Ultrafast Optics and Spectroscopy
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Lecture - 38
Attosecond Chemical Dynamics 1

Welcome to the module 16 of the course Ultrafast Optics and Spectroscopy, in this module we will go for little more advanced topic which is Attosecond Charge Migration Dynamics and well I will be presenting this work this module I will be mostly following the work which we are doing in our lab in the IPC department inorganic and physical chemistry department of Indian Institute of Science.

And because we would be presenting our work we will try to simplify the presentation as much as possible to make it suitable for the new student who are interested to understand attosecond dynamics or attosecond phenomenon from a chemist point of view.

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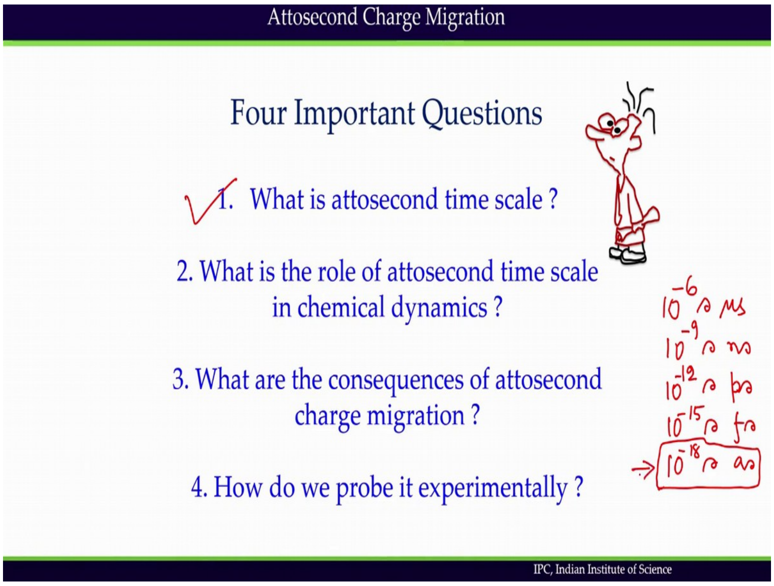

Attosecond Charge Migration

Four Important Questions

✓1. What is attosecond time scale ?

2. What is the role of attosecond time scale in chemical dynamics ?

3. What are the consequences of attosecond charge migration ?

4. How do we probe it experimentally ?

$10^{-6} \to$ μs
$10^{-9} \to$ ns
$10^{-12} \to$ ps
$10^{-15} \to$ fs
$\rightarrow \boxed{10^{-18} \to \text{as}}$

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In this module there are four important questions, what is attosecond time scale? That is the first question we have. What is the role of attosecond time scale in chemical dynamics? That is the second question. Third question, what is the consequences what are the consequences of attosecond charge migration? And the last question we have is how do we probe it experimentally?

And as I told you that mostly I will be presenting our work which we are doing in the IPC department inorganic and physical chemistry department. So, some of the results which we have got from our lab we will be presenting in a manner that anybody can understand the meaning of this attosecond science from a chemist point of view.

Now, before I get into the first question, what is attosecond time scale, I remind that there are different short time scales we have already encountered 10 to the power 6 second which is microsecond, 10 to the power 9 second which is nanosecond, 10 to the power minus 12 second which is pico second, 10 to the power minus 15 second which is femtosecond and 10 to the power minus 18 second which is attosecond and the discussion in the present module will include this time scale 10 to the power minus 18 seconds.

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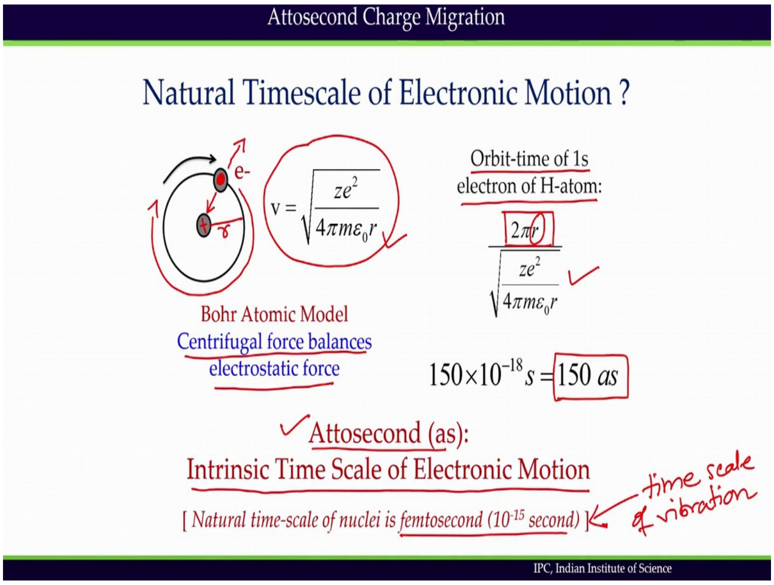

Attosecond Charge Migration

Natural Timescale of Electronic Motion ?

$$v = \sqrt{\frac{ze^2}{4\pi m\varepsilon_0 r}}$$

Bohr Atomic Model

Centrifugal force balances electrostatic force

Orbit-time of 1s electron of H-atom:

$$\frac{\boxed{2\pi r}}{\sqrt{\frac{ze^2}{4\pi m\varepsilon_0 r}}}$$

$$150\times10^{-18}s = \boxed{150\ as}$$

Attosecond (as): Intrinsic Time Scale of Electronic Motion

[*Natural time-scale of nuclei is femtosecond (10^{-15} second)*]

time scale of vibration

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So, what happens in this attosecond time scale? It is very easy to understand what happens in attosecond time scale if we try to understand the natural time scale of 1 s electron from Bohr Atomic Model. Bohr atomic model is the simplest electronic structure theory, which suggests that I have a positively charged nucleus and an electron which is considered to be an particle it is orbiting around this positively charged nucleus.

And when it is orbiting we know that there is an electrostatic force because negatively charged electron will be attracted by the positively charged nucleus. So, electrostatic force will be acting along this side this way this direction and because it is orbiting there is a centrifugal force which will be acting outwards this way and according to Bohr atomic model we know that these two forces will be equal because that is the way we can have the atomic model sustaining atomic model.

And because these two forces are equal then from those two forces after equal after getting those equal forces we can actually once the centrifugal force balances the electrostatic force we can get the velocity of that electron. That is very simple to understand and perhaps this is the first kind of quantum mechanical study we had in our 12 standard.

So, this velocity can be calculated very easily from this equation and once we know the velocity we know the radius of this of the circle that is the Bohr atomic radius and because we know the radius we will be able to find out the total path it covers that is the 2 pi r is the path it covers. So, I know the distance it travels I know the velocity it has.

So, I will be able to get the orbit time of 1 s electron if we consider hydrogen atom, an orbit time what does it mean by orbit time I have positively charged nucleus here and electron is orbiting. So, what I want to know is that, what is the time it takes for the electron to make one complete rotation and that is called the orbit time.

So, if we calculate that orbit time then we get very easily we get this number 150 attosecond, 150 attosecond is going to be the natural time scale of the electron which is orbiting around the nucleus and that is why attosecond is considered to be the intrinsic time scale of electronic motion.

Electron is very lighter element heavier element heavier sorry heavier particle is nucleus, nucleus is heavier than electrons and it is a 3 order magnitude heavier than the electron and that is why electron because it is lighter mass it can travel very quickly and the timescale of it is motion is very very fast is going to be at a second time scale. Natural time scale of nucleus on the other hand is going to be femtosecond that we have already seen, when you talk about natural time scale of nucleus it is nothing, but manifested by the vibration of a bond.

A bond is vibrating and when a bond is vibrating we can find out from the frequency of that vibration we can find out how long does it take from going from equilibrium point to stretch then recompress to that point, how long does it take and that time scale is going to be femtosecond time scale.

So, this time scale this is the time scale of vibration that is manifesting the nuclear motion this is the time scale of vibration and time scale of electronic motion is attosecond. So, we see that there is a 3 order magnitude difference between the motion of electron and motion of nucleus.

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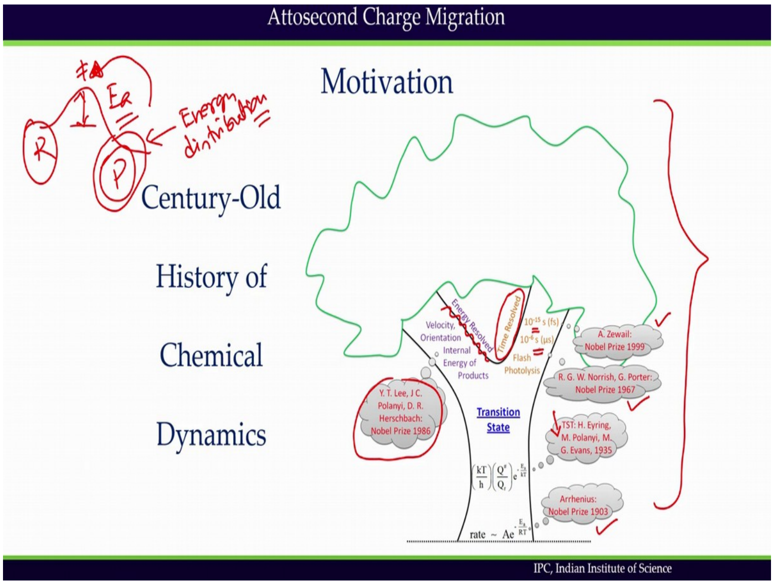

Attosecond Charge Migration

Motivation

Century-Old History of Chemical Dynamics

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Now, when we talk about this attosecond dynamics we immediately get an idea that we are thinking about chemical dynamics and this is a historical perspective of chemical dynamics which we have already discussed in the beginning of this course. We have said that ultra fast spectroscopy is it is a time resolved study of chemical dynamics and we have already given the historical perspective of chemical dynamics study in the time domain it to remind ourselves it started with the idea of chemical dynamics does the whole study we started with Arrhenius equation perhaps in 1900, 100 years back Arrhenius proposed that there is a activation barrier to the reaction.

So, if I have a reaction going from reactant to the product this is reactant this is the product then I have an activation barrier Ea and this Ea is related to the activation barrier this Ea is going to contribute to the timescale of that reaction. Then there is a theory called transition state theory this was proposed by Eyring Polanyi and Evans in 1935, they said that this Ea is associated with a transition state an activated complex and this transition state has one frequency or one normal mode of vibration which is unstable.

So, if I have a molecule with n number of normal modes let us say then n minus 1 number of modes will be stable it will not be let us say dissociative, but one mode will lead to the reaction, one mode will be connecting this reactant and the product at that transition state it is true at the transition state. So, transition state is characterized by a single normal mode of vibration which is unstable and which will help this transformation from reactant to the product.

So, in 1935 when we realized the idea that one normal mode is actually involved in the reaction at the transition state at the activated complex. We immediately realized what would be the timescale based on which we can operate and time resolve study. If we want to monitor the passage for going from reactant to the products what would be that timescale or what would be the experimentally operated time we need in order to observe this transformation from reactant to the product and that is nothing, but the vibration because in the transition state it is suggesting that one normal mode of vibration is involved.

So, our aim or our goal in studying chemical dynamics in the time domain was focused on the nuclear dynamics effectively, because we would like to know the passage from reactant to the products and this whole passage would be dominated by the nuclear dynamics. So, with this goal for the first time in 19 by 1960s we were able to monitor reactions or chemical transformation in the microsecond time scale done by Norrish and Porter which discuss these things.

And by 1990s 1980s a Zewails contribution and others contributions enabled us to understand or monitor chemical dynamics in the femtosecond time domain. So, that was the time resolved study of chemical dynamics. There is another domain we already discussed that is called energy resolved study of chemical dynamics what does it mean, these two domains of studying chemical dynamics was initiated almost simultaneously.

A group of scientist started looking at chemical dynamics from energy resolved perspective, a group of another group of scientists started looking at chemical dynamics from our time resolved perspective. So, this 2 branches were initiated almost simultaneously and in energy resolve study what we do. We thought that when we get the product then we can analyze the energy distribution in the product, this is the energy distribution of the product energy distribution.

So, let us say a molecule having certain amount of energy, after dissociation it will distribute the energy in the product molecules it will be distributing energy in the product rotational, vibrational and translational degrees of freedom. So, if we analyze the energy distribution in the product then one can predict what might happen in the transition state or how the reaction happened.

So, that was the basic idea behind this energy resolved study Y T Lee, Polanyi, Herschbach they are the scientist who pioneered this field of energy (Refer Time: 14:56) of study of chemical dynamics and this I have mentioned before also, in this course we are not discussing energy of study of chemical dynamics we are mostly focused on the time resolved perspective of chemical dynamics.

So, if you look at the time resolved perspective of chemical dynamics we started with microsecond then we ended up with femtosecond. Now, question is after studying chemical dynamics in the femtosecond time domain, what is next?

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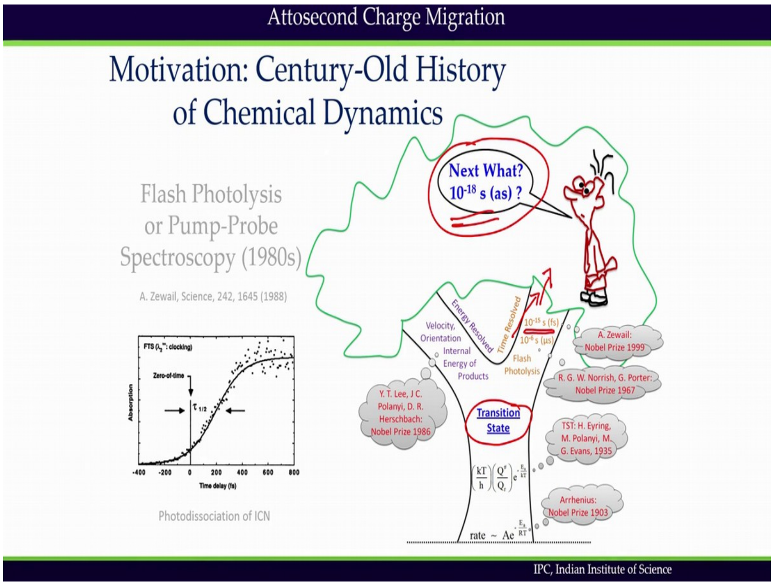

Attosecond Charge Migration

Motivation: Century-Old History of Chemical Dynamics

Flash Photolysis or Pump-Probe Spectroscopy (1980s)

A. Zewail, Science, 242, 1645 (1988)

Photodissociation of ICN

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Is it going to be the and attosecond that is the question we have and this is an important question because there is big reason why we ask this question. We ask this question because we started with an idea that in the end effectively if we want to monitor chemical dynamics it is nothing, but understanding transition state it is nothing, but understanding the passage through the transition state and passage through the transition state is nothing, but nuclear motion.

And nuclear motion happens occurs in femtosecond time scale that is why it might give an idea that once I have studied chemical dynamics in femtosecond time domain we have we are done with the chemical dynamics, there is no chemical dynamics which can occur in the attosecond time scale. So, that might be one opinion. Another opinion is that if we keep decreasing if we started decreasing this time scale slowly then the next frontier of chemical dynamic study should be attosecond. Now question is there any relevance of attosecond time scale in the chemical dynamics study.

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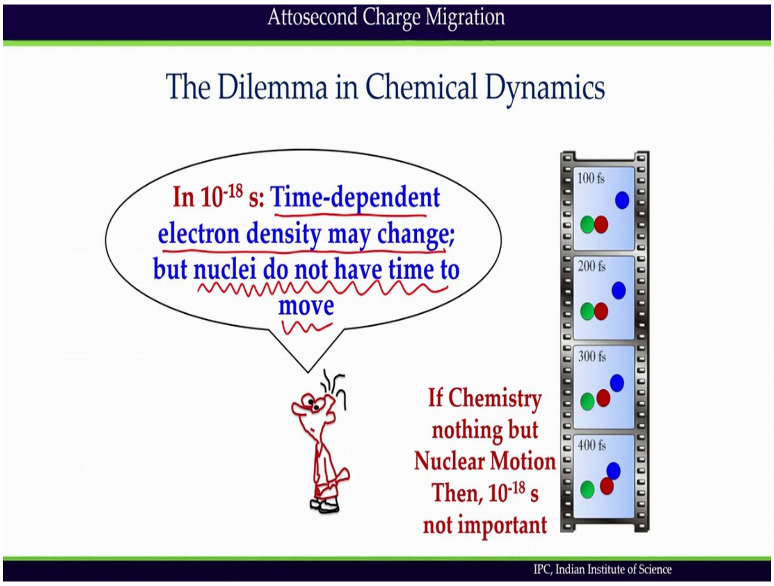

Attosecond Charge Migration

The Dilemma in Chemical Dynamics

In 10^{-18} s: Time-dependent electron density may change; but nuclei do not have time to move

If Chemistry nothing but Nuclear Motion Then, 10^{-18} s not important

So, this is an important question and we will clarify this point, as I have told you that attosecond time scale is nothing, but intrinsic time scale of the electronic motion, which means that in attosecond time scale time dependent electron density may change, but nuclei because they are heavy; they are heavy heavier than electrons they do not move at all or almost they do not move in this time scale and as a chemist. If we cannot imagine any chemical reaction without nuclear motion then attosecond time scale is not an important time scale for chemical dynamic study.

In chemical dynamics traditionally we have discussed we have viewed chemical dynamics from a transition state point of view and transition state is nothing, but manifestation of a process where one non one unstable normal mode of vibration is involved and normal mode of vibration is nothing, but nuclear motion.

So, if we try to follow the tradition traditional chemical dynamics which is dominated by transition state, then we must have nuclear motion and if we must have nuclear motion in the discussion of chemical dynamics then attosecond has no role in the chemical dynamics viewed through the transition state.

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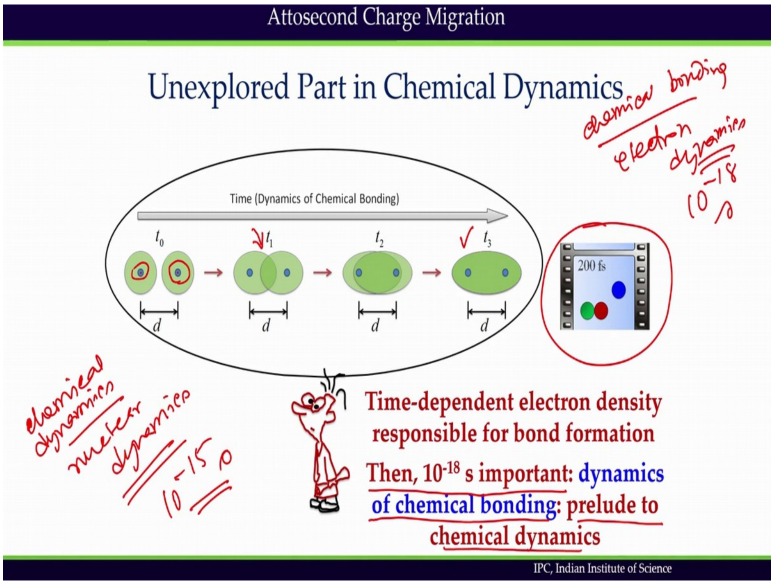

Attosecond Charge Migration

Unexplored Part in Chemical Dynamics

Time-dependent electron density responsible for bond formation

Then, 10^{-18} s important: dynamics of chemical bonding: prelude to chemical dynamics

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But, if we try to capture or freeze the nucleus, we freeze the nuclei first and try to see how the chemical bonding going on. In the end we have to remember that nuclei move on a potential energy surface created by the electron, it is the electrons which are involved in chemical bonding. That is manifested here in this cartoon diagram we have 2 hydrogen atoms, let us say nucleus is represented by these blue dots and electron density is represented by this green color the region.

Now, these two nuclei are separated by d distance and that distance we are not changing we have fixed it the distance and if we somehow get an opportunity to initiate the chemical bonding what will happen. Electron will start sharing the space and in the end we end up with getting a bonding between 2 nucleus and this bonding is done purely by the electrons.

So, time dependent electron density is responsible for any bond formation. So, attosecond time scale when you think about the relevance of attosecond time scale in chemical dynamics we only point out or we only mean that part of the chemical dynamics where nucleus do not move nuclei are fixed at a point at a at positions at their positions. It is the electron density which is started moving and attosecond chemical dynamics will involve only that part of the chemical dynamics.

So, if we try to specify that part of chemical dynamics as chemical bonding, because it is nothing, but chemical bonding which we can see in 10 to the power minus 18 second it is nothing, but the prelude to the chemical dynamics. So, I will now distinguish these 2 terminology, chemical dynamics; chemical dynamics; chemical dynamics is nuclear dynamics and chemical bonding is all about electron dynamics and this may happen in 10 to the power 18 second, but this occurs only in 10 to the power minus 15 second.

So, it is not that we will be able to contribute a lot to the chemical dynamics with the help of attosecond metrology and attosecond science, but we will be able to understand many unknown phenomena of chemical bonding or dynamics of chemical bonding as it occurs or of electron density changes as a function of time. So, attosecond time scale is all about dynamics of chemical bonding or to see how electrons are reorganizing in the intrinsic time scale.

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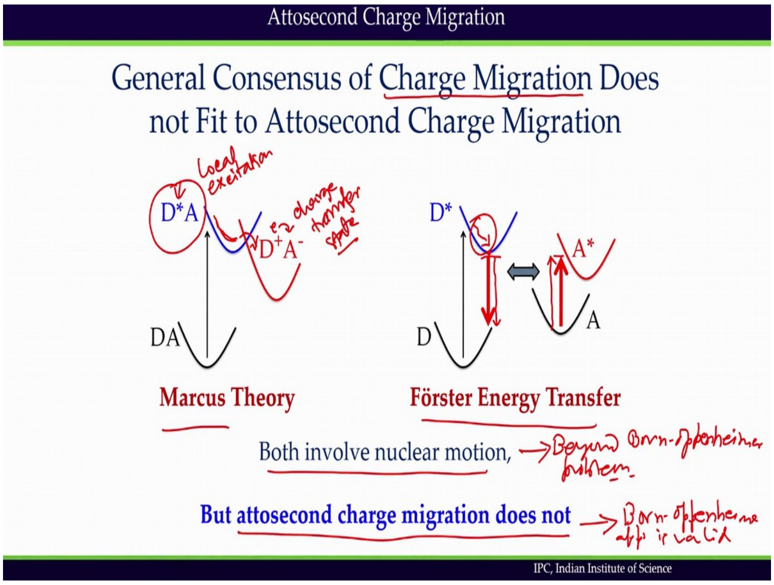

Attosecond Charge Migration

General Consensus of Charge Migration Does not Fit to Attosecond Charge Migration

Marcus Theory

Förster Energy Transfer

Both involve nuclear motion, → Beyond Born-Oppenheimer problem

But attosecond charge migration does not → Born-Oppenheimer app is valid

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Now in the context of electron reorganization or charge transfer or charge migration we often we talk about these 2 terminologies charge migration and charge transfer in chemistry. So, in the context of charge migration and charge transfer we already have 2 important theories established in chemistry; one theory is based on Marcus theory, another theory is based on Forster energy transfer mechanism.

Now in Marcus theory what we how the electron transfer occurs or how electronic density changes as a function of time we consider that we have a donor acceptor complex. These donor acceptor complex is first excited to the local excited state and that is why I am showing star on D only in donor I have done the electronic excitation, acceptor is not electronically excited; however, they are joined together.

So, this is why this is called local excitation. So, this is called local excitation electronic excitation, now this donor acceptor complex is under first has undergone this local excitation and after this local excitation donor acceptor complex will change it is nuclear configuration and because of that change it will start evolving on the potential energy surface and there is a chance that it can hop to a charge transfer state this is called charge transfer state charge transfer state.

So, if it is hoping to charge transfer state then what might happen, electron can migrate from one to the other from donor to the acceptor and that is nothing, but electron density change. But we have to understand that this electron density change is different from the attosecond electron density change. Here this electron density change is a slow electron density change it is not an attosecond electron density change, this kind of change can only happen when electron is slowed down from it is intrinsic time scale to the nuclear motion.

Why is because, the system has to evolve on the potential energy surface and electron has to wait until donor acceptor locally excited donor acceptor complex makes a decision to hop from the local excited state to the charge transfer state. So, electronic reorganization will depend on nuclear motion and that has to be slow, because nuclear motion itself is slow that is why electron has to wait until nuclear motion and that is why electronic motion in this kind of behavior this Marcus theory has to be slow.

On the other hand Forster energy transfer mechanism what happens again we take donor acceptor complex, but in donor acceptor complex we electronically excite the donor first and donor will start evolving on the potential energy surface and then it might happen that this donor is de excited. When this de excitation occurs this amount of energy the same amount of energy can be taken by the acceptor complex and acceptor complex can be electronically excited.

Here also I have some change in electron density, electron density going from donor to the acceptor right. It is not going to the donor through the acceptor, but there is a change of electron density in the accepter and there is a change of electron density in the donor, because it is undergoing donor is undergoing de excitation and acceptor is undergoing at the same time acceptor is undergoing excitation.

But this de excitation an excitation process will occur only when donor has changed it is electron nuclear configuration significantly so, that it can de excite at this point. So, this process is a slow process this is a nuclear dynamics and it is a slow process. So, acceptor in order to get excited to the electronically excited state acceptor has to wait until donor adopts our nuclear configuration for the de excitation process. So, again the whole electronic rearrangement which occurs in this donor or acceptor besides, they have to depend on the nuclear dynamics.

And once a process has to depend on nuclear dynamics that process has to be slow, that is why one thing we have to clarify here that the existing idea of electron transfer or electron migration or charge migration or time dependent change in electron density based on Marcus theory and Forster energy transfer mechanisms they both involve nuclear motion and that is why it is electronically non adiabatic process.

On the other hand attosecond charge migration is does not depend on nuclear motion, it is well separated from nuclear motion, this is much faster than electronic motion, that is why in this case we have born Oppenheim approximation is valid and here it has to be beyond Oppenheimer problem. So, it is going to be electronically non adiabatic problem. So, this distinction should be clarified at the beginning of the discussion of attosecond chemical dynamics which is nothing, but attosecond chemical bonding.

Because in many situations or in many occasions in chemistry we study time dependent change of electron density, but those changes are very slow changes because those changes in electron density depends directly on the nuclear dynamics which is slow, attosecond dynamics is entirely different from those changes.

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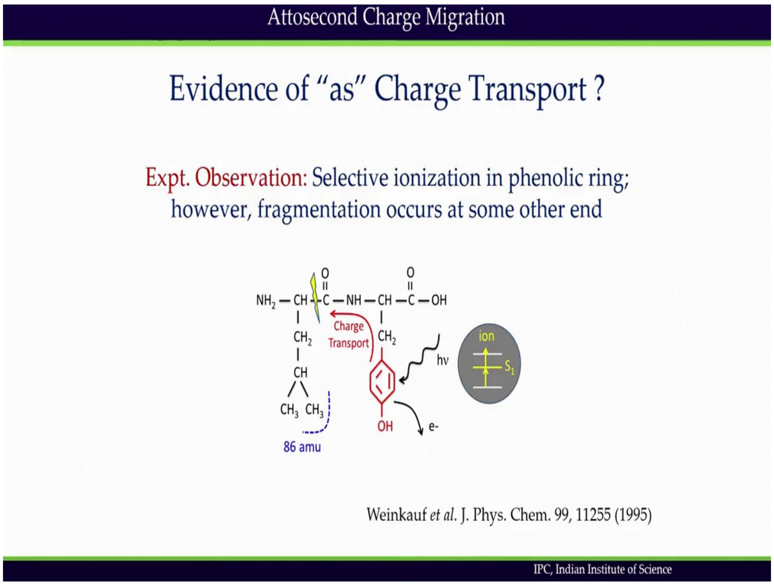

Attosecond Charge Migration

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 and we will continue this session in the next lecture.