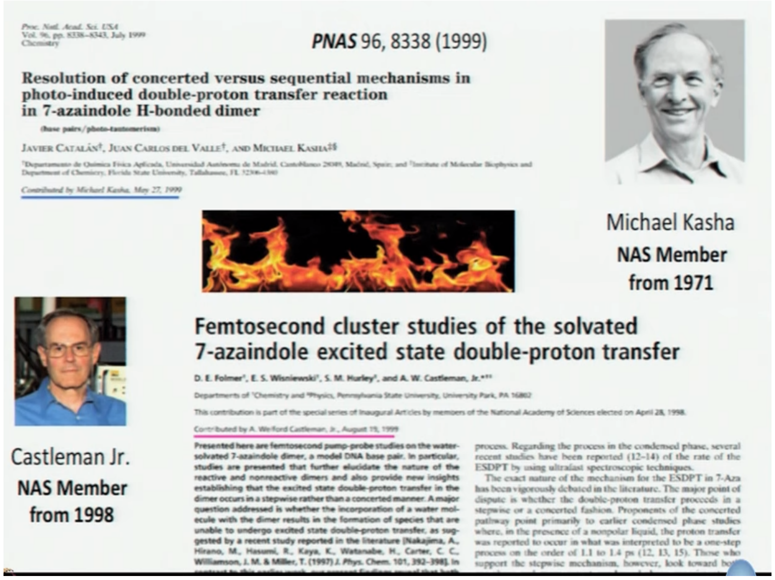

Proc. Natl. Acad. Sci. USA
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Chemistry

PNAS 96, 8338 (1999)

Resolution of concerted versus sequential mechanisms in photo-induced double-proton transfer reaction in 7-azaindole H-bonded dimer

(base pairs/photo-tautomerism)

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Contributed by Michael Kasha, May 27, 1999

Michael Kasha
NAS Member
from 1971

Femtosecond cluster studies of the solvated 7-azaindole excited state double-proton transfer

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This contribution is part of the special series of Inaugural Articles by members of the National Academy of Sciences elected on April 28, 1998.

Contributed by A. Welford Castleman, Jr., August 19, 1999

Presented here are femtosecond pump-probe studies on the water-solvated 7-azaindole dimer, a model DNA base pair. In particular, studies are presented that further elucidate the nature of the reactive and nonreactive dimers and also provide new insights establishing that the excited state double-proton transfer in the dimer occurs in a stepwise rather than a concerted manner. A major question addressed is whether the incorporation of a water molecule with the dimer results in the formation of species that are unable to undergo excited state double-proton transfer, as suggested by a recent study reported in the literature [Nakajima, A., Hirano, M., Hasumi, R., Kaya, K., Watanabe, H., Carter, C. C., Williamson, J. M. & Miller, T. (1997) *J. Phys. Chem.* 101, 392–398]. In

process. Regarding the process in the condensed phase, several recent studies have been reported (12–14) of the rate of the ESDPT by using ultrafast spectroscopic techniques.

The exact nature of the mechanism for the ESDPT in 7-Aza has been vigorously debated in the literature. The major point of dispute is whether the double-proton transfer proceeds in a stepwise or a concerted fashion. Proponents of the concerted pathway point primarily to earlier condensed phase studies where, in the presence of a nonpolar liquid, the proton transfer was reported to occur in what was interpreted to be a one-step process on the order of 1.1 to 1.4 ps (12, 13, 15). Those who support the stepwise mechanism, however, look toward bo

Castleman Jr.
NAS Member
from 1998

But this was immediately followed up by paper on Castleman where he stood his ground and sort of defended that stand. So this is like a war of giant Michael Kasha was a member fellow of national academic of science USA since 1971. Castleman had just become at that time fellow of the academy. And this really got eyeballs.

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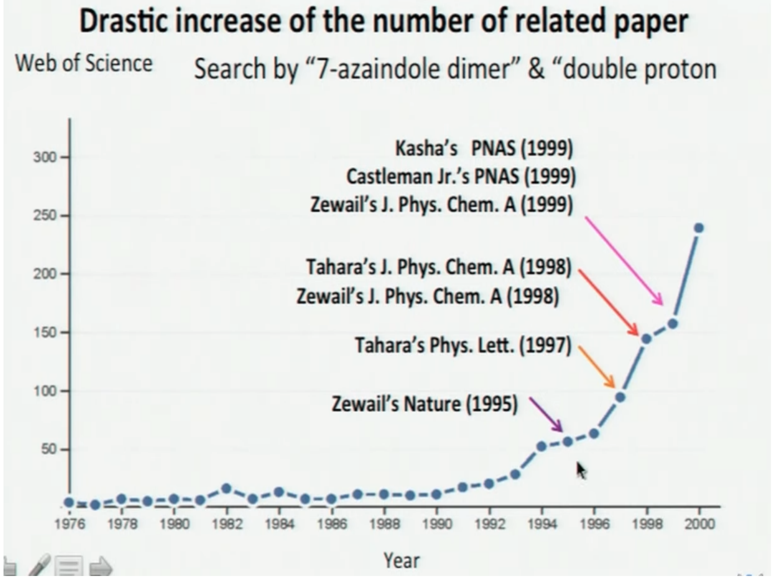

Drastic increase of the number of related paper

Web of Science   Search by "7-azaindole dimer" & "double proton

And this is something I usually do not show in any presentation but in this case just to bring out how the kind of interested generated I show you how drastic was it increase in number of papers in the related fields until 90 to nothing. Slowly it goes up and from here it takes off. And most of this work was about this debate is it concerted it is stepwise? Then Tahara's group did some experiment what they said is fine. We are saying that when we excite to two different state. So now if I change the excitation wavelength then what happens?

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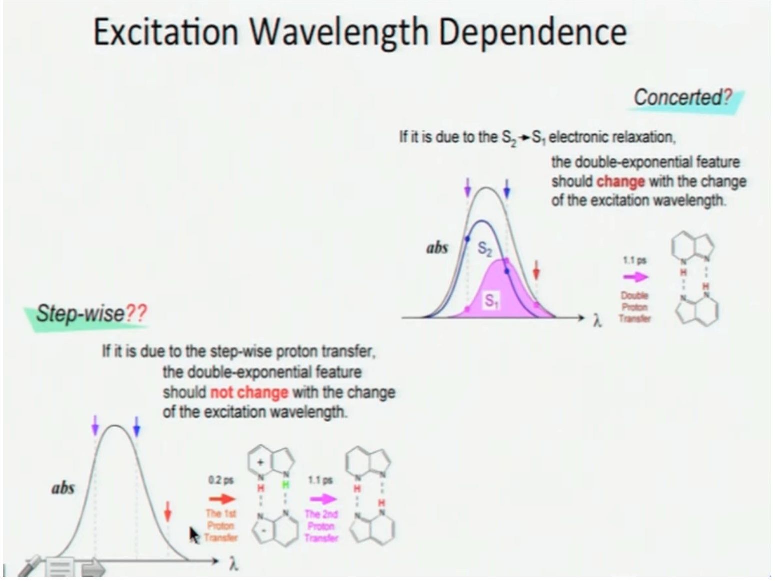

Excitation Wavelength Dependence

Concerted?

If it is due to the $S_2 \rightarrow S_1$ electronic relaxation, the double-exponential feature should **change** with the change of the excitation wavelength.

Step-wise??

If it is due to the step-wise proton transfer, the double-exponential feature should **not change** with the change of the excitation wavelength.

If you have something like this where the absorption spectrum is made up of absorption spectra for S0 to S2 and S0 to S1 transitions. And this is of course a cartoon representation their contention was if I excited here then I will excite primarily to S2. If I excite here I will excite primarily to S1. So when I excite here that is 0.2 picosecond should be seen if it is S2 to S1 transition.

If I excite in the red end of the absorption spectrum it should not be seen. However if it is only one state that excited to if the proton transfer is actually sequential then no matter where do you excite you still see 2 time constant 0.2 picosecond and 1.1 picosecond. Of course this is easier said than done.

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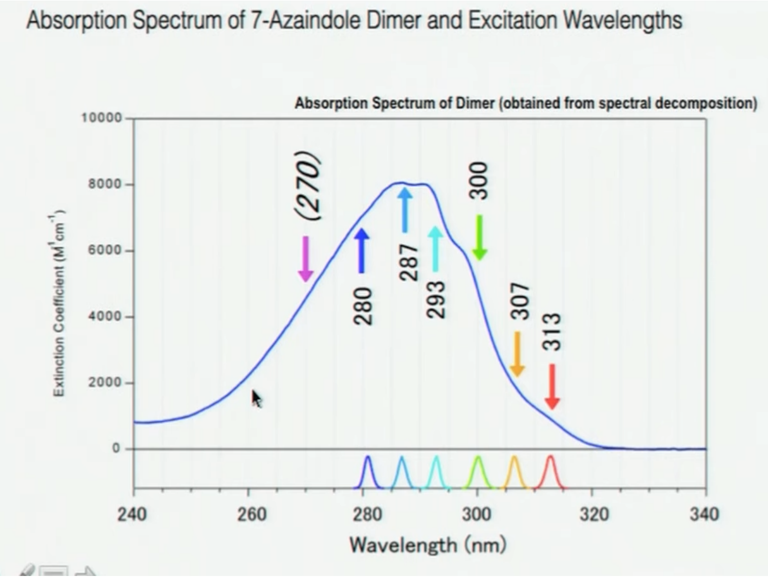

Absorption Spectrum of 7-Azaindole Dimer and Excitation Wavelengths

This is what you want to do? This here the absorption who want to excite at different places that is what they did? They started with 270 nanometer then 280, 287, 293, 300, 307, 313 now do not forget that the problem here is that again saying the same thing again and again your exciting with an ultrafast pulse it is not monochromatic ok. So it is important to do a lot of experiments and when you excite here 270 nanometer you cannot go here you cannot go to 260 because there is hardly an absorption.

So this is a difficult experiment not at all an easy experiment and data analysis was also not at all easy. But I will show you what they get.

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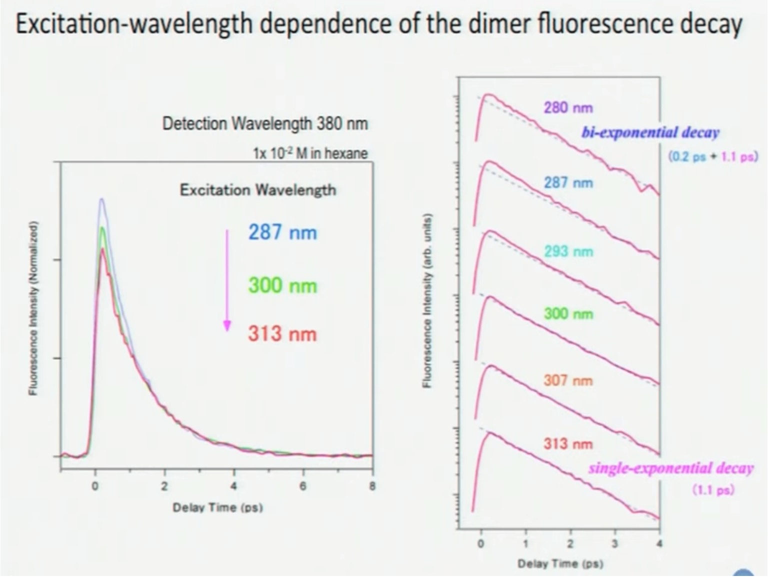

Excitation-wavelength dependence of the dimer fluorescence decay

This is what they got they what is compared here is the decay is of up conversation femtosecond up conversion upon excitation of 287 nanometer, 300 nanometer, 313 nanometer. And look at the decays these are not normalized. This is, are not peak normalized. If anything that tail matched so see that tails are matched very nicely what is this tail? 1.1 picosecond component so if the second case is correct that 0.2 as well as 1.1 picosecond both are associated with proton transfer the first one and the second one.

Then these decays should have become super impossible at tail match decay also get peak normalized a peak normalized decay also get tail matched. That is obviously not the case and when you excited 287, nanometer and when you excited 313 nanometers what is the difference? Contribution from the ultrafast component is more when you excite at 287, nanometer.

And next step is how you represent your data? It is not enough to have data what you say is important? How you say it also important? Right so they did it beautifully by making log normal plots and it log normal plot this is the data right actual data yet to get this kind of data in up conversion third harmonic excitation is very difficult you would not understand that. So this required very careful experiment and then in semi log plots what they did is this lines that you see this lines come when you have this 1.1 picosecond time constant right.

So in semi log plot 1.1 picosecond time constant decay would look like a line with corresponding slope. So for 313 nanometer excitation you see the decay is coincidence with this line. As you go towards blue I mean higher energy excitation there is a deviation in the smaller time scale. That is because when excite at 280 nanometer the decay is bi exponential. You get 0.2, picosecond as well as 1.1 picosecond. When you excited 313, nanometer the excitation wavelength you remember the decay is single exponential. Only 1.1 picosecond component is there right.

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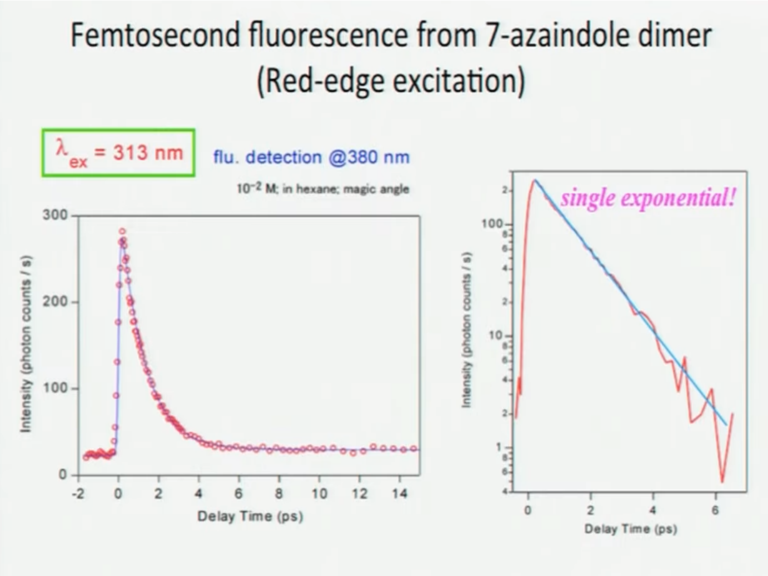

Femtosecond fluorescence from 7-azaindole dimer
(Red-edge excitation)

λ_{ex} = 313 nm

flu. detection @380 nm

10^{-2} M; in hexane; magic angle

single exponential!

So this is the thing moreover they also looked at anisotropy.

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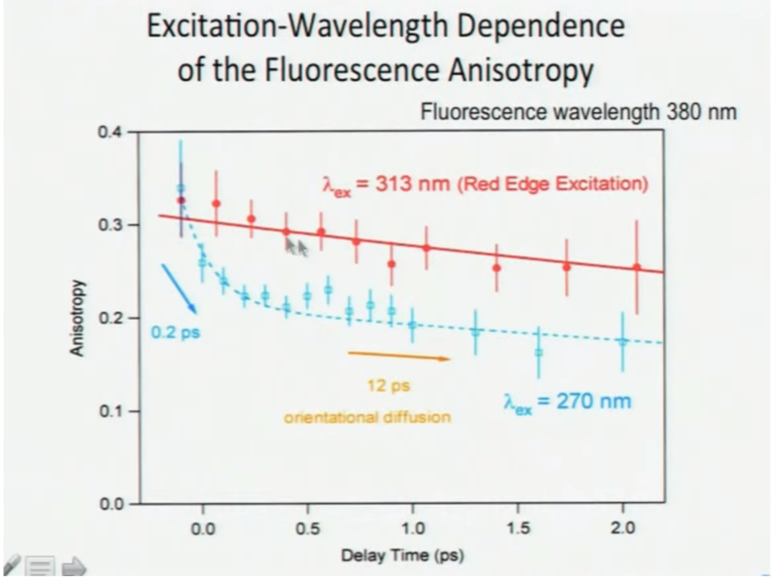

Excitation-Wavelength Dependence
of the Fluorescence Anisotropy

Fluorescence wavelength 380 nm

When 1 excite at 313, nanometer anisotropy decay also is almost single exponential and long lived associated with that 12 picosecond component which is for rotation. When they excited at 270, nanometer you see there is an initial ultrafast component 0.2 picosecond. So that 0.2 picosecond turns out to be the time constant as well as the time constant associated with anisotropy decay.

That is what is telling you that 1 state gives makes way for the other with this 0.2 picosecond time constant. That is associated not with not only with decay of population but also change in direction of transition moment integer well transition dipole moment. That is why you see it here. So this see in long time this 2 are almost parallel right. That is due to rotation anyway but in short time if you get something like that tells you that in that time scale some excited state process is happening.

And that is seen only for well not only for that is seen prominently for excitation at higher energy not seen for excitation at lower energy which means that when you are excited 313 nanometer you are not exciting the S2 state you only excite the S1 state. When you excite at 270 nanometer you too excite the S2 state right.

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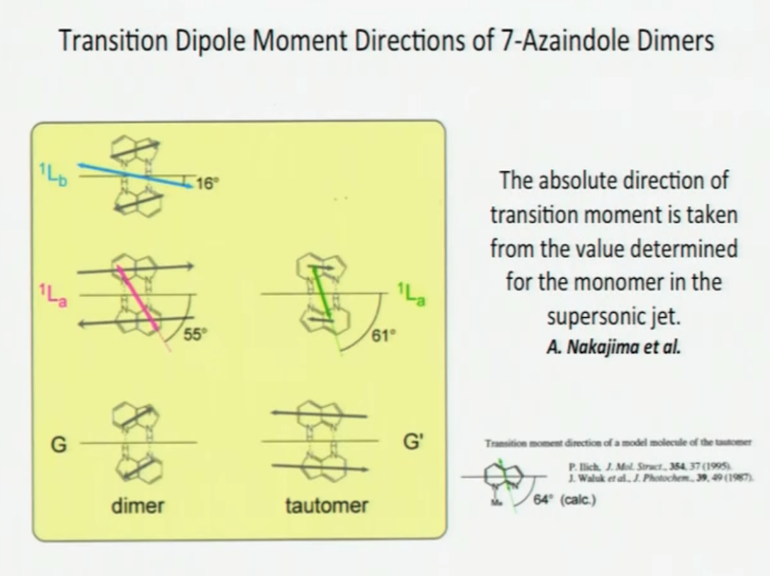

Transition Dipole Moment Directions of 7-Azaindole Dimers

The absolute direction of transition moment is taken from the value determined for the monomer in the supersonic jet.

A. Nakajima et al.

Transition moment direction of a model molecule of the tautomer

P. Ilich, *J. Mol. Struct.*, **354**, 37 (1995).
J. Waluk *et al.*, *J. Photochem.*, **39**, 49 (1987).

So that was explained knowing the directions of all these transition moment integrals from calculations by Nakajima et al and other people like Waluk and all.

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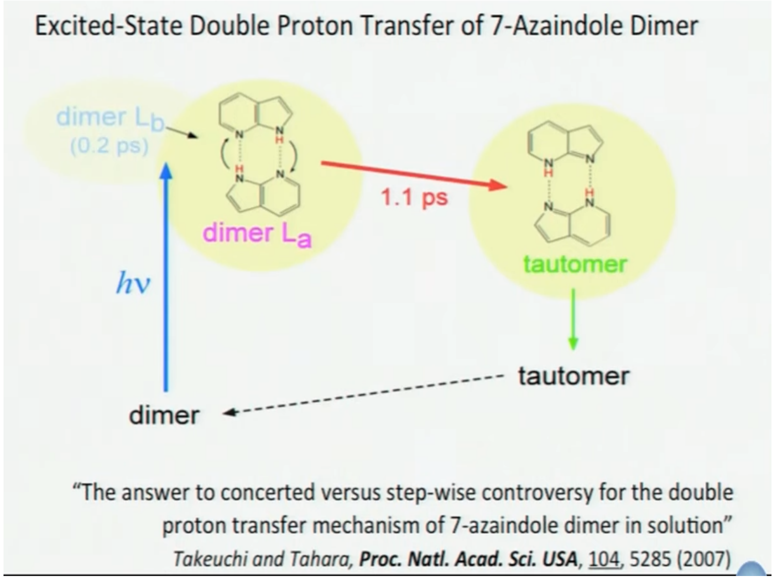

Excited-State Double Proton Transfer of 7-Azaindole Dimer

"The answer to concerted versus step-wise controversy for the double proton transfer mechanism of 7-azaindole dimer in solution"

Takeuchi and Tahara, ***Proc. Natl. Acad. Sci. USA***, 104, 5285 (2007)

And finally this was the PNAS paper published in 2007 10 years after the debate started. And there the title of the paper I think is something like the answer to concerted versus step wise controversy for the double proton transfer mechanism of 7, Azaindole dimer in solution and the answer is so simple. This is the answer to attain a long debate and so from here they said that yes, it is definite that S2 involvement is there and see the change in quality of the paper also that starting from Chem Phys paper 1997. Here we have this last paper in PNAS.

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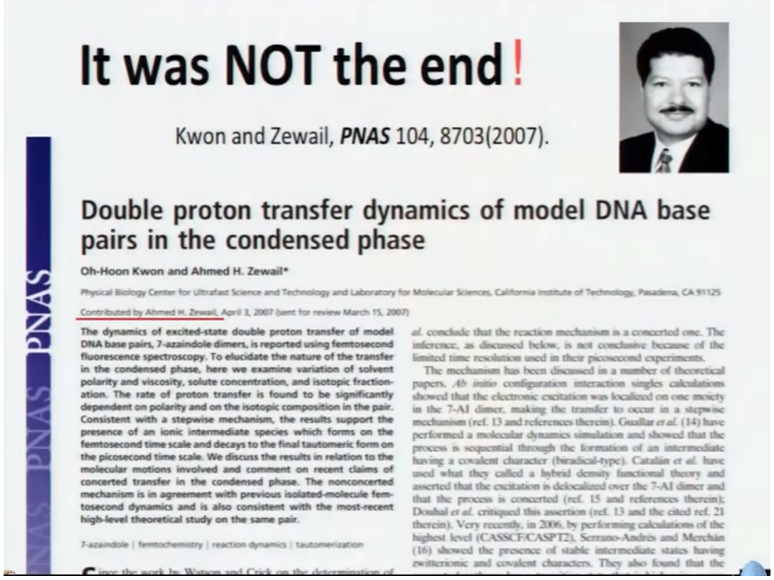

It was NOT the end!

Kwon and Zewail, ***PNAS*** 104, 8703(2007).

Double proton transfer dynamics of model DNA base pairs in the condensed phase

Oh-Hoon Kwon and Ahmed H. Zewail*

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Contributed by Ahmed H. Zewail, April 3, 2007 (sent for review March 15, 2007)

The dynamics of excited-state double proton transfer of model DNA base pairs, 7-azaindole dimers, is reported using femtosecond fluorescence spectroscopy. To elucidate the nature of the transfer in the condensed phase, here we examine variation of solvent polarity and viscosity, solute concentration, and isotopic fractionation. The rate of proton transfer is found to be significantly dependent on polarity and on the isotopic composition in the pair. Consistent with a stepwise mechanism, the results support the presence of an ionic intermediate species which forms on the femtosecond time scale and decays to the final tautomeric form on the picosecond time scale. We discuss the results in relation to the molecular motions involved and comment on recent claims of concerted transfer in the condensed phase. The nonconcerted mechanism is in agreement with previous isolated-molecule femtosecond dynamics and is also consistent with the most-recent high-level theoretical study on the same pair.

7-azaindole | femtochemistry | reaction dynamics | tautomerization

al. conclude that the reaction mechanism is a concerted one. The inference, as discussed below, is not conclusive because of the limited time resolution used in their picosecond experiments.

The mechanism has been discussed in a number of theoretical papers. *Ab initio* configuration interaction singles calculations showed that the electronic excitation was localized on one moiety in the 7-AI dimer, making the transfer to occur in a stepwise mechanism (ref. 13 and references therein). Guallar *et al.* (14) have performed a molecular dynamics simulation and showed that the process is sequential through the formation of an intermediate having a covalent character (biradical-type). Catalán *et al.* have used what they called a hybrid density functional theory and asserted that the excitation is delocalized over the 7-AI dimer and that the process is concerted (ref. 15 and references therein); Douhal *et al.* critiqued this assertion (ref. 13 and the cited ref. 21 therein). Very recently, in 2006, by performing calculations of the highest level (CASSCF/CASPT2), Serrano-Andrés and Merchán (16) showed the presence of stable intermediate states having zwitterionic and covalent characters. They also found that the

It was not the end of the debate because alright this is 2007 PNAS page number 5285, 2007 PNAS page number 8703 where Zewail's group published one more paper defending their stand. I am not going into what they said because by the time actually this is not really the debate raging on it is just that well the Taharas paper were actually concludes.

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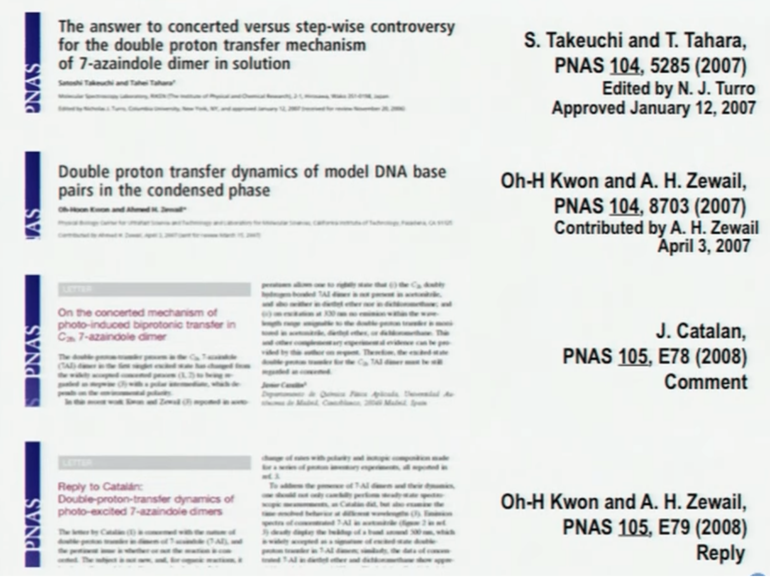

The answer to concerted versus step-wise controversy for the double proton transfer mechanism of 7-azaindole dimer in solution

S. Takeuchi and T. Tahara,
PNAS 104, 5285 (2007)
Edited by N. J. Turro
Approved January 12, 2007

Double proton transfer dynamics of model DNA base pairs in the condensed phase

Oh-H Kwon and A. H. Zewail,
PNAS 104, 8703 (2007)
Contributed by A. H. Zewail
April 3, 2007

On the concerted mechanism of photo-induced biprotonic transfer in C_{2h} 7-azaindole dimer

J. Catalan,
PNAS 105, E78 (2008)
Comment

Reply to Catalán: Double-proton-transfer dynamics of photo-excited 7-azaindole dimers

Oh-H Kwon and A. H. Zewail,
PNAS 105, E79 (2008)
Reply

Still some more papers are published I have already referred to Takeuchi and Tahara 2007 PNAS and Kwon and Zewail 2007 PNAS. Then Catalan, remember Catalan and Kasha has written a paper remember. So Catalan wrote a comment in responds to Zewail's paper 2008 and here since the slides are from Tahara's son is actually written that the excite time line. This paper was accepted in 2007 January 12, Zewail's paper on April third same here.

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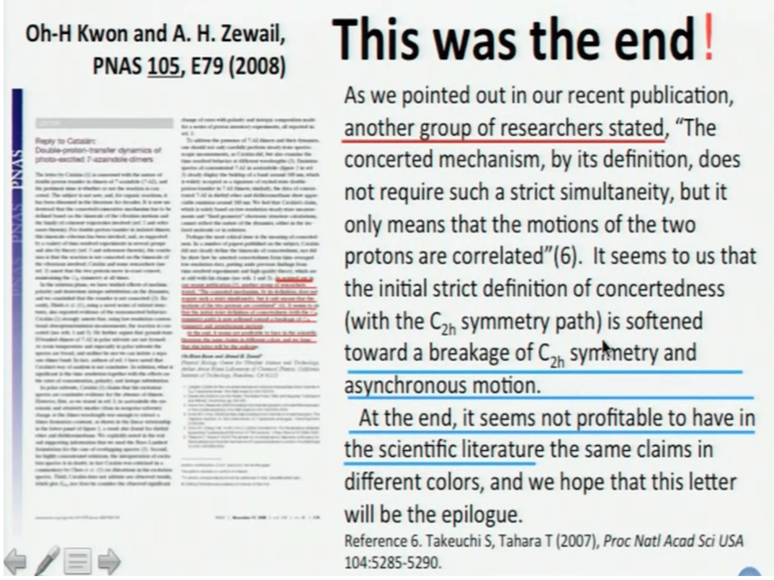

Oh-H Kwon and A. H. Zewail,
PNAS 105, E79 (2008)

This was the end!

As we pointed out in our recent publication, another group of researchers stated, "The concerted mechanism, by its definition, does not require such a strict simultaneity, but it only means that the motions of the two protons are correlated"(6). It seems to us that the initial strict definition of concertedness (with the C_{2h} symmetry path) is softened toward a breakage of C_{2h} symmetry and asynchronous motion.

At the end, it seems not profitable to have in the scientific literature the same claims in different colors, and we hope that this letter will be the epilogue.

Reference 6. Takeuchi S, Tahara T (2007), *Proc Natl Acad Sci USA* 104:5285-5290.

So Catalan wrote this comment, encourage you to read it and Zewail wrote a responds to the comment and that was the end of the debate. So well this very small print you can read it here it is blown up for a benefit. So what Zewail said is here that as you pointed out in our recent publication another group of researchers stated the concerted mechanism by its definition does not require such a strict simultaneity.

So what it had boiled down to is it really concerted or the both going out exactly at time t = 0 with attosecond resolution. So Tahara had said no who is saying that? It might be that there is little bit of difference, but you cannot make out. The fact remains that the initial 0.2 picosecond component is not the first proton transfer. So they discussed a little bit of symmetry breaking and then this is where these are the statement of yielding at the end it seems not profitable to have in the scientific literature the same claims in different color.

And we hope that this letter will be the epilogue and it was. So that brings us to the end of this decade long discussion on what seem to be what might seem to be an outsider a debate of no consequence. But actually, that is very wrong approach this is an engrossing debate because it teaches you several things some scientific and at least one philosophical. The scientific thing that we learn is we learn how to handle situation like this where you have closely lying states.

What are the experiments you need to do? How do I analyze is your data to come up with an explanation that is that differentiates states the difference of which is really subtle a less careful experiment would completely miss this. So this body of literature that has been produced teaches us specifically those in the ultrafast dynamics field but also generally in other field of how experiment should be done?

How data should be analyzed and how question should be asked to understand a problem that is not easy to solve. And the philosophical outcome of this is published paper is not gospel truth. Just because somebody has said something in a paper we cannot say that is published so it is right. That is completely wrong science progresses as a result of series of mistakes. People do something they interpreted in such a way and more often then not it is wrong Rutherford theory was wrong.

Was it completely wrong? It was not completely wrong because they are after all there is in a nucleus and there is an electron outside the nucleus. But this planetary motion and all that is wrong. Both theory was wrong but where did not done we would not have raised the present state of the art. So somebody who has won Nobel prize or is about to win Nobel prize it is not necessary that whatever he says is the absolute truth.

And even if you are Goliath or less that Goliath in front of that David if you are convinced about what we are saying we should have the metal of taking it forward and following through until the epilogue comes right. So that is why I am really very fond of this debate and I thought we will discuss it as a part of this course. That brings us to an end of whatever we wanted to say about molecules of course what we have presented on the molecules again is the tip of the iceberg.

We have not discussed the fast body of literature that exist on say things like photo isomerization that is another story in itself you can teach half of a course on it. So all that I leave to you to read but since in any case we are coming to end of the course in a few more modules may be 15 more modules. What we will do is we will move on to metal nanocluster after this and to metal nanoparticles and semiconductor nanoparticles.

And then we will discuss 2D electronic and IR one of those spectroscopy and perhaps we will come back to Tahara sons work as well. And we will discuss what is called some frequency generation at the surface. That is again a classical problem that has been reinvented a new sites have been achieved in the last 15 minutes. That will bring us to the end of the course.