# Ultrafast Processes in Chemistry

Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

## Module No # 09
## Lecture No # 46
## Snapshots of Bond Breaking

Well over the last many modules we have discussed we have gone into lot of detail but we discussed the working principles of the instruments used commonly in ultrafast dynamics ultrafast spectroscopy. Now we want to come back to the discussion that we originally started we know a little bit about the instruments now fine what do you do with this instruments? What is it that you study? What kinds of system you study?

So once again the answer is that you can do a lot of things and what we will do in the next few modules is that we are going to present few selected problems that as captured the attention of a lot of researches over the last few decades. To start with we will talk about molecules then we will present briefly about ultrafast processes that take place in semiconductor nano crystals and metallic nano crystals.

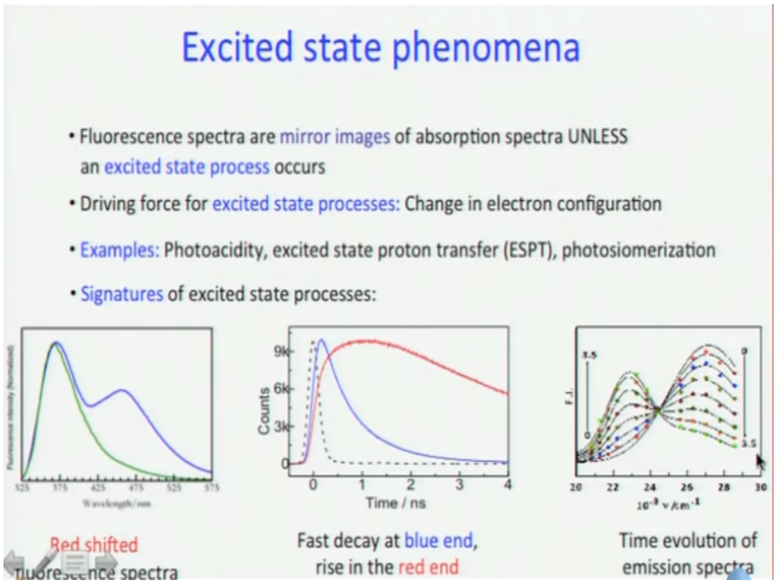
And then we will go over and discuss depending on how much time we have some other techniques. Mainly now we are going to talk about results of your femtosecond optical gating and pump probe. So next we are going to go on and talk about 2D IR spectroscopy at least 2D IR and 2D spectroscopy and then let us see how it unfolds? So what we do usually using this instruments and using this techniques is that we try to study chemistry beyond ground state chemistry.

Now most of the chemistry that goes on all around the world for lot of times is that you when you say chemistry what you really think is that you mix something with something else and produce a new substance. So in fact if you read ancient text book like that by Ladli Mohan Mitra you see that he has written that I like chemistry this is the only science in which you can create something new.

And that has really been the focus of the chemistry but then there is a lot of chemistry that can take place not in ground state but in the excited state and it taking place all around us as we have discussed earlier. So what we try to do using these lasers and all is that you try to understand chemistry that take place beyond ground state and many times we use this chemistry beyond ground state to initiate reactions and see how they proceed okay.

So in this module what we will do is we will remind you of what we had perhaps presented little sketchily in the first 4, 5 modules. You might remember that we had said that excited state phenomena are reflected in certain properties spectral properties of the molecules.

**(Refer Slide Time: 03:03)**



## Excited state phenomena

- Fluorescence spectra are mirror images of absorption spectra UNLESS an excited state process occurs
- Driving force for excited state processes: Change in electron configuration
- Examples: Photoacidity, excited state proton transfer (ESPT), photosiomerization
- Signatures of excited state processes:

Red shifted fluorescence spectra

Fast decay at blue end, rise in the red end

Time evolution of emission spectra

To start with if you doing fluorescence spectroscopy one thing that you learn first of all is Khasa's Rule. Khasa's Rule says that a fluorescence spectrum is a mirror image of should be a mirror image of the absorption spectrum and it holds very nicely for well-behaved fluorophore like Pyrene. Fortunately it does not hold good for many molecules because if it did then we could not have made a living out of being fluorescence spectroscopy in 2019. If every spectrum would have been a mirror image of the absorption then it would be very nicely organized and absolutely boring.

Fortunately Khasa's Rule is a rule that is mean to be broken in many cases so most of our research goes into studying this rule breaking game. So what happens when the rule is broken? What happens when a new state is produced post excitation then the certain signatures are obtained in this spectral and temporal features. As we have discussed earlier so we will not repeat now the driving force of this excited processes is change in electron configuration.

As chemist we know that it is electron configuration that decides reactivity is not very difficult to understand that when we perform a an excitation of course electron configuration changes that is why you go from an electronic state to another electronic state and here let me repeat at the risk of saying it several times for a simple in this course I do not know I do not remember if I said it but many times we ask people to draw Jablonski diagram they draw it and then we ask what is going from S0 to S1 and everybody says electron that is wrong.

So please we should be actually conscious about this electron goes from some molecular orbitals to some other molecular orbital. Not necessarily from Homo to Lumo very often is not even allowed some occupied molecule orbital to some un-occupied molecule orbital. That is where the electron goes okay the molecule goes from S0 to S1 or whatever it is please do not forget S0 S1 T1 is SNTN all these are electronic states of the molecule determine bi-enlarge by the configuration.

I say bi-enlarge by the configuration because even configurations talk to each other you have what is called configuration interaction. For a brief introduction to this phenomenon one may refer to our course which is now online is available freely in YouTube the NPTEL course on Symmetry in chemistry. So there we have discussed in detail the case of naphphthalein and there we have talked about how configuration of same symmetric and interact.

But roughly you can say that it is a configuration determines the state so it is not just 1 electron all the electrons together which orbital that occupied. That is what determines the state of a molecule remember a electronic state is the state of a molecule and not of 1 particular electron alright. So that I am sure I have repeated myself but it is an important point and I see that even people coming for faculty interviews I have no idea about this so it I think it is better that we say it is specially it is hope that this course will reach a wider audience right.

So what are the signatures of excited state processes first of all fluorescence spectra this let us say if you can read the X axis this is actual spectra record in our lab many years ago X axis in wave length. So if you go from left to right 325 nanometer to 575 nanometer from left to right energy decreases in a reciprocal manner. So this one this spectrum is the mirror image spectrum so that is the characteristic spectrum of the locally excited state.

And the red shifted band that you get is the characteristics of the what I like to call nascent state the state that is formed as a result of the excited state reaction or excited state process whichever you want to call it okay. So what happens is when you excite this is the state that is populated initially over time this state depletes not only to back to the ground state but also to populate the state responsible for this red shifted emission.

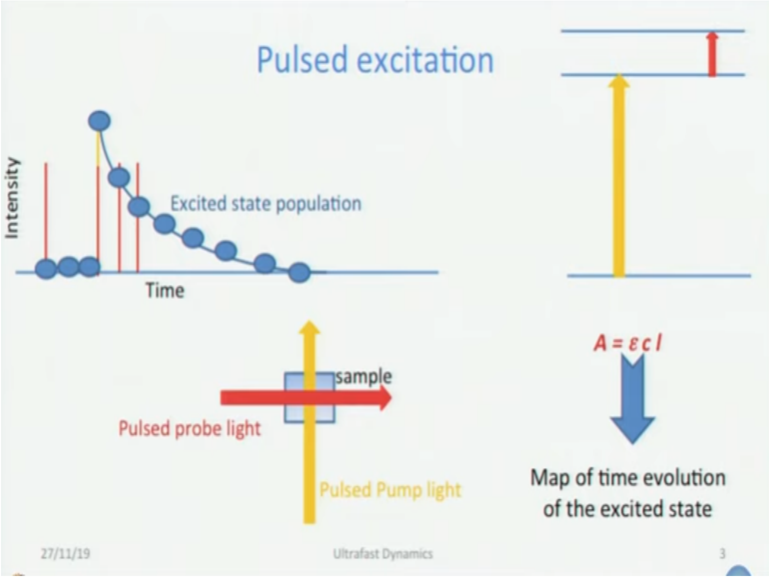
So now if you record fluorescence decays in the high energy side of the spectrum or as you like to call the blue side of the spectrum and the low energy side of spectrum as you like to call red side of the spectrum then what do you expect to see. The species responsible for emission in the high energy side has an additional deactivation pathway and that is the excited state process. So you expect a fast decay of fluorescence's in the blue end of the spectrum like what is shown here.

And this the state responsible for this emission is not even there at the moment of excitation it grows over time as a result of the excited state process that depletes the locally excited state. So you see an initial rise followed by a decay of codes an excited state as should decay eventually okay. So if you go back to our chemical kinetics knowledge this is sort of this red emissive state is sort of like the intermediate remember how the population of the intermediate evolves over time it goes up and the goes down reactant goes down all the way and the product goes up all the way okay.

So this state is like an intermediate that is why there is rise followed by a decay and then using these 2 I think we have discuss this one can construct the time dissolved emission spectrum whereby you can see that you can see how the emission spectrum itself evolves overtime. And this is a very useful thing to know as we are going to discuss not in this module but may be a couple of modules later.

And nowadays in many instruments you do not really need to record this steady state spectrum and the decay separately. If you use 2 dimensional detectors as we have discussed earlier in this course you can actually get the time evolution of the emission spectrum in the next module we are going to show you an example of such a piece of data where you record this spectra fast and then from there you obtain the decays.

**(Refer Slide Time: 09:45)**



Pulsed excitation

Map of time evolution of the excited state

27/11/19 Ultrafast Dynamics 3

Okay now fluorescence is not the only technique that we have studied the commonly used technique which we have whose components we have studied in great detail is pump probe or transient absorption. Here what you do is you excite your sample by a laser pulse an intense laser pulse which causes an excitation to some higher excited state. And then what you do is you look at the excited state population that is going to decay with time.

How do you follow the time evolution here? If you remember very basics of spectroscopy one can use your Lambert Beer's law as you are going to say. But before that do this is how you do the experiment this is your sample this is the pulse pump light the light that is responsible for populating the excited state and along with that you put in a pulse probe light. Probe light is usually of much less intensity compared to pump light because the job of it is just to probe it should not disturb this excited population too much.

So what you do is if monitor the absorbance of this probe light let us say well probe light can have any wave length. But let us say we have a probe light which matches an absorption of the excited state. Now as we know that a absorbance is epsilon cl so if you can follow the time evolution of absorbance of this wave length then that will give you an idea of time evolution of the population or concentration of the excited state.

And you might remember we talked about this in one of the earlier modules so just recapping because it is been such a long time what you do is that you look at this probe pulse right and basically change the delay between the pump and probe pulses. So if the probe pulse arrives before the pump as arrived in this scenario what will happen no it will not be absorbed because you have chosen a wave length let us say that is absorbed by the excited state but not by the ground state.

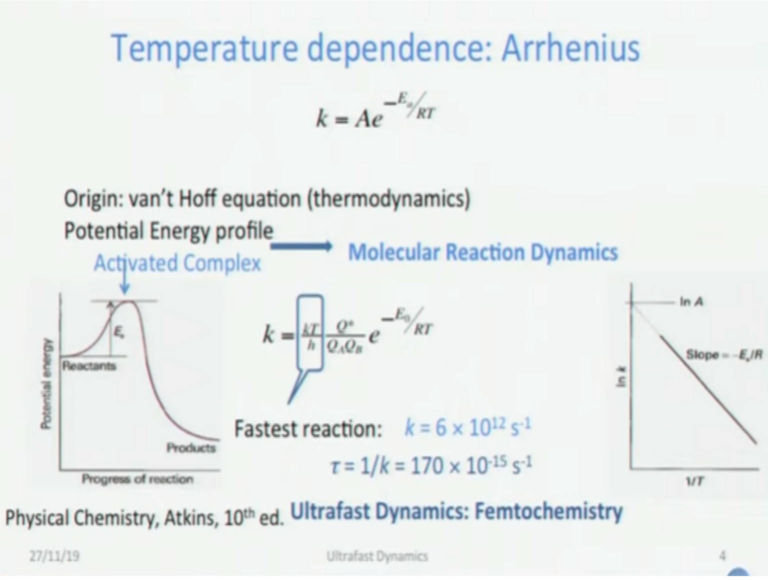
I am not talking about multiplex detection here I am talking about using a mono-chromator and a detector. And pretending as if I a have only one wave length of probe right not a spectrum. So absorbance is there is going to be 0 now suppose you have decreased the time delay little bit it is still 0 absorbance is still 0. Now you keep on changing the delay there will be a time when you will achieve time 0.

Time 0 means the delay of the pump and the probe are exactly matched and that is when the probe light will encounter the maximum possible population of the excited state and absorbance will shoot up okay. So in this cartoon this circle denotes the absorbance is measured at specific delays and this line shows you the time evolution of the excited state population. So if the pump pulse is delayed further it will come a little later now what will happen?

Population would have decrease let us say from here to here okay so epsilon will not change ‘c’ will change accordingly. So your absorbance so if this is when the pump pulse the probe pulse comes absorbance will decrease proportionate to the decrease in population right. This way as you change the pulse as you change the delay of the delay between the pump and probe pulses you generate essentially a map of the time evolution of the excited state population.

That is how the pump probe works of course I hope you have discussed what happen when you probe is tune to the absorption of the ground state and not the excited state then you get something called ground state bleach and if it is tuned to the absorption of an excited state that is formed as a result of sorry excited state that is formed as a result of excited state process then you are going to see arise time okay.

**(Refer Slide Time: 13:51)**



Temperature dependence: Arrhenius

$$k = Ae^{-E_a/RT}$$

Origin: van't Hoff equation (thermodynamics)

Potential Energy profile → Molecular Reaction Dynamics

Activated Complex

$$k = \boxed{\frac{kT}{h}}\frac{Q^*}{Q_AQ_B}e^{-E_0/RT}$$

Fastest reaction: $k = 6 \times 10^{12}\ s^{-1}$

$\tau = 1/k = 170 \times 10^{-15}\ s^{-1}$

Physical Chemistry, Atkins, 10th ed.

Ultrafast Dynamics: Femtochemistry

27/11/19 Ultrafast Dynamics 4

And let me also remind you even though we have said it earlier why is it that we so obsessed with femtosecond. What is so great about femtosecond? And why not attosecond why not stop at nanosecond? We are obsessed with femtosecond because if you look at chemical kinetics once again you are familiar with this Arrhenius equation right? So origin of that is Van't Hoff equation with thermodynamics and we are all familiar with this kind of energy profile right?

Where you have reactants and your product and there is an activation barrier only when there is an activation barrier you are going to have a temperature dependence of the rate constant okay. And this is the activated complex study of activated complex opens up this field of molecular reaction thermodynamics. We are more familiar with the theory part of it perhaps () but what we are trying to do essentially is that we are trying to do experiments by which one can follow reaction to dynamics right.

Now if you have studied this activated complex theory and all you are would be familiar with this equation which equation is this? ionic equation so ionic equation expresses the rate constants in terms of the theoretical quantity right. kT/h k were Boltzmann constant what are Q's, partition function Q star divided by QA QB where the reaction is A + B2 products kind of reaction and e to the power e0 / Rt where your e0 is the activation energy.

So what can be maximum value of k? Let us talk about the exponential part what is the maximum value of the of e to the power –e/Rt and when do we get it? I want to know when k has the maximum value largest rate constant with correspond to this smallest possible time associated with the reaction. So can you tell me? What is the best possible value of e to the power minus e0 /rt you are right it is 1 and when does that happen? When e0 = 0 that means activation energy is 0 that is the best possible scenario right.

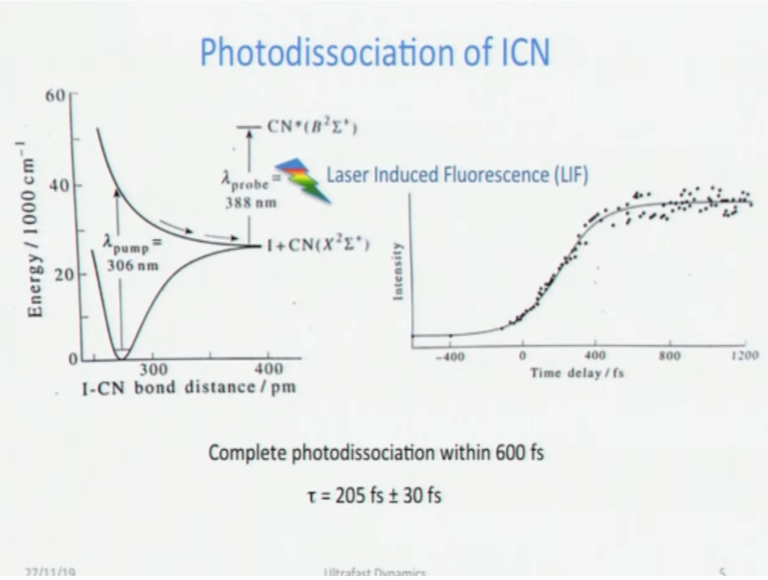
As activation energy goes higher and higher reaction becomes slower and slower okay now and so that would be 1 in the best possible case what is the best possible case that I can get with the partition functions? Again 1 okay so the largest value of the rate constant that one can get is KT/h and at room temperature 300 kelvin or something this value turns out to be value of fastest reaction this turns out to be 6 into 10 to the power 12 per second.

So if this is rate constant what would be the time associated with it the reciprocal the time turns out to be 170 femtosecond we have said it at the beginning of the course just reminding you 170 femtosecond. So from theory the expectation is that the fastest possible chemical process would require about 170 femtosecond that is why femtosecond times scale is so important that is why we want femtosecond pulses because we expect that there is no chemistry faster than that.

Nowadays people study attosecond spectroscopy as well but that is really state to state dynamics and all it is very highly interesting. But chemistry sort of stops at femtosecond and I will show you why we say that right. So that is why this generator lot of interest in 1970’s and 80’s even 90’s and that give rise to the field called femtochemistry. In fact whenever you say one name that you come to your mind many names can come to your mind but one name that definitely comes to your mind is Ahmed Zewail got is Noble price in 99 for femto chemistry.

In fact he has some books name femto chemistry and femto biology and so on and so forth so when you are talking about femto chemistry it would only be proper to show you at least some of the huge amount of highly interesting, and phenomenal results obtain in Zewail group.

**(Refer Slide Time: 18:25)**



Photodissociation of ICN

Complete photodissociation within 600 fs

τ = 205 fs ± 30 fs

27/11/19 Ultrafast Dynamics 5

I will show you just 2 this is not text book material you can find this in common physical chemistry text books like McQuarrie and Simon or Atkins okay so first piece of data what are what is the question we are asking? You want to know can we experimentally determine the rate constant of the fastest possible chemical process what is the fastest possible chemical process? Breaking of a bond how much time does it take? To steady that many experiments where done the data we are going to show you is photo dissociation of ICN.

So sometimes when you show data like this people are so what uses this why ICN? Why not benzene? But these are all invalid questions really this is demonstration of the phenomenon we have to work with something that you can get the interesting result form there is no point asking why you are not taking more complex molecule for more complex molecule perhaps since would become more complicated and you would understand.

So this even though ICN is not a molecule that you encounter every day the reason why ICN was used is this. The energy diagram of ICN is like this so you have this bonding anti-bonding kind of energy diagram right. You have this first electronic excited state which has a minimum and there is this excited state that is dissociative I hope you are familiar with dissociative excited state dissociative states electronic states that do not have a minimum.

So you populate it what will happen is molecule will break and it is well known by that time it was well known that if you excite by 306 nanometer or any wavelength that takes you here then you can go from the bonding lowest energy state to a dissociative state and the dissociation takes place like this I+CN. CN bond does not break IC bond breaks okay so what are the photo dissociation products? I + CN let us now worry about the term symbol at the moment and also this is the pump probe experiment without a probe.

Somewhere we can call it only a pump experiment it is a without a probe because one can use a probe but good thing is it is also known that if you look at the CN fragment that can be excited well that can be excited with 388 nanometer it is not a pump experiment pump probe experiment but you look at something different. So here the probe is also acting as a sort of a pump what happens is first you have a 306 nanometer pump you populate this state and then the probe light is tune to 388 nanometer.

So 388 nanometer is a wavelength that causes a transition of CN to CN star and there is a corresponding emission and as we know it is easier to look at emission then at absorption will you agree with me? Because when you look at when you do emission spectroscopy even 1 photon is enough when you do absorption it is all about difference in absorbance so you have Avogadro's number of molecules even in 1000 molecules are excited that may not be good enough change in absorbance.

But if you even 1 molecule emits right your comparison is darkness which is 0 so even 1 divided by 0 is infinite. So what they did is that they looked at not at transient absorption as such but they looked at emission of Cyanide star excited state of CN which arose due to excitation of the CN fragment by the probe light at 388 nanometer. So pump probe geometry pump as 306 nanometer probe as 388 nanometer and you will observe that these are all ultra violet colors right.

And the lasers they used at that time I think they used Ti sapphire laser also but mostly that time the lasers they used are the type that we are not even discussed in this course they are called CPM lasers it is colliding pulse mode laser that was the technique by which ultra-short pulses were produced before the advent of Titanium Sapphire laser good thing about Ti-sapphire laser is that it gets mode locks by itself just have to disturb it little bit and you have to give it the big enough cavity.

But before that in the era of dye lasers you have to actually make these laser pulses collide with each other and form from ultrafast pulse it was a much more complicated technique. So using this laser what they observed was what is called laser induced fluorescence and since pulse laser were being used they could follow the dynamics of laser induced fluorescence okay. What do you expect? What kind of time evolution do you expect for the laser induced fluorescence in this graph?

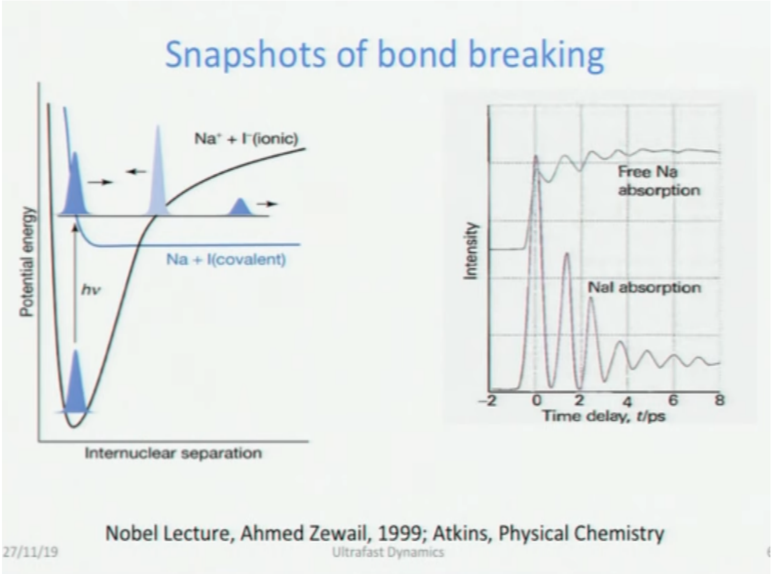
See the moment you excite it should you get any laser induced fluorescence? No because the ground state is what ICN molecule when you excite at the moment of excitation you still have ICN then it takes some time for IC bond to break. And as the IC bond breaks the emissive CN fragment is produced. So what we expect to see here is a rise okay and that is what they absorbed I have dramatized a little bit but they did observe a rise in the laser induced fluorescence signal characteristic of this CN start fragment okay.

So what do you observe? You observe that the photo dissociation is complete look at the times here this is 0 time this is 1200 femtosecond 12 picosecond. In fact if you go here from here onwards it is flat right. So within 600 femtosecond the fragmentation is actually done and when you fit it to arise the time constant that you get is 205 femtosecond plus minus 30 femtosecond hence proved.

Expected value is 170 femtosecond experimentally observed value is 205 femtosecond plus minus 30 femtosecond. So this is the very good match as good as it gets between experiment and theory okay. So this is a phenomenal results because this vindicates the theory and tells you should gives you the evidence of how much time it actually takes for the bond to break the fantastic result.

In fact this perhaps would have been good enough for his noble prize but then they actually studied many other things then they try to understand this process in very great detail and they obtain what they called snap shots of bond breaking.

**(Refer Slide Time: 25:47)**



## Snapshots of bond breaking

Nobel Lecture, Ahmed Zewail, 1999; Atkins, Physical Chemistry

27/11/19

Ultrafast Dynamics

Perhaps I should have dramatize this slide a little more but since I did not i just explain from here. So what they did is this studied different molecules one of the things they studied was NaI sodium iodide okay now let me ask you a question? Everybody has done flame test yes what is the color of flame that you get for sodium? Yellow right what is the color of sodium vapor light? Sometimes there in street side now it is being replaced widely by LEDs yellow right.

So that yellow I think everybody knows about sodium Dline is not it? It is used in your polarimeter and all that. Now see this yellow light is actually characteristic of sodium Na not Na+ but then you take some sodium chloride and put it flame you get yellow color which is characteristic of Na and Na+ why is that so? That is so because you have this kind of an energy diagram here.

You have NaI which is called covalent and then you have Na+ + I- ionic one and of course ionic one as a lower energy this is Na+I is actually dissociative right. But then what you see is if you can populate this somehow then you will get this characteristic sodium light sodium dline so that is what happens when you heat and all when you put in the flame from Na+I some amount of Na is formed and that is what gives you the yellow color again emission.

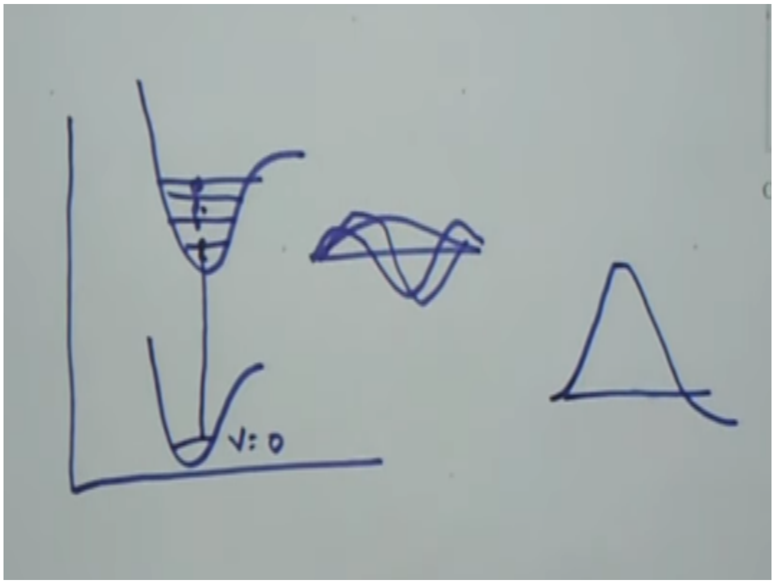
So what they did was they took Na++I- and then the excited using a laser pulse and they used laser pulse that would take the system from Na++I- surface to Na+I surface okay that is dissociated. So you can think that the moment is taken to Na+I surface dissociation would have taken place okay.

So if you follow the same transient absorption what should you see you should see a rise for free Na absorption and you should see a decay for NaI absorption right.

What this see is this and it is extremely and it is not it is extremely let us say not difficult but it it extremely non trivial to get data that looks like this thing that you see is not noise this is real data what you see is for NaI absorption yes there is a decay but the decay is associated with oscillations for free Na absorption there is a rise but the rise is associated with oscillation periodic increase and decrease why is that so?

That is so because once again will not go into the intricate details of this but this is something that anybody working in field of ultrafast dynamic should know. So encourage everybody to read papers on this, papers and books so what happens is remember the property that we studied of ultrafast pulses how do you produce ultrafast pulses what is the technique? Mode locking is not it? So when your mode lock what happens to the spectrum? Ultrafast pulses are the monachromatic or do they have broad spectrum? They have a broad spectrum because many as many modes you lock shorter pulse you produce more modes are lock shorter pulse you produce okay.

**(Refer Slide Time: 29:52)**



So what happens is when you excite using a ultrafast pulse then let us say this is your ground state of course here it is your dissociative state but it is easier to understand if it is if the excited state is also something it goes to minimum. So this states are associated with this vibrational levels and you know the V = 0 state is the only one that is populated at room temperature.

So if you excite using a highly monochromatic light then you can go from V=0 or V=1 or V=2 whatever the energy is but then if you excite using a broadband light the light you are ultrafast pulses then you cannot selectively excite 20 dash is not it? You cannot selectively excite 1 dashed or 2 dashed you end up populating many of this levels 2 different extent right. So what is the wave function of the lowest one like something like this the one above that is something like this one above that you have one more so on and so forth okay.

So what do you do is and all this states get populated at the same instant right so what you form then is not a particular wave but a wave packet a coherent wave packet. A wave packet means a packet of waves you can think like that when the wave function is not a single wave function but really a super position of many wave functions then it is called as wave packet and you know what happen when you super impose many waves what will happen localization will take place is not it that we have I think we discussed earlier.

At time t = 0 if they are in step then as time passes then they will get out of phase so you will get end up getting something like this alright. And more the number of waves you mix narrower will this distribution of the wave packet be. So once again for a fundamental idea of wave packet you can read something like Atkins. In fact they have used the idea of wave packets to discuss uncertainty principle where they talk about momentum base it is an interesting read I encourage you to do that.

So when you excite using an ultrafast pulse you end up creating wave packets and wave packets are stationary they oscillate okay. So that gives rise to this interesting phenomenon called coherent wave packet dynamics okay I will not go further into that but just be aware that here we have an example of coherence wave packet dynamics which is a very important field of study in ultrafast dynamics I encourage you to read up on that and essentially what it means is that the oscillations means that you have produce so you see this is a wave packet okay.

Now this wave packet oscillates between Na++I and Na+I that is why there is rise but then there is a fall as well why? Because this are dissociated now it is coming back then it dissociates again and it comes back. So the system oscillates post excitation between a dissociated and undissociated state and that is what gives rise to oscillation in this signal as well as it is oscillation as period of 1 picosecond oscillation.

So it is not as if you break the bond and that is the end of the story breaks gets made breaks again get made again and finally it does not come back after a point of time is like a damped oscillation okay. So this is the extent to which you can follow molecular processes using ultrafast processes ultrafast techniques okay you can get snapshots of bond breaking and that is what Ahmed Zewail got is noble prize. So we will stop here now and we will come back and we will talk about another phenomenon.