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

Lecture – 40
Attosecond Chemical Dynamics 3

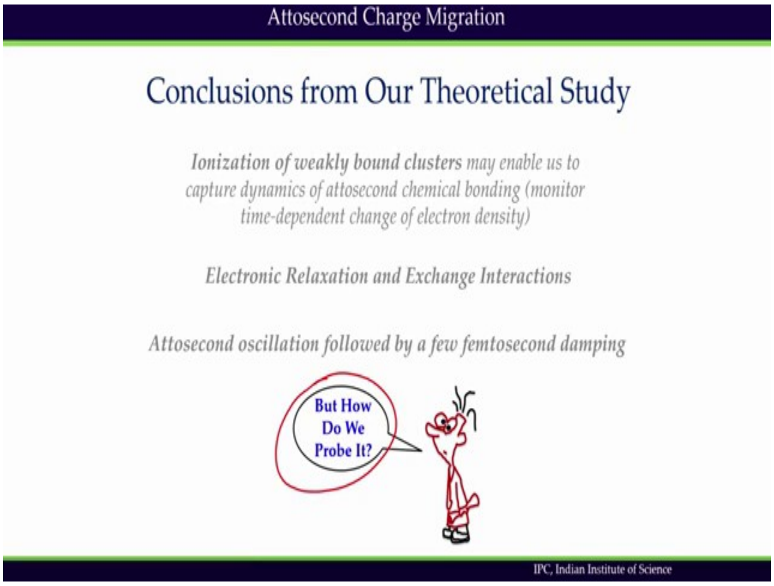
Welcome back to module 16 in this module, we will continue the discussion on the attosecond charge migration. We have already pointed out that this is an advanced topic and then I was perhaps many ways one can represent the advanced topic. And here we are representing, or we are presenting the most of our work which we do in Indian Institute of Science. And we are providing mostly our perspective to look at attosecond charge migration from a chemist point of view.

What we have discussed so far is the meaning of attosecond time scale it is 10 to the power minus 18 second that is the time scale we are talking about. And we have already seen that in this time scale only electron density can change as a function of time, nuclei which is heavier mass which having heavier mass than electrons nuclei do not have time to move in this time scale.

And we have seen that mostly attosecond dynamics is not representing chemical dynamics which is necessarily dynamics of nuclei or dynamics of the transition state. Attosecond dynamics is representing the dynamics of chemical bonding which is nothing, but time dependent change of electron density during the chemical bonding. And we have already shown that two different molecules when they are bound together, I can take molecule and molecule they are weakly bound together.

And this bonding, this intermolecular bonding is called non covalent bonding. And if we take two different molecules which are weekly bound together then we can selectively ionize one of them, we can remove our electron from one molecule and we can try to monitor how the electron density getting reorganized or new non covalent bonding interactions can be formed after the ionization of these two different molecules which are weakly bound. So, that is the strategy we used in the theoretical exploration of different aspects of attosecond charge migration.

(Refer Slide Time: 03:13)



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

But How Do We Probe It?

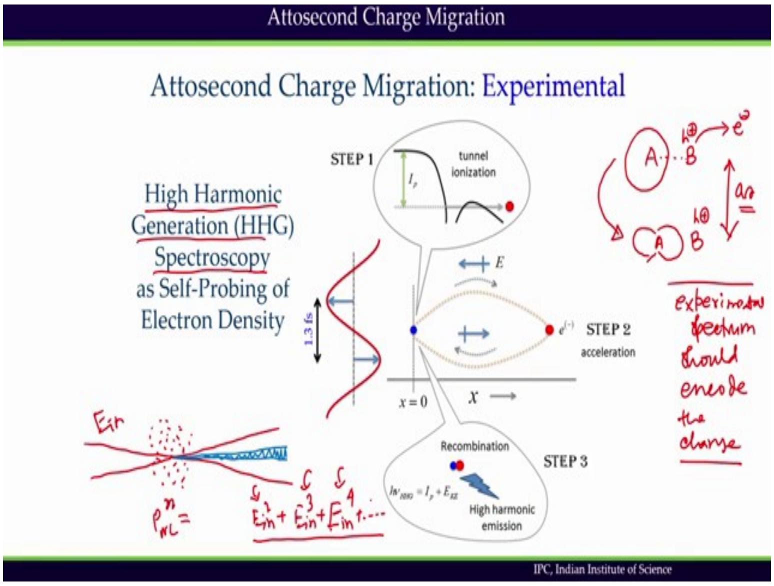
IPC, Indian Institute of Science

There are many information we have in our hand right now. Ionization of weakly bound clusters may enable us to capture dynamics of attosecond chemical bonding to monitor time dependent change of electron density. Electronic relaxation and exchange interactions both are going to contribute to the attosecond charge migration.

And we have seen that there is an oscillation in the few 100 attosecond timescale there is an oscillation of the charge density from one moiety to another moiety followed by the damping which occurs in the femtosecond time scale. Within 10 femtosecond the charge oscillation will stop because of the vibrational motion before the ionization.

So, these interesting informations are already evident from theoretical work. Next question is how do we probe it? That is an important question because any theory is based on certain approximation and we have to confirm within that approximation whether our predictions are right or wrong.

(Refer Slide Time: 04:22)



Attosecond Charge Migration

Attosecond Charge Migration: Experimental

High Harmonic Generation (HHG) Spectroscopy as Self-Probing of Electron Density

experimental spectrum should encode the change

IPC, Indian Institute of Science

So, with this idea we move to the, we will move to the experimental part of the attosecond charge migration dynamics. The technique which we need to follow should be able to monitor the change of the electron density. So, let us say there is a there is the process here where I have two dissimilar molecules, A B molecules, they are weakly bound. Very weakly bound species they are attached together, but they are weakly bound that is called non covalent bond.

Now, if I remove an electron from B, then what I create a whole charge which is missing electron charge or whole charge I create in B and due to this creation, the electron density which we had in A may change. And it may so happen that finally, the electron density should may look like this, this is just an imagination. Due to this whole charge density this electron density in A is changing and if electron density is changing in a then we have to probe it.

So, the technique which we would like to implement here in this discussion, and this change we know that is going to be several attosecond. So, I should have an attosecond resolution in the experimental technique as well as the technique should be sensitive enough to see the changes, the changes which is occurring in the electron density in this moiety.

So, going from this to this there will be a change and that change should be encoded in the experimental spectrum. Experimental spectrum should encode the change, the change in electron density that is very important. And the technique which one can imply is called it is called high harmonic generation spectroscopy.

High harmonic generation spectroscopy is a cell probing spectroscopy of electron density. What does it mean? It will be clarified very soon by taking the classical picture of high harmonic, semi classical picture of high harmony generation. High harmony generation is an emission, is an emission of high energy photons.

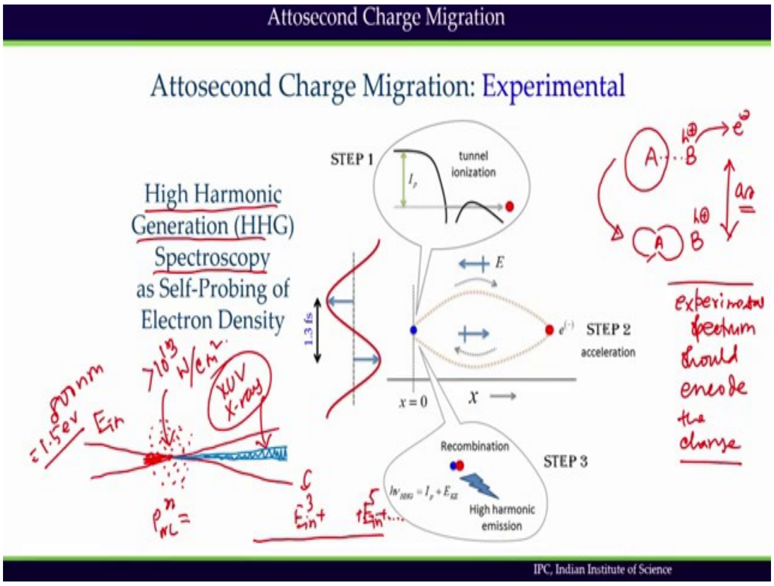
So, if I have let us say 800 nanometer light focused in a gaseous medium, you know this is a gaseous medium let us say. In a gaseous medium if we focus 800 nanometer light then what happens this 800 nanometer propagates like this and at the same time we create a new light and the light is in the X-ray regime and this light is created in the X-ray regime.

So, this light is created due to HHG process. HHG process what does it mean? The polarization, we have discussed the polarization of a system polarization p n, that polarization depends on the electric field, input electric field the plus input electric field square plus input electric field cube plus input electric field 4 like this it continuous that is the non-linear polarization we have discussed.

Now, this linear term does not exist in the non-linear polarization, so I will remove this one. Only non-linear polarization which is contributed by this higher order terms and this input electric field is the field of the input beam, the fundamental beam which is focused to the gaseous medium. When it is focused to the gaseous medium then what I see is that all second harmonic, third harmonic, fourth harmonic all these harmonics can be produced.

Interestingly we have seen that because this is an isotropic medium the gaseous system is an isotropic medium. So, odd harmonics are produced, even harmonics are removed from this and all odd harmonics are produced.

(Refer Slide Time: 09:00)



Attosecond Charge Migration

Attosecond Charge Migration: Experimental

High Harmonic Generation (HHG) Spectroscopy as Self-Probing of Electron Density

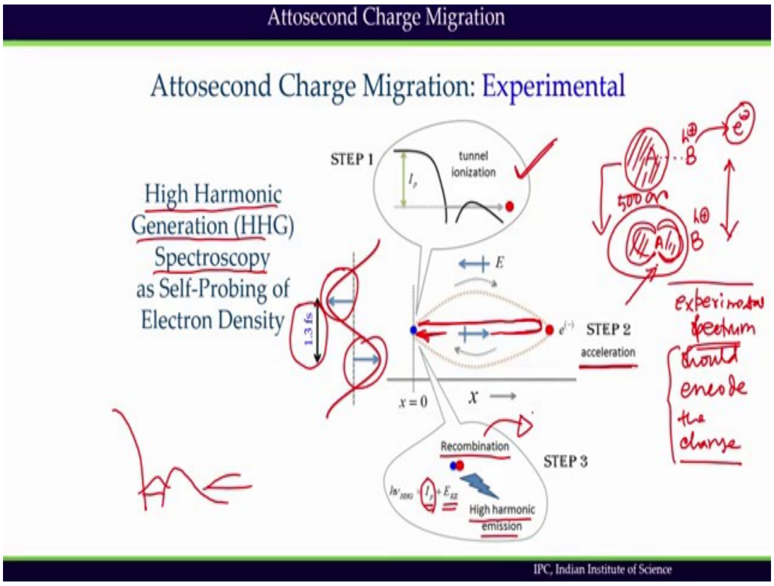
IPC, Indian Institute of Science

So, we get in input to the power 5 plus all other harmonics and this can be extended to the X-ray regime. So, its 800 nanometer pulse center wavelength 800 nanometer pulse which is having almost 1.5 ev photon energy let us say for the central center of central wave length.

This can be converted to even 10 times or 100 times higher photon energy. So, it can go up to XUV regime or X-ray regime. All these regimes can be produced with the help of this HHG process. Now, in HHG process as I told that the 800-nanometer pulse is focused at a particular point and the intensity at that focal point becomes much greater than 10 to the power 13 watt per centimeter square.

So, this is a huge intensity we use, this is a strong field effect which we have already discussed in the non-linear optics. So, in this strong field effect, due to the strong field effect what happens every molecule the when this under the strong field the molecules are ionized, or atoms are ionized in the gaseous system.

(Refer Slide Time: 10:31)



Attosecond Charge Migration

Attosecond Charge Migration: Experimental

High Harmonic Generation (HHG) Spectroscopy as Self-Probing of Electron Density

IPC, Indian Institute of Science

So, if I consider that each atomic potential is like this an electron is staying here only, this is electron atomic potential within atomic potential. Due to the strong field this field is suppressed significantly and due to this suppression what happens this electron tunnels out to the continuum; tunnels out to the continuum and which means that ionized I ionized it.

So, the first step of high harmonic generation is the tunnel ionization, where electron is removed through that tunnel ionization process, due to the barrier suppression, the barrier which is holding the electron to the atomic to the atom that electron is removed from that. So, its suddenly electron is free.

And once an electron is free what happens? So, I have this is the point of focus let us m and the laser beam is going through like this way and this is a gaseous medium. So, I am picking up one molecule or one atomic response. So, I have one atom here at this point this atom will be ionized. So, I have three electron and the positively charged the cation I have created.

Now, this free electron will experience this field only, this is that the field is so strong, it is something like in a daylight we do not see stars, does it mean that stars do not exist? They actually exist, but we do not see them because the sunlight is so powerful so glowing that we do not see the very thin light from stars is it similar in taking that analogy we can think about it the beam which is passing through the atom is so strong; so strong field that the cationic field is not experienced by the electron anymore.

Cation as if cation does not exist anymore. So, if I have free electron now, then if the electric field is propagating this way then the field is changing along the perpendicular direction. So, this is the propagation vector direction and the field direction is this way and we know that every half cycle field is changing this finger is changing, it means that the force directions is changing. So, what will happen electron will try to.

So, at this point electron I have produced and that electron will try to go away from the from that point where it is produced and then within half cycle the field has changed the direction to the opposite direction. So, electron will come back, when it is coming back there is a possibility that this electron can recoiled with the with (Refer Time: 13:12) cation and that is called collision acceleration and collision step.

So, tunnel ionization is the first step of removing an electron, then acceleration is done by the field itself. Field is nothing, but a force. So, if a force is acting on a charged particle that will be accelerated immediately and that acceleration will not go along a particular direction, it will just change every half cycle. See the field is changing the direction in every half cycle.

So, electron will try to go away from the cation and then come back to the cation and when its coming back there is a possibility of recombination. And the possibility is very low, the probability of recombination is very low. But if they recombine then what will happen? I will have an emission of the light and that emission energy includes the I.P which is the binding energy of the electron, electron; in order to remove an electron I need to give the energy.

But in order to recombine an electron with the cation that elect that energy would be released that is called binding energy of the electron. So, that I binding energy will be released plus the kinetic energy will be released, because electron was traveling in the field. So, this travel has gained the kinetic energy for the electron and then when you see combining when its coming to a stop then it will release the energy. And that energy content would be would include the binding energy of the electron and the kinetic energy which has been gained during this travel.

So, this is called three step model. Now, question is we have to go back to the previous problem. Our problem is that there is a very fast timescale and within this very fast timescale there is a change and this is an artistic imagination. Let us say I have an electron density which is spherical like this and that is becoming like two lobes ok, this to the this is just an imagination.

So, if there is a change of this kind of change in electron density and within this attosecond time scale if there is a change, then we have to understand that if the electron is recombining at this stage the emission will be different, if the electron is recombining at this stage emission will be different. So, in HHG process what we what is going on? In HHG process I have an electron, I have removed when I have removed an electron the electron density was just like the sphere here.

So, I have removed an electron, the moment I have removed an electron the electron density was like sphere. During the travel when this electron was traveling in the field, when I have removed an electron this was sphere and then whoever is traveling this electron density is changing. And when after the change, when the electron is coming back and re colliding its seeing entirely different electron density.

It is just like I have left home seeing my daughter is doing something and then when I came back, I see that my daughter is doing something else and that change I will be able to recognize. Similarly, an electron when its leaving the molecule its seeing one density and it left and then when to do it was coming back and then re colliding it has changed to another density.

And the emission spectrum is very sensitive to the point of the to the electron density which we have at the time of recollision. So, if we need to if we want to employ high harmony generation spectroscopy in the attosecond dynamics, in probing attosecond dynamics then the whole attention should be given in analyzing the spectrum and decoding the information of the change. Because this change is coded in the spectrum or the emission, the emitted light. The emitted light if we analyze it nicely then this change will be encoded in that.

So, all we need to do is that we have to iterate the idea and then understand, how that change was implemented in the spectrum how to analyze the spectrum. Now, second question is that if I mean this process this removing an electron and then re colliding with the same cation, how long does it take? Because we know that this process, this elect this electron reorganization takes almost let us say 500 attosecond.

So, am I in that timescale? So, let us say it is 500 attosecond, within this 500 attosecond can we recombine, this recombination time is actually 1.3 femtosecond. So, we have pretty much the time scale which we need. So, what will happen during this removal, I remove an electron this electron will travel for 1.3 femtosecond at the center wavelength 800 nanometer.

So, this time is 1.3 femtosecond, after 1.3 femtosecond when electron is coming back if there is a change in electron density then the emission spectrum should encode the change of the electron density. So, we have that time scale necessary time scale which is needed for attosecond dynamics as well as through high harmonic regeneration and we have also the this recollision, this recombination step is actually sensitive to the electron density current electron density which we have in them in the atom or molecule.

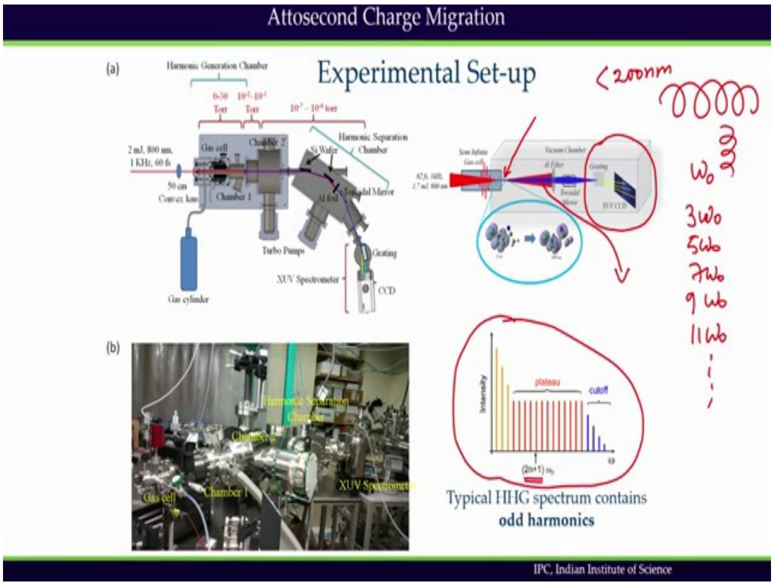
That is why high harmonic regeneration spectroscopy is called cell probing spectroscopy because it is using the probing scheme, it does not require, it is not like a pump probe spectroscopy. In pump probe spectroscopy what we do there is a pump which we which will create or excite the system to the excited state.

And that system will be now evolving and there will be a probe which will interrogate the system how the system is evolving as a function of time. In a pump probe I always need two pulses, but in HHG process I need only one pulse because I come create the electron, that electron is a probe it is coming back to probe the system at different time.

So, let us say instead of 800 nanometer for 800 nanometer my electron trajectory would be this much, but if I take 2000 lesser nanometer; 2000 nanometer 2000 nanometer will have longer oscillation period and that is why electron trajectory would be this much this long. So, in one case I have this long trajectory, another case I have this long trajectory. What does it mean? I am asking the system to relax more.

So, in this system has relax this much so, I can see this. But if I have if I started with this then system has relaxed a lot and then coming to recollision step. So, depending on what kind of central wavelength I can use, I can change the probing time, but it is a cell probing spectroscopy because the electron is actually itself our probe for the HHG process.

(Refer Slide Time: 20:51)



Attosecond Charge Migration

Experimental Set-up

Typical HHG spectrum contains **odd harmonics**

IPC, Indian Institute of Science

So, we use this HHG spectroscopic technique and mostly as I told you that when there is a, when we focus the 800 nanometer pulse in this gas cell I have to create a gas cell and in the gas cell I have to focus the beam. And at the point where the focal point is they are I cannot use any window, because the any window every material will start absorbing above 200 nanometer.

So, if it is greater than 200 sorry, less than 200 nanometer the wavelength, it less than 200 nanometer every material will start absorbing. We do not have a good window for that. So, we have to use a hole so that light can pass through the hole and then I can create the X-ray and then I collect the X-ray.

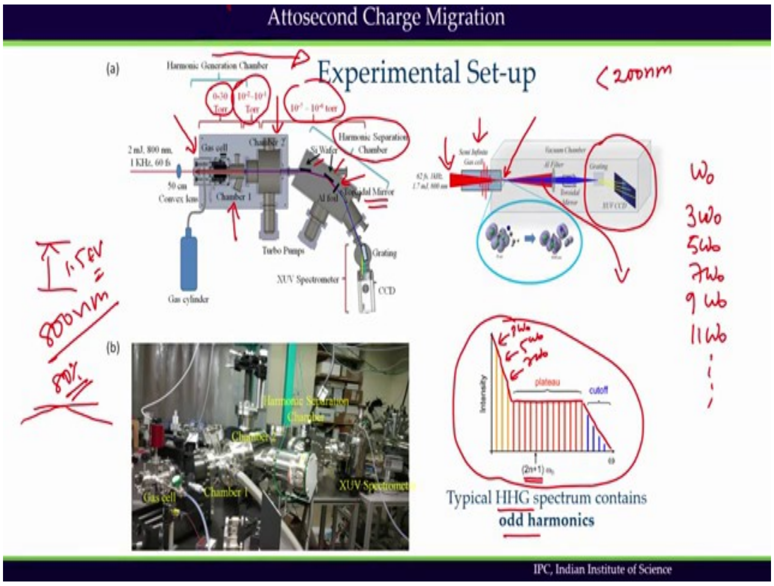
So, that is the that is one important information we should remember and this is the typical spectrum we see. What is the typical spectrum? This is the spectrum. So, what does it mean? It means that once I create this HHG this blue light this blue light can be directed to a grating and CCD, the combination this makes the spectrometer.

In spectrometer what we do depending on the wavelength we disperse the light, we disperse the color and we detect what are the colors we have. And if we check the spectrum then what we see is that this is a typical spectrum and you see that 2 n plus 1, this is the number which we are trying to give for the odd harmonics, all odd harmonics would be created. So, if 800 nanometer I considered to be omega naught then I will create 3 omega naught, 5 omega naught, 7 omega naught, 9 omega naught, 11 omega naught and so on. These are the odd harmonics will always create.

Odd harmonics we are created in HHG process because the medium in which we create HHG is a gaseous medium and any gaseous medium has isotropic property. What does it mean? Optical properties in this direction, in this direction, in this direction, in this direction, in this direction, in this direction every direction optical properties are equivalent. But if I take a crystal, let us say solid state crystal if I go this direction and if I go this direction their properties can be different, it is more like if I go this direction my spring more like this.

And if I go another direction then spring may be like this, I saw something like that. So, so one can imagine that I have a; I have a medium with different springs in different direction, that is called an isotropic medium. But gaseous system any gaseous phase is actually isotropic medium and due to isotropic medium I have to maintain this center of symmetry of the system and that makes this odd harmonic generated.

(Refer Slide Time: 24:01)



Attosecond Charge Migration

Experimental Set-up

Typical HHG spectrum contains **odd harmonics**

IPC, Indian Institute of Science

Now, in odd harmonics so definitely this is going to be my 3 omega naught, this is going to be my 5 omega naught, this is going to be my 7 omega naught. So, up to 7 omega naught there is a sharp decay we see in the intensity. Then there is a plato, there is no change of intensity all this plato are showing up. And then suddenly there will be a cut off, there will be cut off in this and this is a typical spectrum. So, first what we will do in the spectrum we will see a sharp decay in the intensity, then there will be a plato and then there will be a cut off.

So, this is a typical spectrum which we observe from the HHG process from any gaseous system. And we will go over the experimental setup to some extent which we have in Indian Institute of Science. This is not the only way one can generate HHG there are many other ways HHG can be generated. HHG can be generated in a pulse, nozzle, valve, in a pulse nozzle HHG can be generated in a gas tube.

So, here we have used one gas cell. So, what we have here the first thing is the gas cell, this is the gas cell and this is a schematic diagram and the original diagram is here. So, gas cell is actually attached to a xyz translational stage so that we can move the gas cell this way or that way because I have two holes here. So, one gas cell hole and then another wall I have in the wall I have one hole. So, this hole and this hole has to be collinear and that is why we have to use this xyz translational state to adjust the position so that these two holes becomes collinear. So, that the light can go through both holes.

So, I have the first gas cell, then second chamber then third. So, gas cell chamber then chamber 1 and chamber 2, this chamber 1 and chamber 2 these are the we have used to for the differential pumping. Differential pumping is used to let us say I have a very high pressure in this regime so there are chambers. Let us say one chamber, this is this is one chamber, then second chamber, then third chamber, there are 3 chambers I have.

In the first chamber I have a hole let us say and in this chamber I have very high pressure, in the second chamber that is there this a hole on this wall so in the second chamber I again pump it down and I have another hole here. So, on both side I have hole in the second chamber and then third chamber I have hole here, but I do not I have a big hollow tube here on this side. So, what is going on? By taking these three chambers I can reduce the pressure step by step.

So, here in this gas cell pressure can be very high can be few to all let us say, but in this second chamber I have lesser minus 2 torr and 10 to the minus 2 torr and the third chamber I can create 10 to the power minus let us say 6 torr and that is exactly shown here. So, far in the first gas cell chamber is 30 torr it could be, but then I would reduce the pressure to minus 1 and minus 6 as we move to the optics chamber.

So, why we need this vacuum? We need the vacuum because the energy of the XUB beam is very low and XUV is an ionizing radiation. Most of the VUV and XUV radiation which is coming from sun is absorbed by the upper atmosphere, it does not come to us and if it is coming to us we will not be able to survive.

So, XUV is absorbed by the atmospheric molecules and that is exactly what we need to avoid here, because we want to get XUV. So, in order to get XUV we have to create the vacuum and in order to create, but XUV will be generated in the gas cell, but then the XUV beam has to be collected in the vacuum. So, I have to have; I have to have a transition from high pressure to the vacuum and this transition is done with the help of this differential pumping which is showing here the gradual decrease in the pressure.

In the optics chamber, this is the high harmonic separation chamber our optics chamber what we have used we have used a silicon wafer two silicon wafers we have used. Silicon wafers are very interesting, silicon is actually a semiconductor and it has a band gap of almost 1.5 ev. So, this 1.5 ev is comparable to the 800 nanometer energy photon energy.

And for the excitation for the high harmonic regeneration we are using 800 nanometer pulse. So, what will happen this silicon wafer will the when 800 nanometer is propagating like this way it is reflected by this way most of the 80 percent of the beam will be absorbed, what I am doing here is that once I have created HHG both fundamental beam and the XUV beam are collinearly propagating.

My task is to eliminate fundamental beam and only take XUV beam from it. And that is why two silicon wafers we use to reduce 800 nanometer beam as we show here with the help of colors. And then we use one aluminum filter. Why aluminum filter? Aluminum foil filter, we use aluminum foil at home all the time, but the thickness of aluminum foil which we use is probably 10 micron or 100 micron, but what we have used here is 0.6 micron, which is 600 nanometer even less than the one which we use at home.

So, what is the advantage of using an aluminum foil in the beam path is that we know that X-ray penetration depth is much larger than 800 or near IR. So, if I have a metal and if I use X-ray to go through it can actually penetrate through metal, but if I use 800 nanometer or visible light or the light we have in this in the classroom that light cannot penetrate to the metal and we take that advantage, because we have X-ray beam XUV beam and we have 800 nanometer beam.

So, if I use aluminum foil which is very thick thickness needs to be adjusted because thickness will cut down XUV beam as well, but if we adjust the thickness for example, we are using 0.6 micron thick aluminum foil that will allow my XUV beam to go through the foil. But 800 nanometer is now blocked in at the aluminum foil and because it is blocked then we use a toroidal mirror. Toroidal mirror is nothing, but a focusing mirror.

What is focusing mirror? Why do we need focusing mirror because you see that the beam is focused here and slowly diverging here in this point diverging and all the beam is diverging actually and in order to recompress the base sorry refocus the beam to the grating I need a toroidal mirror. Toroidal mirror is actually nothing, but a focusing mirror for the X-ray.

And it is now directed to the grating and grating is dispersing the beam. Grating equation we have seen how grating can disperse the beam, we know that transmission transmissive grating and reflective grating both equations we have seen in the construction of ultra-fast laser system. So, why we need to refocus the beam is because we are focusing the fundamental beam first at this point.

So, every beam when you focus see it first, it will be slowly diverging after the focus. And that is exactly going on with the XUV beam as well here and this XUV beam needs to be refocused with the help of toroidal mirror. Toroidal mirror is nothing, but a focusing mirror which will be directing the beam to the grating and grating equation we have studied already in the construction of the ultra fast laser which disperses the beam as a function of the of the instant angle.

And the finally, the beam will be detected with the help of XUV CCD camera, CCD camera is very sensitive for detecting very low photon energy and that we can we got low intensity light. So, we can detect that one and once we disperse it will be able to get the spectrum like this what we have shown here. We will continue the this session in the next lecture.