Ultrafast Optics and Spectroscopy
Dr. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru

Lecture – 41
Attosecond Chemical Dynamics 4

Welcome back to module 16 of where we are discussing Attosecond charge migration, its experimental setup has been discussed, so far and we have seen that; XUV beam is produced with the help of high harmony generation process.

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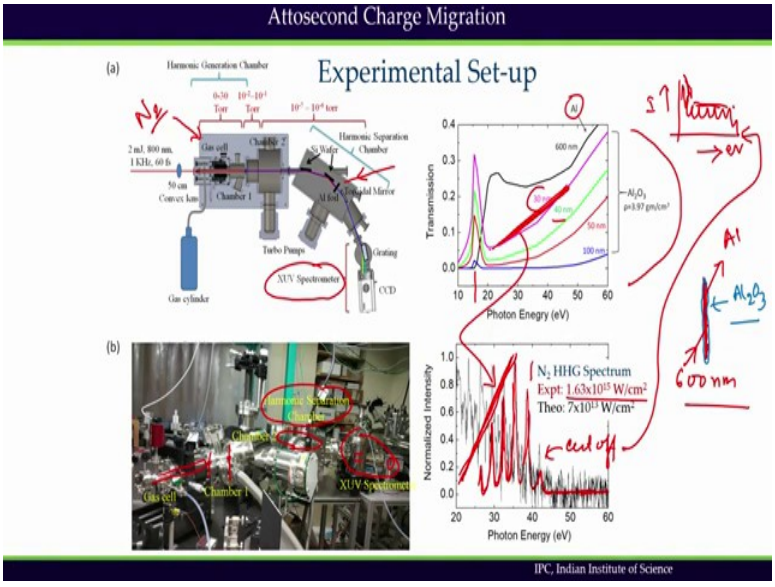

In the high harmony generation process in the experimental setup, which we have here is the one XUV spectrometer, one filter for the XUV beam and one gas cell here situated here.

Now, these are the, with the components, which we use for the XUV spectroscopy. This is the real lab image this is the gas cell which is inserted inside this tube, inside this chamber and then there is a hole here in this point. Then there is another hole here in this point and then the chamber; so, chamber 1 and chamber 2 are actually used for the differential pumping. And the high hammering separation chamber is actually situated here, this one; high harmony generation chamber and this is a spectrometer.

So, we have built this a grating is kept here and the CCD Camera is kept here. So, this is the spectrometer. And we have said that previously that; typically, HHG spectrum should look like this. I have one intensity should drop down like this and then there will be a plateau of intensity and then there will be a cut off. This is the typical intensity and this way you are plotting, let us say energy ev. And this way you are plotting intensity. So, this is the typical HHG spectrum what it should be.

But, when we looked at N2 spectrum, this is the N2 spectrum which means; in the gas cell we have injected N2 gas we have filled with N2 gas. When we looked at N2 spectrum at this 10 to the power 15 Watt per centimeter square, high-intensity; I mentioned that high-intensity we need to tunnel ionize it. And then once I tunnel ionize it; electron will be traveling in the field and it will combine. So, this is a strong field effect; which we see in the HHG process.

Now, when you look at the N2 spectrum, our spectrum is this red color spectrum, which is quite different from what is expected from the HHG spectrum. It does not have plateau, it does not have fast decay, and it; but it has a cut off, this is the cutoff. After this energy; you do not see anything.

So, we see the cutoff, but we do not see any plateau and we do not see any decrease in the first few harmonics. And it is because, we are using aluminum filter; so, once we have used aluminum filter, what we see. This is the transmission curve which is shown here, these curves are transmission curves which mean that how much XUV beam will be transmitted through the aluminum filter. This black color is actually transmission curve characteristics of the aluminum filter. And in the aluminum filter, what we see is that; up to 15 ev with this will be, nothing will be transmitted due to presence of the aluminum filter.

Aluminum filter will transmit only light above 15 ev , and that is why, below 15 ev we will not see anything. But, at the same time we have to understand that; when you take an aluminum filter we say that it is an aluminum filter, but we have any metal we take. If we take iron, if we take aluminum, if we take let us say titanium or gold, gold which I have in my ring. Even any metal I take; due to the oxidizing environment or the atmosphere oxygen, the top surface will be always quoted by its own oxide. It is a general behavior of any metal we take in the atmosphere.

So, this aluminum filter also exposed to the atmosphere. So, obviously although it is an aluminum filter, but its surface is actually coated by is now coated by a thin aluminum film; Al_2O_3 film. So, this red colour one; so, this blue color one is Al_2O_3; this is the oxide of aluminum and the inner material is still aluminum. So, we have to understand the transmission characteristic of alumina, Al_2O_3film as well. But, we do not know.

Unfortunately, we do not know, what is the thickness? Typical thickness of that Al_2O_3 film on that filter, but if we take up let us say general case, that receipts is 30 nanometer let us say, or 400 nanometer. So, this thickness, this aluminum thickness; when you purchase this aluminum filter thickness was 600 nanometer. In the 600 nanometer thick aluminum foil, we may have let us say 30 nanometer thick aluminum film. And if we have aluminum film, we see that from 20 eV to 40 eV or 50 eV it is a sloppy increase in the transmission. And that is exactly what is showing up here 20 to 40 eV is a slopy increase in transmission.

So, this slopy increase in transmission is due to the filter which we use, it is not because of the behavior of the HHG. So, we had; probably if we could somehow analyze the whole spectrum whole light without filtering it, without using the aluminum filter. We could have observed a plateau here in this regime. But we do not see the plateau because, the transmission of Al_2O_3 is a slopy or its slowly increasing as we go to the higher energy photon and that is exactly evident here 20 to 30 eV or 20 to 40 eV, they are slopy increase and then this decrease is due to the cutoff.

So, this decrease we understand it is the cutoff regime; so, this is your cutoff regime; which is nothing but, in this regime, but this slopy part is due to the filter which is affecting the transmission. So, that is the reason why in the end, what we observe is actually a spectrum which looks like this red color spectrum. And all the spectra we observed from different gas molecules, they actually follow similar kind of, this kind of patterns this red color pattern.

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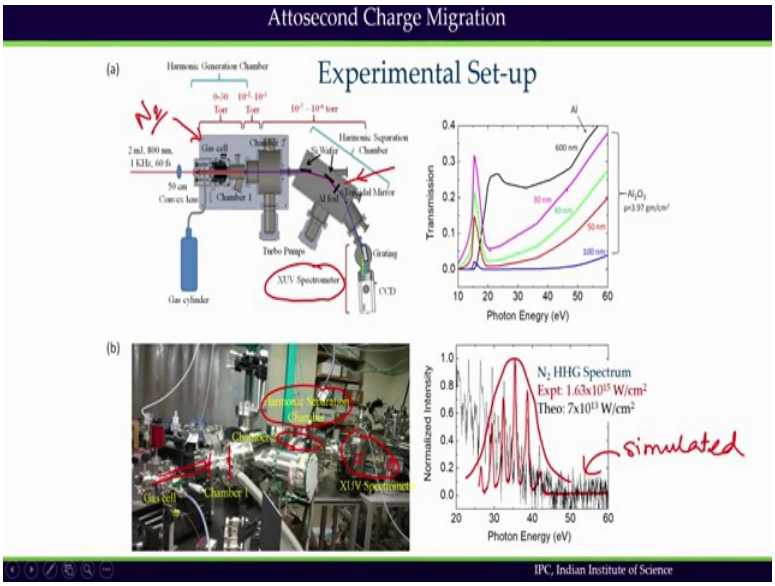

In the background the, this black spectrum is actually simulated spectrum. And in the simulated spectrum we see that the cutoff is matching, but then slowly this part is actually not matching. And this part is not matching is because in the simulated spectrum we do not use any filter. It is actually theoretically simulated spectrum which shows a, which shows a plateau. So, from this point it is a plateau; it is supposed to be a plateau, but we do not see the plateau because of the transmission of, this transmission characteristics of the filter itself.

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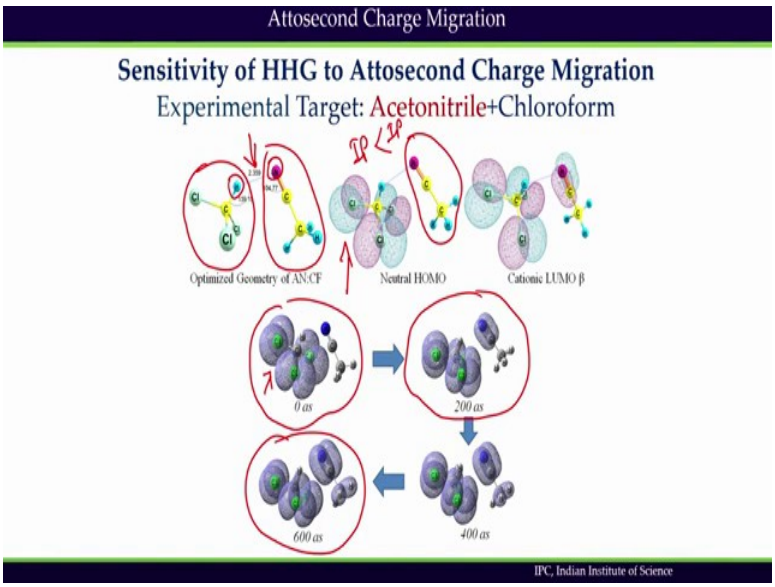

So, with this idea, we started working on this system, and we remind ourself that; our target system was two dissimilar molecule; two different molecules weakly bound together. Here, we are using one of them is chloroform, chloroform this molecule and another molecule is acetonitrile, this molecule. So, these two molecules are weakly bound together by a dotted line. This dotted line is the non covalent bonding interaction. Any molecule in this room, if they are interacting with each other, but their interaction is very weak they are very weakly interacting. And this interaction energy or the interaction the way it is interacting is called non covalent interaction.

So, this minimum distance which is achieved by the equilibrium optimization of this cluster is, this distance is called non covalent bond distance. This is the minimum distance which we can have for between these two molecules. And they are weakly bound by this interaction. Now, what is this interaction? This interaction is an interaction between hydrogen and nitrogen of two different molecules. Hydrogen from chloroform and nitrogen from the other molecule, these two molecules are interacting.

And we know that these two molecules having different ionization potential. Ionization potential of this guy, this molecule is IP is greater than this molecule. So, IP of this molecule is low. And because, this is a low ionization potential I remove and definitely; I remove an electron from this molecule, even they are bound together. Because, this molecule having low ionization potential than this molecule, when I remove an electron when I undergo this tunnel ionization preference preferably electrons will be removed from this molecule only.

And, once we remove an electron, we know that we create a hole, and that is the hole density we have shown at the point of 0 attosecond timescale. And this hole density, if we allow to relax, what does it mean? I have a bucket of, let us say electrons. In a molecule I have lot of electrons and I remove an electron from there. If I remove an electron from there, the whole field has changed. Electrons are charged particles, they are interacting with each other.

So, once you remove an electron from that molecule, the whole electron density has to reorganize one more time. Because the field; effective field or mean field has changed and due to this during this reorganization, I can have this charged migration. The whole charge which I have created only in gum chloroform moiety, it is moving towards the

acetonitrile moiety in 200 attosecond. And then again, if we look at 600 attosecond it is actually the maximum change we see.

So, what is evident from this theoretical investigation; which is a continuation of the previous theoretical presentation which we had previously also in the previous lectures, that I have two molecules; I have two molecules weakly bound. I remove electron from this molecule and that molecule due to remove of an electron from this molecule, I have created a whole charge in this. That charge is now delocalizing. It is moving to the both side of the molecule. So, it is delocalization of charge, and this delocalization of charge occurs within 600 attosecond.

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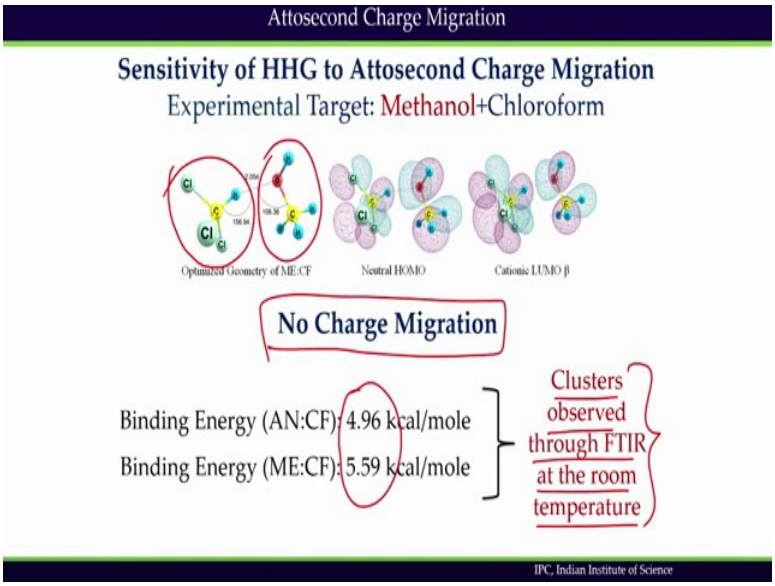

Now, question is, how this is going to affect the HHG process? In order to understand that, what we have used is that, we have taken binary mixture of chloroform acetonitrile and chloroform ethanol, if we look at this; this molecule is retained. In the previous slide we had this molecule, but instead of taking this molecule we have changed the molecule to methanol, two different molecules. Binding Energies are almost equivalent; 4.96 kcal per mole for one of them and 5.59 kcal per mole, kilo calorie per mole. That is binding energies are almost comparable equivalent binding energies. And it has been clusters observed through FTIR at the room temperature.

These clusters, ok; they actually, they form the clusters that was evident through the FTIR spectrum. So, FTIR is pointing out that those clusters are present even at the room

temperature, and their binding energies are comparable. So, they can exist being weakly bound. Question is, when I have changed, so this molecule was fixed this molecule was chloroform, but this molecule instead of acetonitrile we have used methanol. These two combination when we checked we have found that no charge migration occurs, theoretically we have found that; no charge migration occurs from one end to the another end in this combination. And this is an interesting theoretical observation.

In one combination when I have acetonitrile, sorry, I have chloroform and acetonitrile. Both together, I see charge migration attosecond charge migration, when I have chloroform and methanol. Then I do not see any charge migration, this is the prediction we get from theory. And after getting this prediction; we thought that, if we try to observe high harmonic generation from these two different systems; one may respond in a different way another would may respond in little different way.

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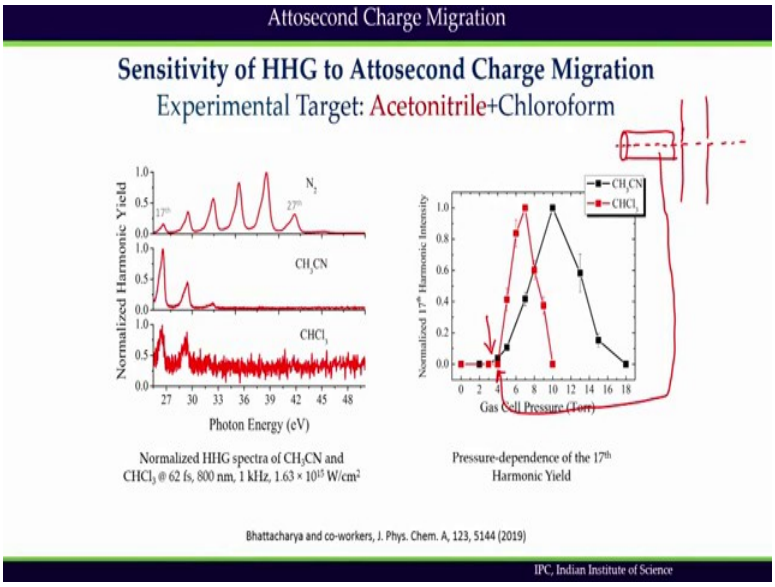

So, we wanted to check the differences between these two systems. In order to check that, what we have found is that at the force torr gas cell pressure. We said that, we have a gas cell first. In the gas cell, then we had another chamber, where we have a hole here. So, this is also, there is a hole here also in the gas cell. We have a hole cold collinear hole and then there is another hole. So, this is the three holes we have and then it go to the beam light beam is propagating through this medium. This gas cell has a window.

Now, this gas cell pressure is varied and we see that at the gas cell pressure of fourth torr, we do not see any signal for HHG; HHG is not produced when individual gas cell pressure is fourth torr; at the footer we do not produce it.

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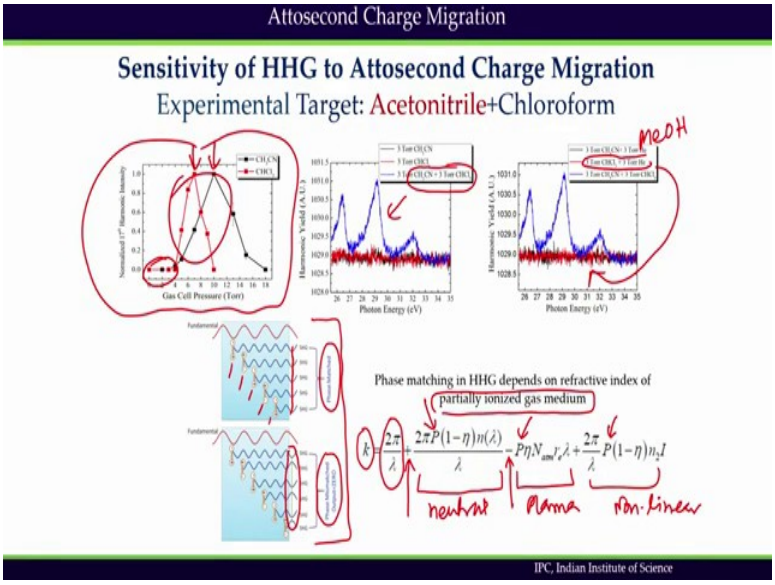

But, when you mix them, let us say 3 torr 3 torr if we mix them; 3 torr acetonitrile to 3 torr chloroform, we see an enhancement in the signal and if we try to comb mix them with 3 torr chloroform, 3 torr helium, we do not see any enhancement. And also instead of helium, if we use methanol also we do not see any enhancement.

So, both methanol, helium many other gas molecules are not doing enhancement in the signal. The only enhancement we see is due to acetonitrile chloroform. Acetonitrile chloroform is therefore, having an unique property with respect to other gas combinations. Now question is, why there should be a pressure dependence in the HHG yield? Previously, we have discussed this one that, HHG process is nothing but, a non-linear process or non-linear frequency conversion.

And in any non-linear frequency conversion, we have to understand the phase matching behavior, because phase matching is the only factor, which will control the efficiency of that conversion, whether I will see a new light or not that depends on whether, I have achieved phase matching or not.

So, what is phase matching? Here, I have given an example one more time taking an example of SHG, Second Harmonic Generation. Second harmonic generation is not produced through HHG, because HHG cannot produce any even harmonics, but we will take an example of a SHG, just to remind ourself. So, what happens I have a medium let us say. I have a medium of this thickness. And that the beam is propagating from this direction to this direction; beam is propagating.

Now in the medium this is a dielectric medium; dielectric medium what does it mean? It does not have any free electrons like metal. It does not have any free electron. So, what happens this, when the fundamental beam is propagating through this medium in this regime; in the beginning, I create a polarization and also in the end I create a pole polarization, because beam is propagating through the medium.

So, I am just considering two different dipoles; one dipole in the beginning of the interaction and another dipole in the end of the medium, these two dipoles. Now dipoles, oscillatory dipoles are actually the source of electromagnetic radiation and that is the, that is creating the new light.

So, what will happen? If this dipole is creating an electromagnetic radiation which is propagating,, and this dipole is creating another electromagnetic radiation; which is propagating. If these two electromagnetic fields are in phase, then we call phase matching is achieved. And the phase matching is achieved and that is exactly exemplified here. So, each dipole is creating new field and those fields are in phase and that is why it is phase matched. But, if each dipole is creating the field and each field is not in phase, they are they will cancel each other. And once they will cancel each other I get a 0 output.

So, there is a non-linear effect in the medium, but output would be 0. So, output in this regime would be 0 just like this. And this regime; I have some output, because I have been able to achieve phase matching. Now the medium which we use here is gaseous medium and partially ionized medium. So, basically, it is a partially ionized gas medium which we use. Partially ionized, why? Because due to strong film ionization I am ionizing the medium as well. So, I have neutral molecules as well as plasma medium as well, it is a mixture of plasma and the neutral.

What is plasma? It is fourth state of matter; I know the matter different states of matter. Solid state, gas gaseous state, liquid phase and plasma phase. Plasma phase is one phase which is creating lightning in the during rainy season. So, plasma phase is nothing, but an ionized phase a gas molecule which are highly ionized, electrons, radicals, they are put together. They are a very reactive state of matter.

And, when you look at the phase matching in the non-linear optics; we have come to know that, we have to think about the magnitude of the wave vector. And how does it depend on the medium refractive index. We know that 2 pi by lambda, this part is coming from the vacuum contribution always there for the vacuum field. Then this part is due to the neutral dispersion. Then this part is due to plasma dispersion, this is neutral dispersion; this is neutral dispersion, this is plasma dispersion, and this is your non-linear dispersion. So, these are the terms we have.

Interestingly, we see that for each term I have P, P and P. P is nothing but, the pressure, which means that pressure is going to contribute to the overall phase matching of the for this high harmony generation. And, we see that the plasma dispersion has a negative term, neutral dispersion has a positive term, which means they will just act in opposite direction.

And two factors, when I am increasing pressure two factors will contribute in opposite direction, which means one of them is trying to break the phase matching another one is trying to bring the phase matching. And in an equilibrium at a particular, we will get an optimum point, optimum pressure at what point we will get the maximum yield. And that is why I see pressure has a maximum value here always, a pressure which will give me the optimum HHG yield.

So, when we see a pressure dependent study, when we see a pressure dependent behavior in HHG always we think that; it could be because of the phase matching problem. Now, if it is a simple pressure dependent phase matching issue, then we could have imagined that when we used chloroform and helium; chloroform methanol, chloroform with other molecules.

All the molecules should have similar kind of behavior, because I am increasing the pressure to the same level. So, it should show me the efficiency, but we do not see that, we see only chloroform and acetonitrile. This combination is giving enhancement in the

HHG yield. In fact, is giving you HHG efficiency. But any other combination; you take out this acetonitrile and use methanol, use helium, use any other molecules it is not giving the enhancement HHG yield. So, it cannot be pure pressure dependent phase matching, which we very easily conclude for the HHG process.

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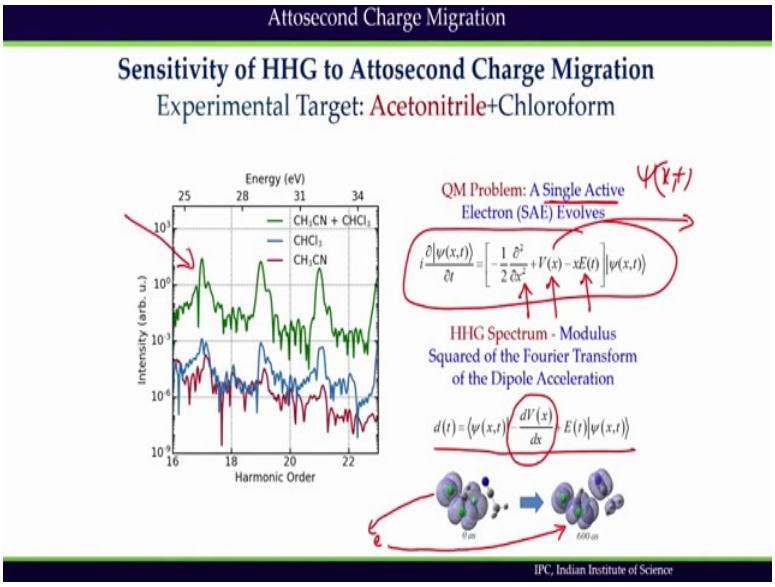

Second thing, second point, which we should clarify is that ok if it is not pure pressure dependent phase matching, then, what is contributing to that enhancement? So, to understand it, we use quantum mechanical time dependent Schrodinger equation, simulation based on time dependent Schrodinger equation.

And the problem is very simple quantum mechanical problem, I have an electron which was bound to the at molecule first. Then that electron is removed or that electron is actually sent to the continuum, so it was actually went to the continuum. Continuum state it does not, it is not localized anymore, it is continuum and then again during recombination is coming back. So, the whole problem is that I had a localized electron; it is going to the continuum and again coming back and recombining.

So, I have an active electron and the wave function of that active electron is psi x, t, this is the time dependent Schrodinger equation. I have kinetic energy component, I have potential component, I have external electric field component. And, what is that potential? Potential is nothing but, the molecular static potential. When electron is away

from the cation, this cation has its own electrostatic potential. Its electrostatic potential it means that, it is actually affecting the electrostatic environment of the system.

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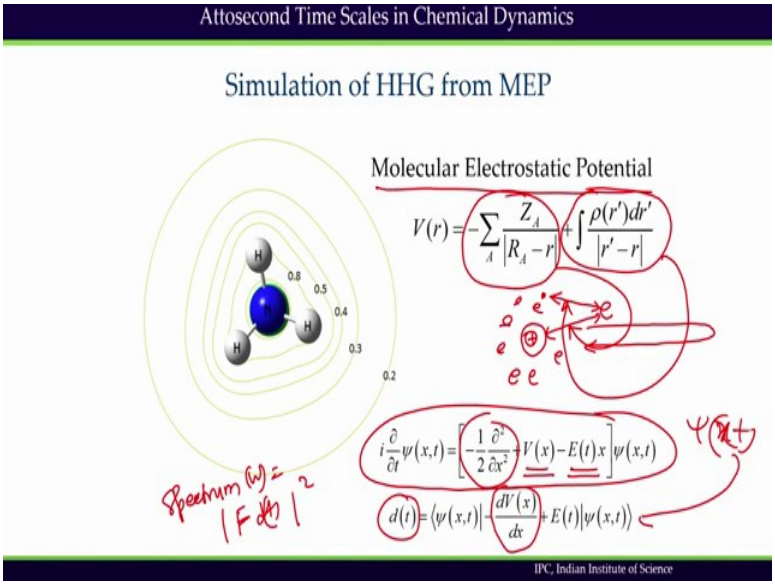

So, this is the molecular static potential which we can define molecular static potential is the interaction, so interactions between; so, I have in and let us say I have an atom, in an atom I have nucleus and then I have lot of electrons here. And one of the electrons I have removed. So, I have removed this electron let us say. This electron is making a journey going away and then coming back and rejoining it. When it is doing it, then the electrostatic potential which is calculated is actually an interaction between this electron with the electron density at this point. Electrons are not particle anymore; electrons are actually represented by its own density.

So, I have to find out the electrostatic interaction between electron density and this electron and that is represented by this term. And electron will be interacting with the positively charged core of a nucleus as well. So, this electron will be interacting with this. So, this is the electrostatic potential between, electrostatic potential represented by this and this is the electrostatic potential represented by the interaction between the density at that point with the electron; incoming outgoing electron and that is the electrostatic potential.

So, with this electrostatic potential; we want this is the electrostatic potential. This is the kinetic energy operator in one dimensional problem and this is the electric field; under

which it is undergoing the acceleration. Finally, if we solve this equation numerically, then I get x t value at different time, psi x t value.

If I plug that in; in this dipole acceleration term dt term then what I get is actually the spectrum is square modulus of Fourier transform. Fourier transform of; this is Fourier transform of dt so, that I get in terms of omega. That we have seen always. If I have time dependent part, I can convert to frequency dependent part and spectrum is nothing, but the Fourier sorry, square modulus of the Fourier transform of the time domain part. And that is the way we get the spectrum.

So, dipole acceleration term is used to for that, and we see that in the dipole acceleration term we have a derivative term. That is with respect to x V is changing. And, why I should have a change in the spectrum is because. now we see that; this dipole acceleration term is affecting. So, once I remove an electron from here when electron is making the journey away from it and then coming back to this.

During the comeback it is does not see this electron density is actually seeing this electron density. So, there is a change in potential and due to this change, now I have the enhancement in the spectrum in the HHG spectrum.

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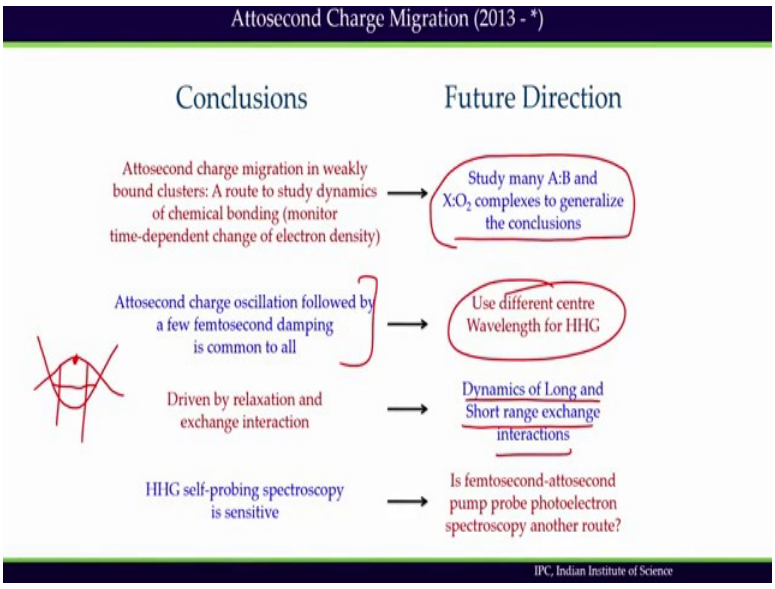

So, with this, there are many conclusions one can make from both, from theoretical work which we have done and the experimental work which we have done. The conclusions

are following attosecond charge migration in weakly bound clusters is a route to study dynamics of chemical bonding, we can monitor time dependent change of electron density.

So, we will we have to focus on weakly bound clusters because, weakly bound clusters gives an opportunity to remove an electron selectively from one moiety and to see how electron density is reorganizing after remove an electron from that, from 1 moiety. So, this is already evident and we would like to continue this work with the different kind of Van der Waal complexes, halogen bonded complexes, little bonded complexes different weekly bound species. Attosecond charge oscillation followed by a few femtosecond damping is common to all, we are always seeing that.

So, once I remove; if I take an equilibrium geometry, one geometry which is an equilibrium geometry and if we remove an electron, I see always an oscillation and that oscillation will be damped because equilibrium geometry is not the only structure which we see in the, at the room temperature. If we consider room temperature, we can have this structure, we can have this structure, we can have this structure, there are many combination, and that is due to the fact that first vibrational state; ground vibrational state is represented by a Gaussian.

Center of the Gaussian is the equilibrium geometry, but it has many other configurations as well. And one can sample the different geometries from Wigner distribution, many other ways one can sample it and check how this with, finite with before finite width of the vibrational wave function before ionization can affect it. We see that, it can actually damp the oscillation.

So, this oscillation can be probed with the help of different center wavelength for HHG that is one conclusion we have made driven by relaxation and exchange interactions. We have seen that this charge migration between these two weakly bound species is driven by relaxation and exchange interactions. And for the; and because it is driven by exchange interactions and relaxation one can think of studying dynamics of long and short range exchange interactions. These are very important for cold chemistry.

When I have two species, how they are interacting with each other. That is an important question; I have neutral species, let us say I have a neutral molecule. And one ion there is a positively charged molecule is going through the neutral molecule let us say, and when

its going through the molecule near the molecule. In the near vicinity of this molecule they will interact with each other. They may exchange charge and one can think about ok, what is the typical distance of that exchange of the charge? Can I go this way and still they can exchange can I go this way and still they can exchange.

So, this is the dynamics or long range and short range exchange interactions, which are very important for fundamental physical chemistry that can be studied with the help of this relaxation and exchange interactions within attosecond charge migration. And finally, we have already shown that HHG cell probing spectroscopy is very sensitive to the attosecond charge migration, is it the only technique can we use femtosecond, attosecond, pump probe photoelectron spectroscopy as an another alternative route to the investigation of this additional charge migration. So, with this big hope and little conclusions we will stop here for this module. We will meet again for the next module.