Ultrafast Optics and Spectroscopy
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Lecture - 39
Attosecond Chemical Dynamics 2

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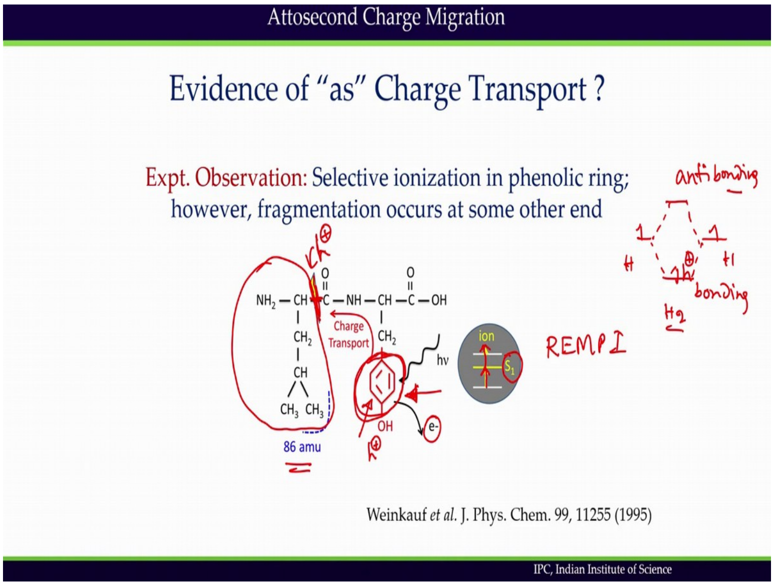

Attosecond Charge Migration

Evidence of "as" Charge Transport ?

Expt. Observation: Selective ionization in phenolic ring; however, fragmentation occurs at some other end

Weinkauf *et al.* J. Phys. Chem. 99, 11255 (1995)

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Next question is that is there any evidence of Attosecond charge transport in chemical reactivity or the influence of attosecond charge transport in the chemical reactivity. I will give you two examples from literature; one example is based on the Weinkauf work. What they did? They took this a molecule a big molecule and then they have selectively ionized this molecule.

They know that the selective ionization they know that the local ionization occurred in this moiety. Because this ionization was done through the REMPI scheme resonance enhance; REMPI Resonance Enhance Multiple Ionization scheme. What does it mean? It means that, this moiety or this chromophore has a particular electronic state that is the characteristic S 1 state.

So, they have undergone this ladder climbing through this S 1 state and then they have ionized the molecule which means that they have selectively ionized the molecule at this end of this molecule. So, they have removed an electron from here and when they looked at the fragmentation pattern of this molecule. They have found that this is the fragment which is having 83 amu mass channel this is the fragment they have observed.

Based on this observation Weinkauf and co workers they concluded that this electron when you remove an electron we create a hole charge hole positive charge which is nothing, but an missing electron. That has to transport to a bond where the bond will be broken. Now, just imagine I have this two we know that that this is the way we can have bonding and I can have this bonding and antibonding orbital's ok.

Now, if we remove one electron from bonding. So, this is your bonding let us say this is again hydrogen atom two hydrogen atom making hydrogen molecule. And this is the emo diagram we can construct very easily this is bonding this is antibonding. Now and these are very preliminary chemical problem we have. This is the how we construct the bonding in the hydrogen molecule the hydrogen molecule.

Now, we know that if you remove an electron from bonding then bond order will decrease, which means I am placing one hole charge here. If I remove an electron from bond from an energy level or from a molecular orbital then we create a hole charge density in it. And if we create a hole charge density the bond order will decrease and the bond will be weak.

And with this argument Weinkauf and co worker said that ok because we are removing an electron from this end of this molecule this hole charge has to migrate to this end. And sitting probably in this bond and that is why we are breaking this bond. So, this is an very indirect evidence of role of attosecond charge migration in the reactivity of in the chemical reaction.

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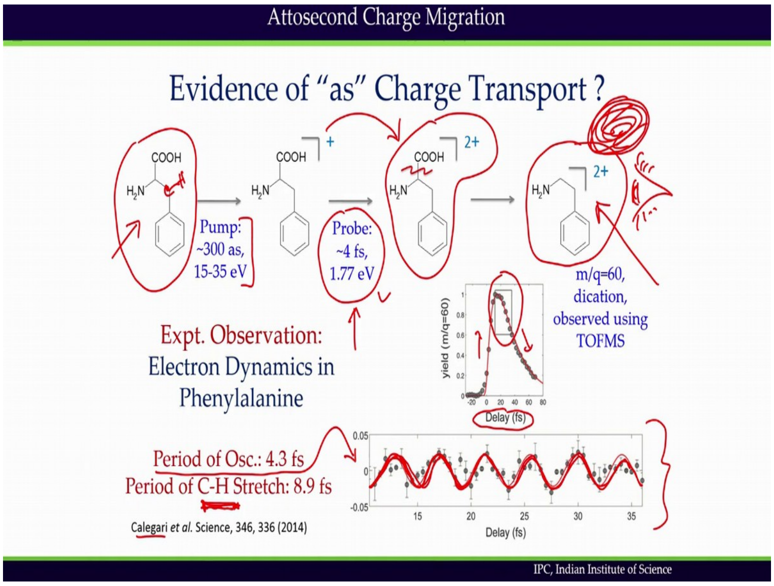

Attosecond Charge Migration

Evidence of "as" Charge Transport ?

Pump: ~300 as, 15-35 eV

Probe: ~4 fs, 1.77 eV

m/q=60, dication, observed using TOFMS

Expt. Observation: Electron Dynamics in Phenylalanine

Period of Osc.: 4.3 fs
Period of C-H Stretch: 8.9 fs

Calegari *et al.* Science, 346, 336 (2014)

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There is an another example we will we have picked up here. In this example this is an experiment done by calegari and co workers, they have ionized this molecule this molecule by a pump pulse. Then they have double ionized this molecule which means this ion has to be doubly again ionized with the help of a probe pulse this one.

And once they have formed this doubly ionized product, they have seen a fragment of this and they are monitoring this fragment in the mass spectrometer. And when they looked at the fragment mass channel intensity as a function of delay between pump and probe what they have seen that, slowly they have an increase and then there is a decay this is there an increase and then there is a decay in the positive delay.

If in the negative way they know that the probe cannot ionize the molecule that is why when probe becomes earlier than pump, then you can you do not produce this iron. We produce this ion only when the pump comes earlier in time as compared to the probe. And that is why they have a build up signal this is the transient ionization spectrum. We have already gone over similar kind of transition transient spectrum before in this course.

Now, when they looked at closely at this regime of this transient ionization spectrum, they have seen an oscillation this is the oscillation they have observed as a function of time delay. And this oscillation what does it mean by this oscillation. Let us say I have a process going on the process is nothing, but the production of this ion we are creating this ion.

Now, when we are creating this ion there must be a probability of creating that ion. And that probability is getting modulated by the pump probe delay time. What does it mean? It means that its some oscillatory behavior of the molecule is affecting the probability of producing this double charged cation. There we see the probability goes high low; high low this is the way it happens.

So, one can visualize like this way. Let us say in a molecule what kind of oscillatory behavior I can have simplest oscillatory behavior is the vibration. So, I in a molecular a molecule is vibrating like this way. And when the molecule is vibrating like this way then in this configuration I can have higher probability of producing that ion that is why I have a higher yield.

Then low yield then high yield low yield, high yield, low yield, high yield and that is why we can have this oscillatory behavior of the of the ion signal. And one can imagine that in a molecule the simplest oscillatory behavior is going to be vibration which is nuclear motion which is oscillatory.

So, they looked at the period of the oscillation for the C H stretching vibration that is the fastest vibration one can imagine for this molecule for we have C H bonds this is a C H bond. So, they thought that ok, this oscillation could be because of this C H 1 vibration. So, what is the period of the C H 1 vibration? The bond is going to be 8.8 femtosecond.

But then looked at they looked at this oscillatory behavior and then they found that the period of oscillation experimentally observed oscillation is going to be is actually 4.3 femtosecond. So, their observed oscillation is much faster than the fastest possible vibration that is C H vibration in the molecule. What could be other kind of oscillation in the molecule? There must be some kind of electronic oscillation which is going on in the molecule after ionization.

And based on this Calegari and co workers concluded that the after the ionization we there must be some superposition of electronic states they are creating. And that electronic superposition is changing the electron density and affecting the cross section of this reaction. And that is why they have seen even faster oscillation faster than the possible fastest vibration in the molecule.

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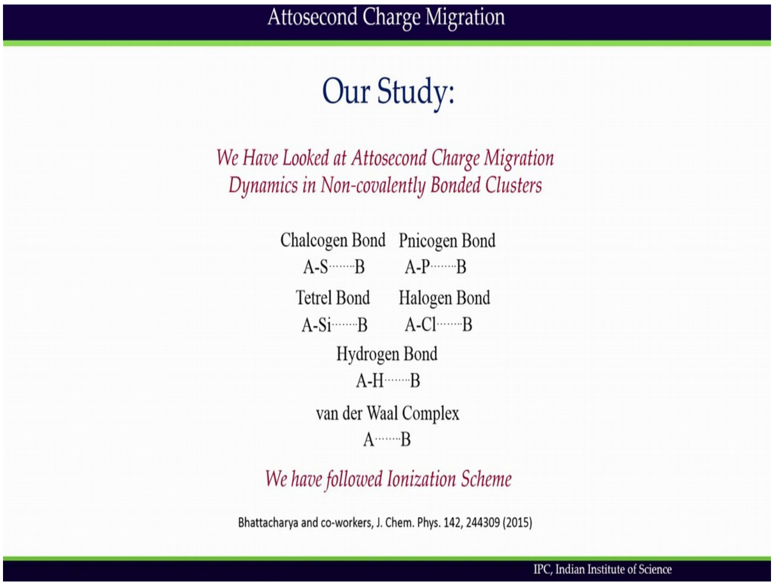

Attosecond Charge Migration

Our Study:

We Have Looked at Attosecond Charge Migration Dynamics in Non-covalently Bonded Clusters

Chalcogen Bond
A-S·······B

Pnicogen Bond
A-P·······B

Tetrel Bond
A-Si·······B

Halogen Bond
A-Cl·······B

Hydrogen Bond
A-H·······B

van der Waal Complex
A·······B

We have followed Ionization Scheme

Bhattacharya and co-workers, J. Chem. Phys. 142, 244309 (2015)

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So, this two examples are directly pointing out in. In fact, indirectly pointing out that there is a role of attosecond charge oscillation and charge migration in the molecular reactivity. Is there any direct evidence of attosecond charge migration we have in the chemical reactivity yet? There is no experiment to the best of my knowledge has been performed.

So, for which shows directly experimentally demonstrate that there is an influence of attosecond charge migration in the chemical reactivity. So, with this idea we started working in inorganic chemistry in the department of inorganic and physical chemistry Indian Institute of Science. And we selected a binary complex these two molecules can come closer.

They are they can be weakly bound sometimes they are called (Refer Time: 10:11) complex sometimes they called non covalently bonded complex. What kind of interactions? They have we are not interested. But what we are interested is that if we take two dissimilar molecules let us say one is methanol another one is water. If we take this two dissimilar molecules and try to ionize one of them we know that ionization potential will vary depending on the molecule. This molecule may have different ionization potential than this molecule.

So, depending on the ionization potential we can selectively ionize one molecule. And then we can try to monitor whether there is a hole charge which is which might be delocalized over the over the entire molecule. So, initially I might create a hole density here and then slowly that hole density delocalized over the entire molecule. And that is the goal which we had when we initiated this attosecond program in Indian institute of science.

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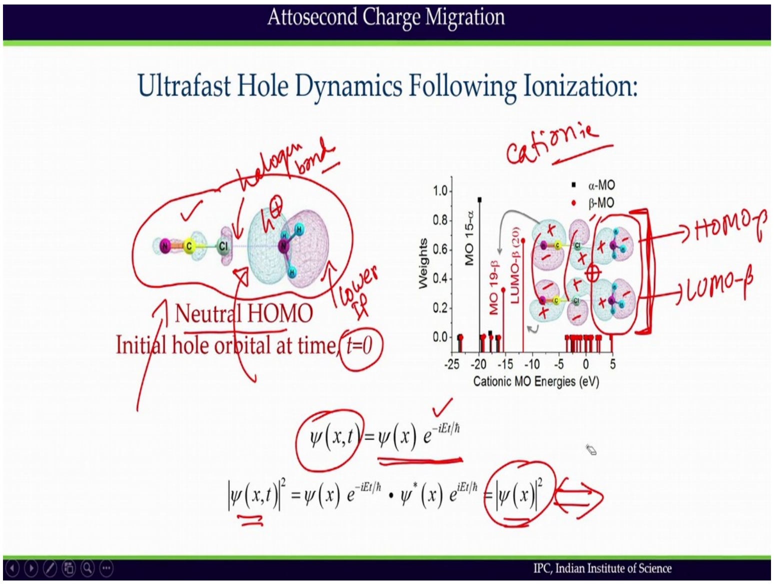

Attosecond Charge Migration

Ultrafast Hole Dynamics Following Ionization:

Neutral HOMO
Initial hole orbital at time, $t=0$

$$\psi(x,t) = \psi(x)\, e^{-iEt/\hbar}$$

$$|\psi(x,t)|^2 = \psi(x)\, e^{-iEt/\hbar} \bullet \psi^*(x)\, e^{iEt/\hbar} = |\psi(x)|^2$$

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This is an example quickly we will be able to understand what does it mean by this electron delocalization attosecond electron delocalization we are talking about. This is the non covalently bonded system we selected and in this cluster this is a binary mixture. So, we have c l c N this is one molecule and ammonia is another molecule. This is another molecule two molecules are bound by this dotted line this dotted line is called halogen bond.

Now, they are they are attractive attraction this is an this is an attractive interaction. So, this two molecules will not fall apart as we give the energy ok. So, they will be staying close to each other is just like a bonding ok, but its a very weak bonding and that is why they stay close to each other. Now, we know that ammonia has lower ionization potential which means that lower than this molecule, which means that to remove an electron from ammonia it requires more energy than cl c N. That is why its quite obvious that if we ionize this molecule molecular cluster we will be able to create a hole charge density in the ammonia end.

But this hole charge density which we have created is going to be at t equals to 0 immediately after ionization. If we create a hole in the electron density effectively the main field of the hole electron. So, let us I have an electronic cloud which is optimized with the help of acf iteration that is the cell constant field scheme. So, I have an electron density and I remove one electron from this density.

If we remove an electron from this electron density. Then we create a hole charge density in the cloud which means, the mean field experience by other electrons will change. And because it has changed the mean field we have to re optimize the mean field. When we are re-optimizing the mean field we have to remember that we are not changing the nucleus. Nucleus is fixed nuclei do not change it is the mean field which will change and we are trying to optimize it.

After optimization in the cation state of the mean field we see that there are two orbitals we get and this two orbitals are nothing, but LUMO beta and homo beta. So, this is homo beta and this is LUMO beta. LUMO stands for lowest unoccupied molecular orbital. I have removed my electrons that is going to be lumo and homo beta stands for highest occupied molecular orbital. Now, if we so this is the cationic orbital optimize cationic orbital.

And this is the neutral homo which is representing the initial hole orbital at time t equals 0. What we see from this two diagram is that, we can represent this initial state by linearly combining this two orbitals. If we combine this two linearly we see that different colors are representing the different phases of the wave function.

So, this is your negative, this is your positive, this is positive, this is your negative, this is your positive, this is your negative, now this is your positive, this is your negative. Now this is positive, this is negative, this is positive, this is negative, this is negative, this is positive. So, if we linearly add them what will happen this negative positive part will cancel out this negative positive part will cancel out. So, in the end electron density will be localized in this moiety and that is exactly what we can do mathematically.

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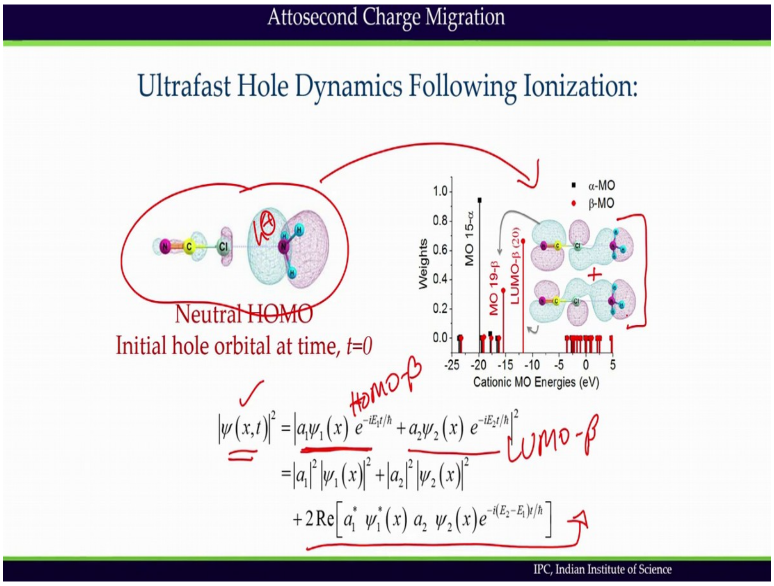

Attosecond Charge Migration

Ultrafast Hole Dynamics Following Ionization:

Neutral HOMO

Initial hole orbital at time, *t=0*

$$|\psi(x,t)|^2 = |a_1\psi_1(x)\, e^{-iE_1t/\hbar} + a_2\psi_2(x)\, e^{-iE_2t/\hbar}|^2$$

$$= |a_1|^2 |\psi_1(x)|^2 + |a_2|^2 |\psi_2(x)|^2$$

$$+ 2\mathrm{Re}\left[a_1^*\ \psi_1^*(x)\ a_2\ \psi_2(x) e^{-i(E_2-E_1)t/\hbar}\right]$$

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Mathematically, when we create a superposition state quantum mechanics suggest that. If we create a if we if the wave function can be time dependent for any quantum system wave function can be time dependent. But its density may not be time dependent because it a pure state and for density it is psi psi star and that is why we get time independent density. And remember all the experimental observables in all the experimental observables in a atomic or molecular chemistry those observables are always connected to the density of to the density.

So, this density is somehow connected to the experimental observable not the wave function we do not see the wave function. We always see the expectation value which is related to the density show all the wave function can be time dependent for a pure state in the intensity cannot be time dependent. So, experimentally we will not be able to see any time dependence we see time dependence in density when we create a superposition state something like this.

So, this state initial state can be expressed as linear combination of these two cationic states cationic molecular orbitals. And that is exactly what we are doing one state we created by the help of with the help of this superposition states. So, this is one state which is let us say, this is HOMO beta and this is LUMO beta.

So, this two states I have combined together once we combine together we get the density and then density depends on you see that, density will depend on the time and so time dependent density will see. So, this is a basic quantum mechanics we do not see time dependent change in density. if it is a pure state. We see time dependent change in density when we create a superposition state and superposition state we are creating after ionization. The initial hole orbital will be represented with the help of a superposition of the cationic orbitals and that is why we see the change in density.

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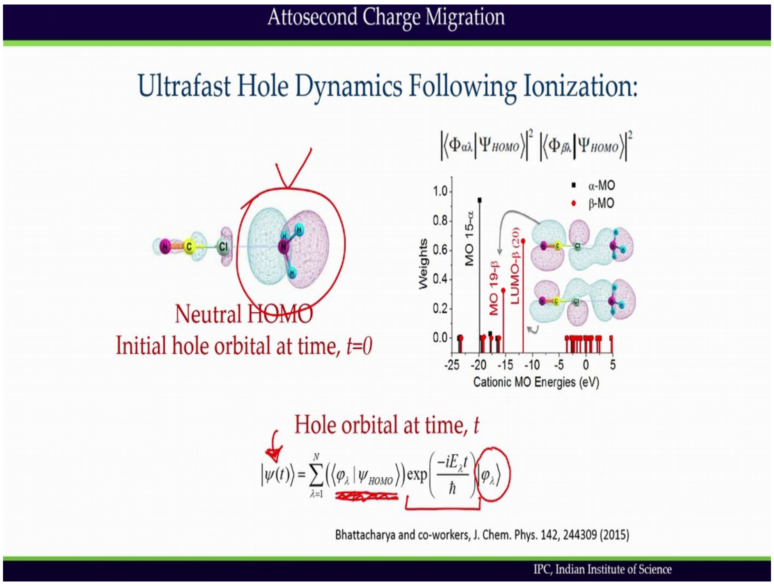

Attosecond Charge Migration

Ultrafast Hole Dynamics Following Ionization:

Neutral HOMO

Initial hole orbital at time, $t=0$

$$|\langle\Phi_{\alpha\lambda}|\Psi_{HOMO}\rangle|^2 \quad |\langle\Phi_{\beta\lambda}|\Psi_{HOMO}\rangle|^2$$

Hole orbital at time, t

$$|\psi(t)\rangle = \sum_{\lambda=1}^{N} \left(\langle\varphi_\lambda|\psi_{HOMO}\rangle\right) \exp\left(\frac{-iE_\lambda t}{\hbar}\right) |\varphi_\lambda\rangle$$

Bhattacharya and co-workers, J. Chem. Phys. 142, 244309 (2015)

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Now, the these are the details of the theory we can go over the details little bit what we are doing now is that, the initial state or the hole orbital can be represented as a linear combination of all cationic orbitals. So, this is the cationic orbitals representing the cationic orbital. And the expansion coefficient for this expansion is taken to be the overlap mattress between the cationic orbital and the homo psi homo; psi homo is this orbital.

So, all we are doing is that we are taking this neutral homo orbital and projecting onto all cationic orbitals all the metals and that is exactly what we are doing. So, if this densities are similar, then we get this expansion coefficient densities are different in delay then this expansion coefficient will go 0. And then we add this time dependent factor time dependent phase factor, which is coming from the general description of the wave function time dependent wave function.

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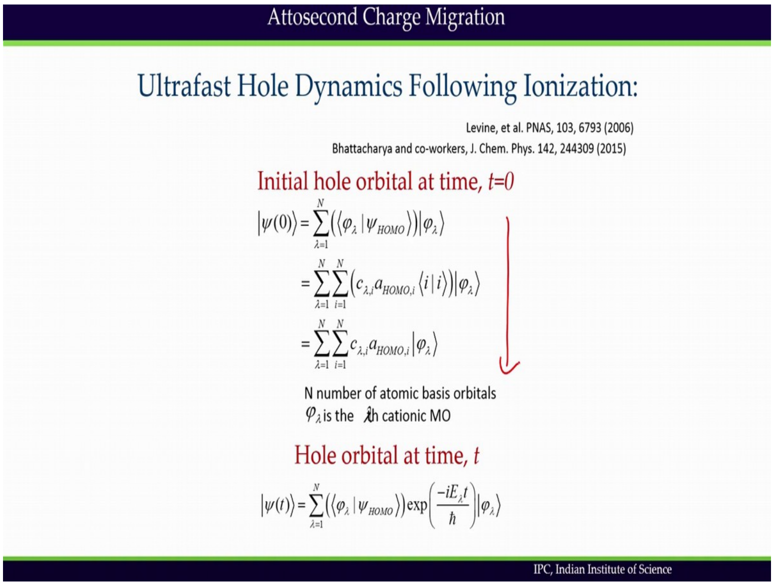

Attosecond Charge Migration

Ultrafast Hole Dynamics Following Ionization:

Levine, et al. PNAS, 103, 6793 (2006)
Bhattacharya and co-workers, J. Chem. Phys. 142, 244309 (2015)

Initial hole orbital at time, *t=0*

$$|\psi(0)\rangle = \sum_{\lambda=1}^{N}\left(\langle\varphi_\lambda|\psi_{HOMO}\rangle\right)|\varphi_\lambda\rangle$$

$$= \sum_{\lambda=1}^{N}\sum_{i=1}^{N}\left(c_{\lambda,i}a_{HOMO,i}\langle i|i\rangle\right)|\varphi_\lambda\rangle$$

$$= \sum_{\lambda=1}^{N}\sum_{i=1}^{N}c_{\lambda,i}a_{HOMO,i}|\varphi_\lambda\rangle$$

N number of atomic basis orbitals
φ_λ is the λth cationic MO

Hole orbital at time, *t*

$$|\psi(t)\rangle = \sum_{\lambda=1}^{N}\left(\langle\varphi_\lambda|\psi_{HOMO}\rangle\right)\exp\left(\frac{-iE_\lambda t}{\hbar}\right)|\varphi_\lambda\rangle$$

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By this way we are representing the hole orbital if we represent the hole orbital like this way.

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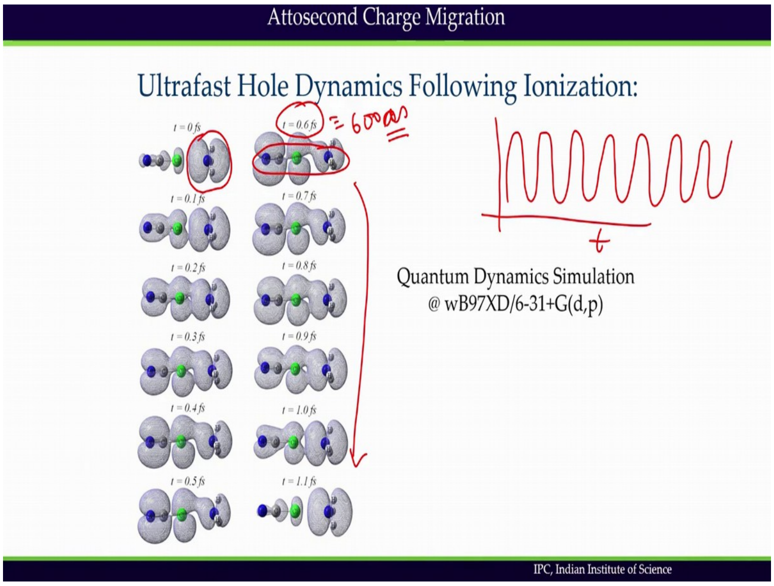

Attosecond Charge Migration

Ultrafast Hole Dynamics Following Ionization:

Quantum Dynamics Simulation
@ wB97XD/6-31+G(d,p)

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Then we can reduce down slowly and finally, we can actually get this results we will go to this results directly. Here what we see that at t equals 0 time hole density mostly localize in the nh 3 moiety and within 600, 0.6 femtosecond is nothing but 600 attosecond. Within this 600 attosecond we see that the hole density is delocalized over the entire complex.

But again this is going back to its origin where the hole was created and this is kind of an oscillatory behavior. So, if as a function of time if we draw the hole density how it should look like? It should look like an oscillation it just look an oscillation total hole density on ammonia is just an oscillation as a function of time. And this will continue forever unless there is an important information we include we will discuss that information very soon.

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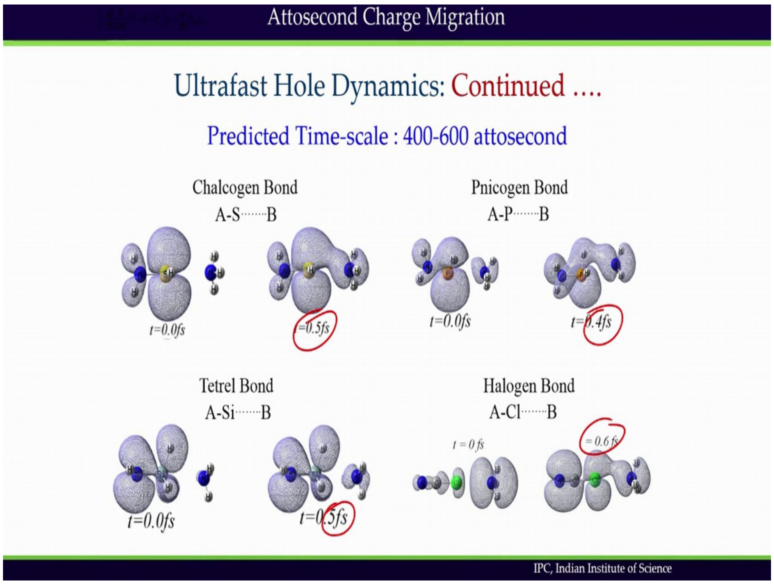

Attosecond Charge Migration

Ultrafast Hole Dynamics: Continued ....

Predicted Time-scale : 400-600 attosecond

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But what we will do right now is that we will continue and check other non covalent bonded systems. Previously we have talked about halogen bond; halogen bond where this the definition of hydrogen bond we do not need to know the definition immediately.

But we can change this X atom this if it is an X atom A X interacting with B. Now, depending on what kind of X atom I have it is in halogen atom then it is called halogen bond, if it is chalcogen atom then its chalogen bond, if it is pnicogen atom then it is pnicogen bond, if its a tetrel atom then its called tetrel bond.

And this is the way different definition of non covalent bonds is given in literature we are not interested in the characteristics of different non covalent bonding interactions, we are only interested in, If they are forming these bonds and we selectively ionize or selectively remove an electron from one molecule how the hole density is delocalizing over the entire molecular that is exactly what we are interested in. And we see that within almost 500 attosecond time scale 400 to 500 or 600 attosecond time scale. This hole density is delocalized this is more like an universal response we are seeing for many other system.

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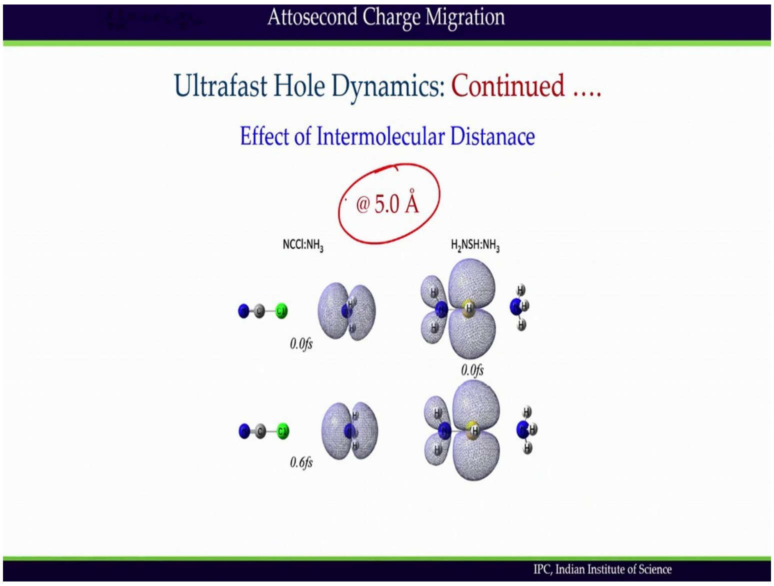

Attosecond Charge Migration

Ultrafast Hole Dynamics: Continued ....

Effect of Intermolecular Distanace

@ 5.0 Å

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If we try to understand what will happen if we selectively we if we will hold this two molecules. And instead of allowing it to be present in the equilibrium configuration, if we just separate them at a long distance. Then again we selectively ionize it we ionize it from this moiety we remove an electron from this molecule.

And we try to find out at this long distance do you have the similar kind of charge migration. And we see that beyond a at a long distance let us say five angstrom distance whenthese two molecules are separated they do not show any charge migration.

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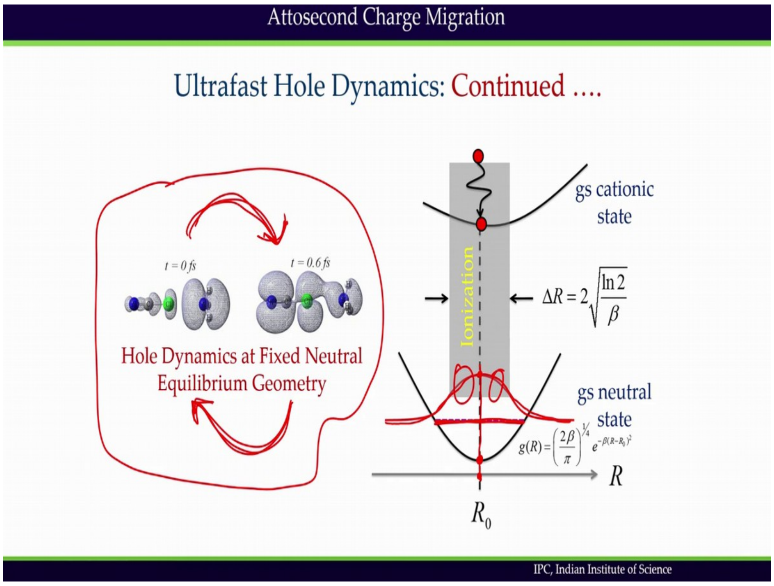

Attosecond Charge Migration

Ultrafast Hole Dynamics: Continued ....

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This is an important observation because at the equilibrium pump this suggest that the equilibrium point only or equilibrium configuration only they are electronically coupled they are electron. And that is why hole can migrate from one moiety to the other moiety. Now, I will come to this important point. We said that this hole migration will be oscillatory and it will exist forever it will just go from one side to the another side partially.

And then again come back and then again go delocalize then localize delocalize localize. So, this will continue forever unless we introduce one important experimental condition into the problem the problem is that. In this discussion in this oscillatory behavior we have considered that the nuclear configuration is R naught, that is the equilibrium point. And anytime when you perform an experiment or when you think about the molecule molecules will always vibrate.

And because of its vibration the 0 point energy state 0 point state is not going to be the other the 0 vibrational state. It means that even at the 0 Kelvin temperature when we are at the ground vibrational state molecule will vibrate any molecule cannot be no molecule can be made vibration less. But a molecule can be made rotational less because 0 point energy of rotation is 0.

But 0 point energy of vibration is not 0 it is some value it has. And at the ground state it has if we take the harmonic potential or harmonic approximation. Then the ground state wave function of vibrational wave function is represented by a Gaussian function. It suggest that at the equilibrium point the probability of finding this configuration is maximum, but other configuration will also contribute.

And one way to incorporate this idea into the dynamics work is that to use vigor distribution vigor distribution with the help of distribution one can sample different nuclear configuration and see what is the ensemble average response for this oscillatory dynamics.

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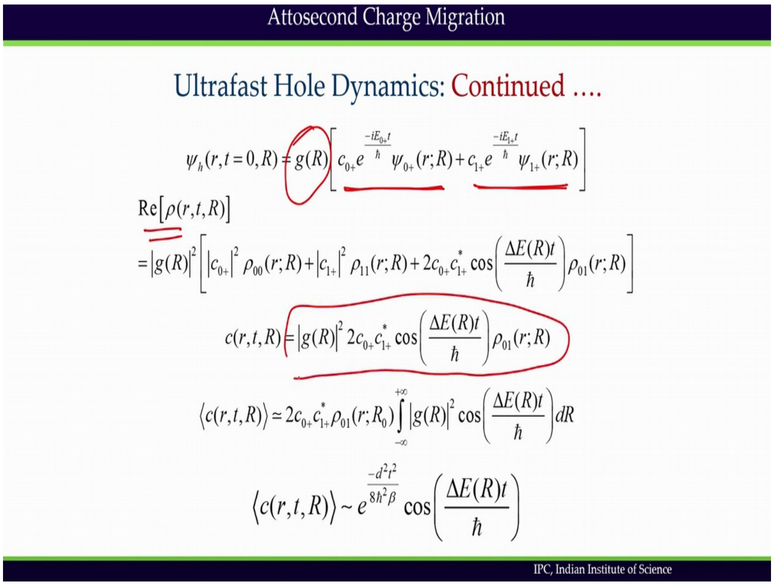

Attosecond Charge Migration

Ultrafast Hole Dynamics: Continued ....

$$\psi_h(r,t=0,R)=\boxed{g(R)}\left[\underline{c_{0+}e^{\frac{-iE_{0+}t}{\hbar}}\psi_{0+}(r;R)}+\underline{c_{1+}e^{\frac{-iE_{1+}t}{\hbar}}\psi_{1+}(r;R)}\right]$$

$$\underline{\underline{\mathrm{Re}}}\left[\rho(r,t,R)\right]$$

$$=\left|g(R)\right|^2\left[\left|c_{0+}\right|^2\rho_{00}(r;R)+\left|c_{1+}\right|^2\rho_{11}(r;R)+2c_{0+}c_{1+}^*\cos\left(\frac{\Delta E(R)t}{\hbar}\right)\rho_{01}(r;R)\right]$$

$$c(r,t,R)=\boxed{\left|g(R)\right|^2 2c_{0+}c_{1+}^*\cos\left(\frac{\Delta E(R)t}{\hbar}\right)\rho_{01}(r;R)}$$

$$\left\langle c(r,t,R)\right\rangle\simeq 2c_{0+}c_{1+}^*\rho_{01}(r;R_0)\int_{-\infty}^{+\infty}\left|g(R)\right|^2\cos\left(\frac{\Delta E(R)t}{\hbar}\right)dR$$

$$\left\langle c(r,t,R)\right\rangle\sim e^{\frac{-d^2t^2}{8\hbar^2\beta}}\cos\left(\frac{\Delta E(R)t}{\hbar}\right)$$

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And for that what we have to do, we already we have shown that we have a superposition state. This superposition state will be multiplied by the ground state vibrational wave function. And then we get the density because that is exactly what we are interested in and we see that density will depend on this finally, depend on this time dependent part.

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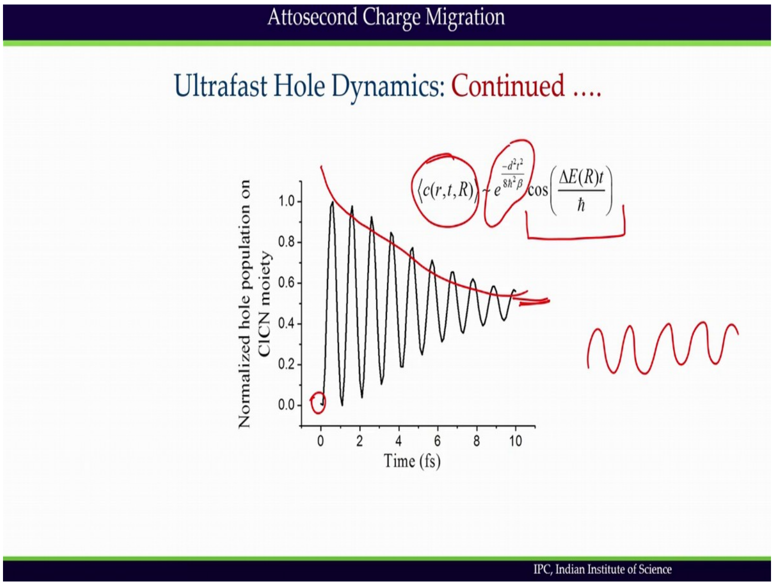

Attosecond Charge Migration

Ultrafast Hole Dynamics: Continued ….

$$\langle c(r,t,R)\rangle \sim e^{\frac{-d^2t^2}{8\hbar^2\beta}}\underbrace{\cos\left(\frac{\Delta E(R)t}{\hbar}\right)}$$

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And if we do this math then what we get is that the density effective the density will depend on two factors. One factory we have already seen this cause that is the oscillatory factor that is the that that causing the oscillation. But this cosine oscillation will be decayed by the by one Gaussian function.

And it suggest that this decay is a Gaussian function and this will decay and what it suggest? It suggest that because of the vibration previously we have not taken vibration. And that is why it will be oscillating always, but because we have now introduced the vibrational affect. The effect of vibration before ionization what will happen within 10 femtosecond it suggest that within 10 femtosecond the charge which I am created in a particular end will be delocalized. And it will stop the it will stop the this oscillation.

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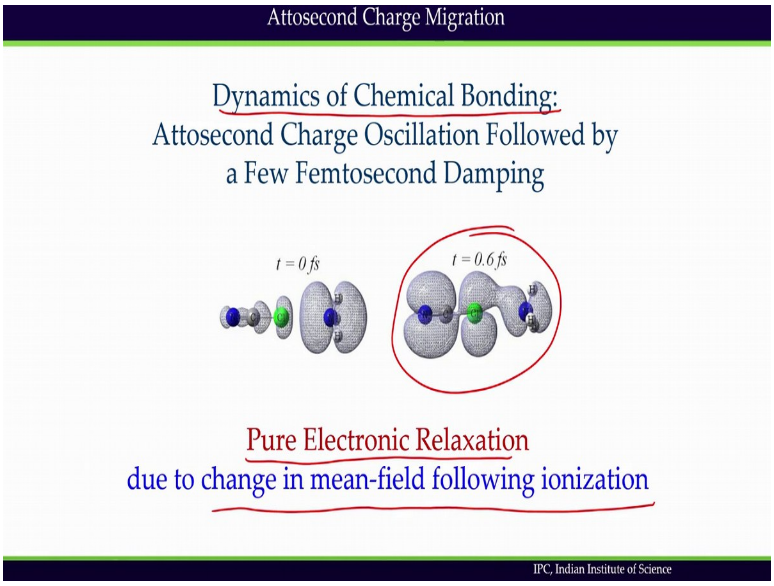

Attosecond Charge Migration

Dynamics of Chemical Bonding:
Attosecond Charge Oscillation Followed by
a Few Femtosecond Damping

Pure Electronic Relaxation
due to change in mean-field following ionization

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So, nuclear packet has a significant effect on the oscillatory behavior of the attosecond charge migration. And this electronic atttosecond charge migration is nothing is driven by pure electronic relaxation due to change in the mean field following ionization. So, this is an important idea which we get and we see that the chemical dynamics of chemical bonding this chemical.

In this problem the chemical bonding is initiated with the help of ionization scheme. And once we ionize it then new chemical bonding is formed the new chemical bonding that is the non covalent bonding is formed between these two moieties. And this is exactly what we are probing and we see that this bonding. Bonding form this non covalent bond is formed with the help of attosecond charge oscillation followed by a few femtosecond damping. And this is very common to all the system we have studied.

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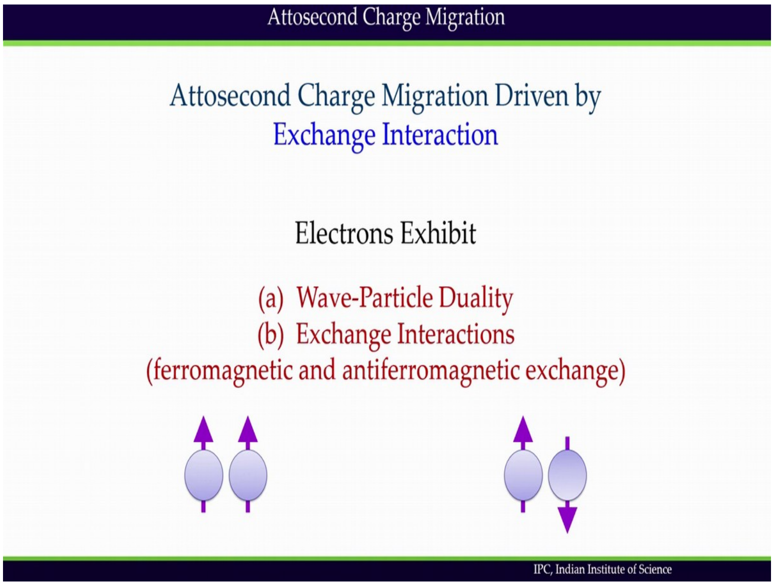

Attosecond Charge Migration

Attosecond Charge Migration Driven by
Exchange Interaction

Electrons Exhibit

(a) Wave-Particle Duality
(b) Exchange Interactions
(ferromagnetic and antiferromagnetic exchange)

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So, far what we have discussed is that attosecond charge migration could be because of the electronic relaxation pure electronic relaxation. The next slide we will talk about it could also be driven by exchange interaction. And exchange interaction is nothing but the behavior of an electron electrons are very interesting particles they have wave particle duality.

And also they exhibits exchange interaction and among exchange interactions. There are two important interactions, which is known ferromagnetic interactions. And anti ferromagnetic interactions these interactions are very important magnetism and also long range electron electron correlation.

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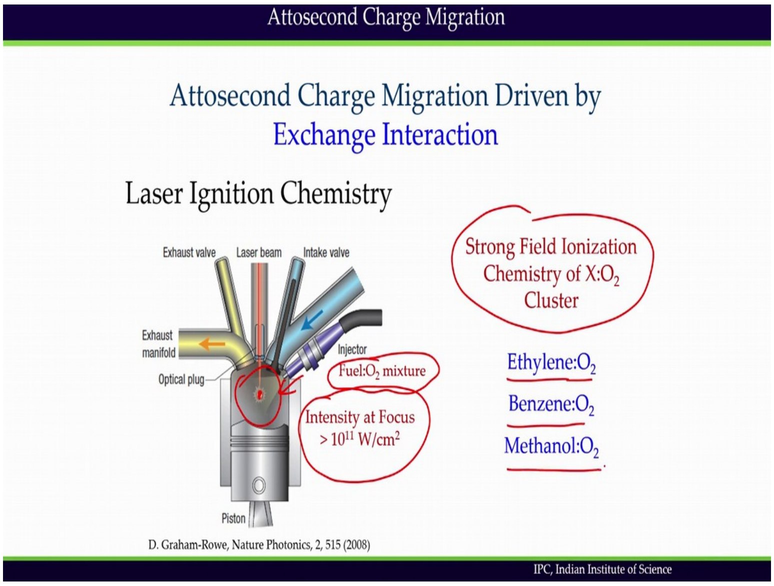

Attosecond Charge Migration

Attosecond Charge Migration Driven by Exchange Interaction

Laser Ignition Chemistry

Strong Field Ionization Chemistry of X:O_2 Cluster

Ethylene:O_2

Benzene:O_2

Methanol:O_2

D. Graham-Rowe, Nature Photonics, 2, 515 (2008)

IPC, Indian Institute of Science

The problems which we discussed this exchange interaction is could be very interesting fundamentally very interesting problem. In the laser ignition chemistry in the laser ignition chemistry what we do? We focus a laser beam in the combustion engine in general all the cars which we drive present at present. They are using spark plug ignition the spark plug what does it means?

I have a container in this container there is a fuel which is injected fuel gasoline or petrol these are vaporized. And then injected in the container and in this container we have a this is spare plug this is the current technologies spark plug best technology. In the internal combustion engine in our car and in the spark plug what you do, we have a two electrodes and in the two in this two electrons we employ very high voltage.

When we employee very high voltage, then what will happened there will be a spark in between these two electrons. And that spark can actually ignite the fuel and it can create the self sustaining combustion. And that is the basic idea of the internal combustion engine. Now, there are many problems in of using spark plug in internal combustion engine and future technology are proposed to be based on the laser ignition chemistry.

So, the spark which is created by the spark plug will be replaced by the laser beam. And what happens? In the laser beam we focus the beam at a particular point in the fuel region in the where the fuel mixture is injected and that will create the self sustaining combustion. Now, the spark will be done by the laser ignition at the very high intensity.

And the kind of intensity of which is used which is proposed to use is more than 10 to power 11 what percent to be the square. This is a very highly intense intensity which is required to initiate that combustion. Now, a when you talk about this in the fuel injection fuel oxidize and mixture is used and in the end fundamentally the hole problem becomes a strong fuel ionization chemistry of fuel oxidize emission.

Mostly when you burn fuel in internal combustion engine we mix fuel with oxygen. And that is why let us say it could be ethylene oxygen mixture, it could be benzene oxygen mixture methanol oxygen mixture. So, these are the mixtures which is used.

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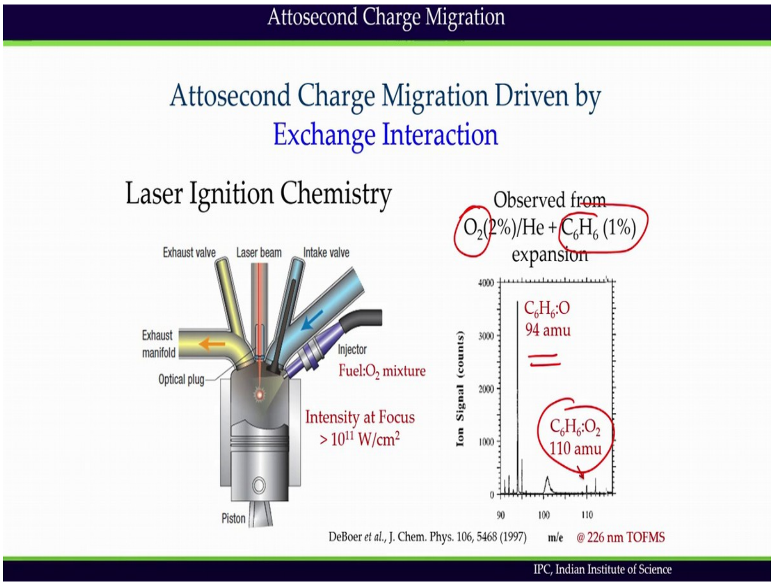

Attosecond Charge Migration

Attosecond Charge Migration Driven by Exchange Interaction

Laser Ignition Chemistry

Observed from O_2(2%)/He + C_6H_6 (1%) expansion

DeBoer *et al.*, J. Chem. Phys. 106, 5468 (1997) @ 226 nm TOFMS

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And it has been found that at when we mix let us say benzene with oxygen, then we see that, there are clusters benzene oxygen clusters which are formed. So, this kind of clusters are formed in the gas phase. And the hole laser ignition chemistry fundamentally can be viewed as strong fuel ionization chemistry of this kind of oxygen fuel cluster.

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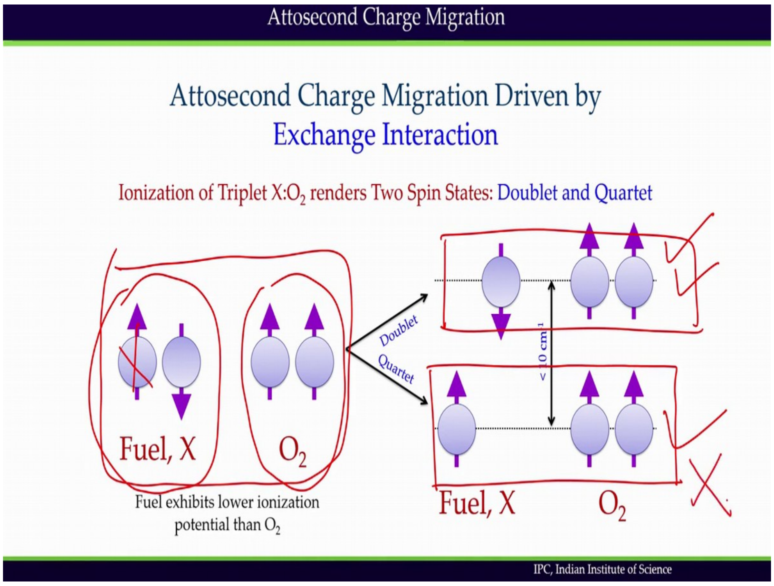
Attosecond Charge Migration

Attosecond Charge Migration Driven by Exchange Interaction

Ionization of Triplet X:O_2 renders Two Spin States: Doublet and Quartet

Fuel exhibits lower ionization potential than O_2

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And when you look at the oxygen fuel cluster fuel is generally they are singlet they are they do not have any unpaired electron but oxygen. When we think about it oxygen is a triplet is a electronically it is a triplet state that. So, when we combine this two system and try to ionize this system, then we can have two opportunities; one opportunity is that one case we can remove this electron and we can a quartet state.

On the other hand we can remove this electron. , we can remove this electron and we can have a doublet state. And we see that this doublet state and the quartet state they are very close lying. The energy difference between these two spin states are found to be less than 10 wave number; 10 wave number could be just an error in the competition.

So, they are very close lying one can say they are very almost degenerate states, what has been found by us that, this doublet state only induces attosecond charge migration. But this state to not show any charge migration; quartet state do not show any charge migration.

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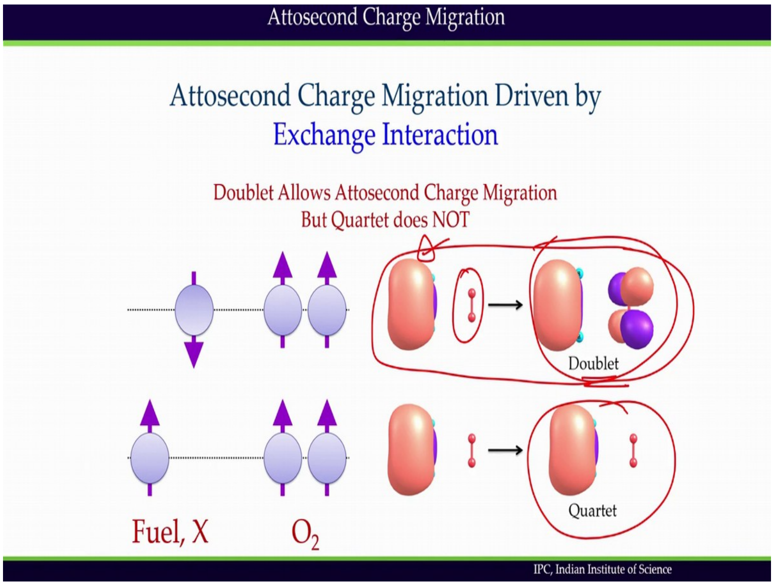

Attosecond Charge Migration

Attosecond Charge Migration Driven by Exchange Interaction

Doublet Allows Attosecond Charge Migration But Quartet does NOT

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But doublet state shows charge migration and that is that is shown here this is the charge which we create. In general fuel molecule shows lower ionization potential than oxygen molecule. And that is why charge is first created in the fuel molecule, which is then delocalized in the hole complex. And that is that happens only in the doublet state this does not happen in the quartet state. And that is why we believe that this is due to the exchange interaction, pure exchange interaction in the in this kind of system.

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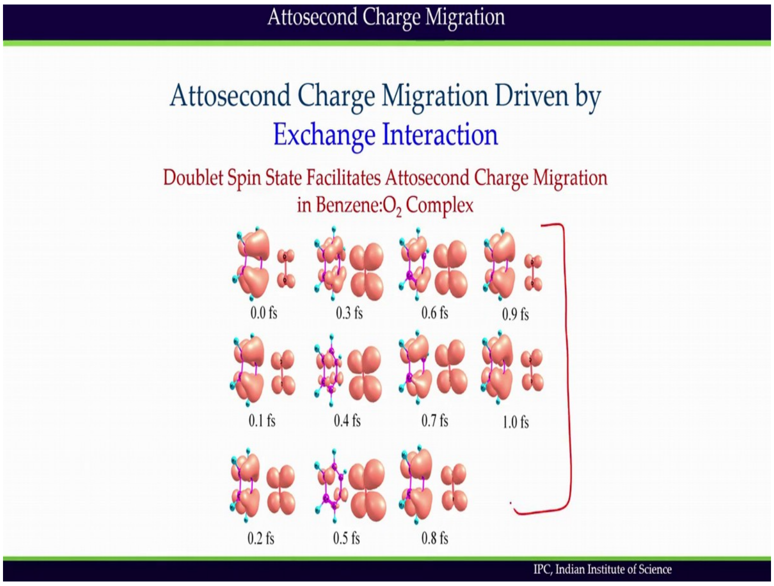

Attosecond Charge Migration

Attosecond Charge Migration Driven by Exchange Interaction

Doublet Spin State Facilitates Attosecond Charge Migration in Benzene:O_2 Complex

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This is just the details of similar kind of charge migration dynamics we have observed.

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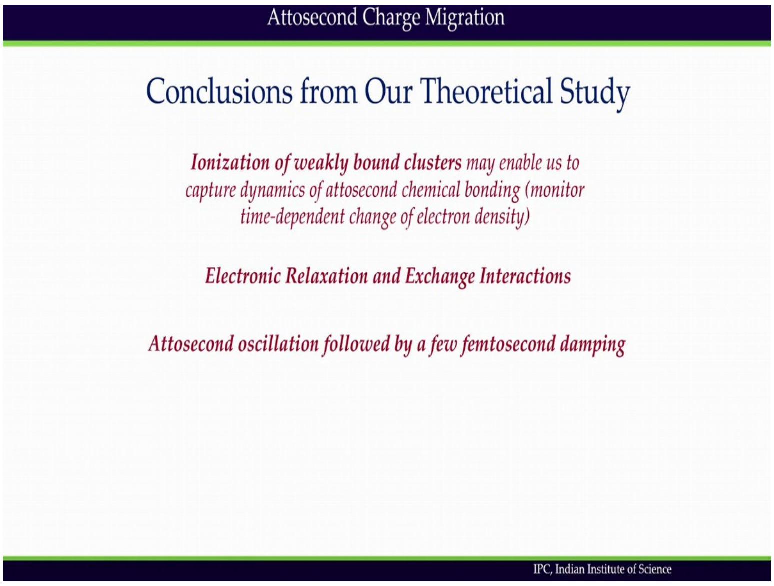

Attosecond Charge Migration

Conclusions from Our Theoretical Study

***Ionization of weakly bound clusters** may enable us to capture dynamics of attosecond chemical bonding (monitor time-dependent change of electron density)*

Electronic Relaxation and Exchange Interactions

Attosecond oscillation followed by a few femtosecond damping

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So, in the end what conclusions we make from our theoretical study. We will discuss the experimental study in the next class. But in the theoretical study what conclusions we have made is that ionization of weakly bonded clusters, actually may enable somebody to capture dynamics of attosecond chemical bonding. Electronic relaxation and exchange interactions both are going to contribute to this attosecond charge migration.

And attosecond oscillation followed by few femtosecond damping is quite common in a in the non covalent bonded clusters. We will meet again for the experimental part of this work. And we will discuss how high harmonic generation this is the technique which can be used to probe or get the fingerprint of this kind of attosecond charge migration in non covalent bonded clusters. We will meet again in the next class.