Advanced Chemical Thermodynamics & Kinetics
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Lecture- 18
Review of Chemical Kinetics

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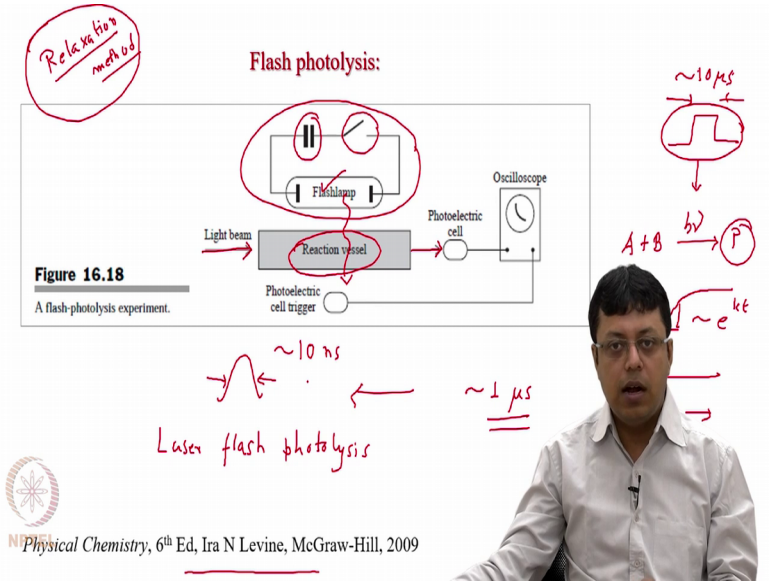

So, now the problem with these relaxation methods is that the time scales are still pretty low like I said it goes up to 1 nanosecond. And the reason is obvious, because if you think that we are using a short pulse of light, let us say a laser pulse of few nanoseconds. But then it initiates the process and then you watch the subsequent events by say absorption or emission of whatever, and which you can directly see on an electronic device like oscilloscope. Now, electronics up their own time skills, it is limited up to say 1 nanosecond or let us say a fraction of a nanosecond something like that but not beyond that. However, the dynamics of molecules have a much much faster time scale, to give you a feeling of how fast you at these dynamics.

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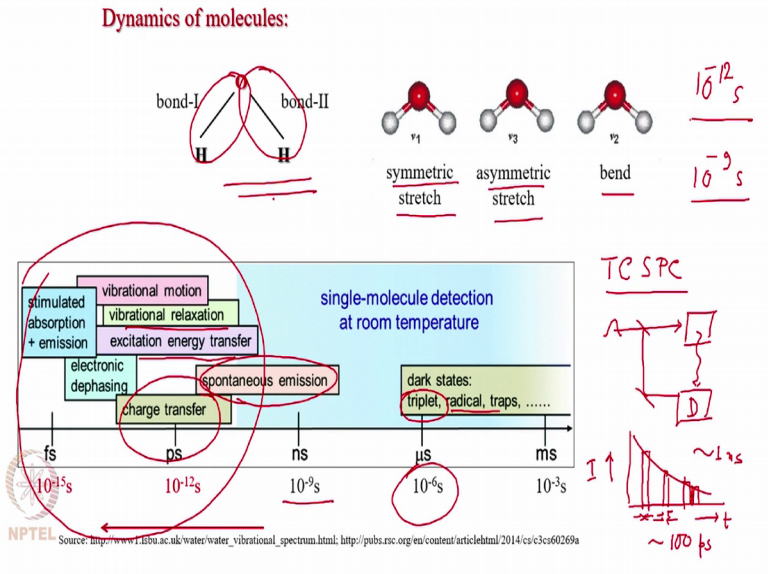

Here, we show you first our water molecule. Now, water molecule is a simple molecule, and as you can see that as you know that it has 2 O H bonds. And then in what happens at any temperature this bonds vibrate, because the molecule has a vibration energy which is a zero point hydration of energy. And you can actually think of these vibrations as the combination of vibrations under, which is known as normal modes of vibration. As a three typical vibration; one is a symmetric stretch, which is shown here. In this animation where you can see that the two bonds of water are stretching or compressing simultaneously, so that is why, it is a symmetric vibration.

Similarly you could have an asymmetric stretching vibration, where actually you have one bond stretching, but at that time the other bond is compressing, so these two vibrations are basically our 2 bond vibrations are out of phase. And similarly, you can have a bending motion, like the water molecule these two bonds are bending like this. Now, these three vibrations have their characteristic frequencies and they also have a characteristic time period associated with that.

Now, these time periods will be on the order of picoseconds, a few picoseconds to a few tens of people seconds; and if it is a low frequency vibration, it can be a few I mean 100s of picoseconds will terra hertz raging, but those timescales are very fast, because now we are talking about picosecond or sub picosecond dynamics which is like 10 to the power minus 2, minus 12 seconds, and earlier well the flash photolysis times if you remember,

it was limited by the electronics, and that was up to 10 to the power 9 second and a nanosecond.

Now, again you see a three order of magnitude improvement or beyond that. And before we discuss, how to tackle this problem which should anyway discuss very briefly. And let us first show you the wide range of chemical and biological processes or what are the timescales associated with these processes. Now, for example what we just said about flash photolysis, with flash photolysis with a microsecond time resolution. You can actually study, the dynamics of long lived triplet states or radical species or some I mean craps if you can create, some ion trap or some other kind of a matrix trap, and then you can actually stabilize those places, and you can increase their lifetime. And you can actually have a look at, you can observe it by electronics.

However, if you look at it carefully, the spontaneous emission of the fluorescence has a knife type of nanosecond. So, or slightly more less than nanosecond. So, in order to understand that you need a device, which actually works a much faster time scale. Now, up to this like a fraction of a nanosecond on the order of say 100 picoseconds and so. We can still use electronics and for example, for fluorescence lifetime measurement, you can actually use a device which is known as a or a method which is known as a Time Correlated Single Photon Counting method which is known as TCSPC method.

And what is done there, is that you first send a light pulse to the system, and then suppose our fluorescent photon is emitted. And, your detector actually knows, when this light pulse was sent, and when this fluorescent photon arrives. And by actually it is even more complicated than the way I am saying, because it involves a lot of intricate details of the electronics, but the overall principle is like you know the point of photon id at the sample, and when the fluorescent photon emitted, and from that you can actually calculate that arrival time of the photons.

If you repeat this experiment for many times, you can actually create a histogram. And from that actually you can calculate, like what is the fluorescence lifetime, and typically these lifetimes are on the order of 1 nanosecond or so few nanoseconds. And the resolution you get for every step is something on the order of say 100 picoseconds or fraction of a nanosecond, 0.1 nanoseconds or so. So, so in this case what you do is that you basically count the arrival time of the fluorescent photon with respect to the

excitation photon. And you calculate how many photons are suppose there, which arrive at say this time, and then how many photons arrived at this time; and then you create a histogram like this. And, if you fit an exponential, that will correspond to the fluorescence lifetime.

But we can actually apply electronics I mean up to this time scale, but not beyond that. So, but you can see that lot of physical and chemical and biological processes happen, which are actually in the sub picoseconds timescale picosecond or sub picoseconds timescale. For example, charge transfer has a typical timescale of 1 picosecond to 100, 100 from the second 1 picosecond. And vibrational relaxation or vibrational energy transfer, all these vibrational motions which we just discussed, they have a typical characteristic time scale of few 10s of picosecond to down to few 10s of femtosecond.

Now, you need of course femtosecond pulse which is a much shorter pulse to initiate the process, but still you have a problem. And the problem is how you observe the subsequent process, meaning you can there are two problems always associated here; one is that you need a very short pulse to initiate the process. If you use a longer pulse, let us say I am using a nanosecond pulse to understand a femtosecond process.

So, during my excitation, because the nanosecond pulse will keep on exciting the system for 1 nanosecond and during this 1 nanosecond time window, the molecule dynamics will also be over, because as I said that the vibrational motion happen in that timescale of picosecond. So, the bond will vibrate a 1000 times, say If it (Refer Time: 07:20) time scale of 1 picosecond, within a time window of 1 nanosecond, it will vibrate 1000 times.

So, you are actually initiating the process, but you cannot observe it, because everything is averaged up. So, you want to just you have to just excite the system, which is during a time scale, which is much shorter than 1 picosecond. And with the advent of these soft picosecond lasers or femtosecond lasers you can do it, but the question is how will you watch the subsequent difference, because electronics also fail in this case. So, the trick is that you actually use the light pulse itself to control.

Now, on the watch these dynamics and this is usually known as femtosecond spectroscopy. And so this is one of the like great achievement technique wise, in is a beautiful spectroscopic techniques and together, we call it as a ultrafast dynamics of molecules by ultrafast usually we mean something like which is lies in the sub

nanosecond time scale. And it does not necessarily mean picosecond or femtosecond; it can be an active second dynamics also, which is 10 to the power minus 18 seconds. And today even nanosecond lasers are available, which can actually enable you to see the dynamics of electronic motions within the molecules our atoms.

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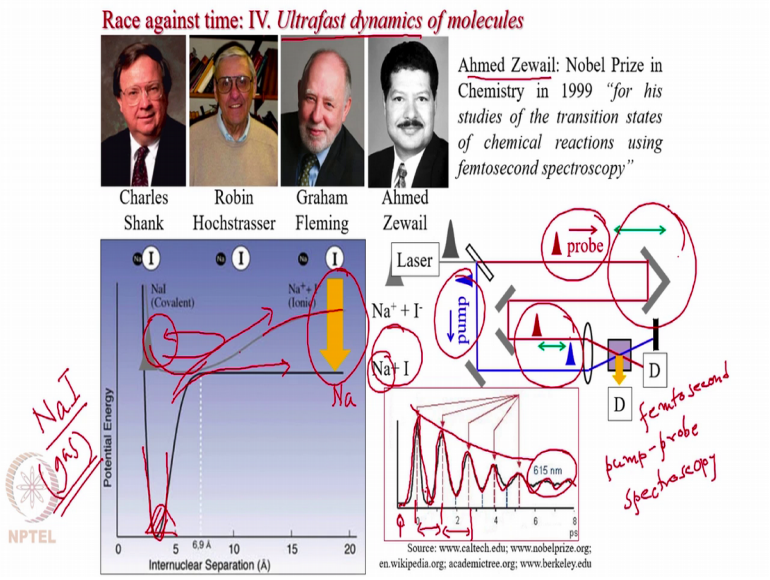

Now this femtosecond spectroscopy was developed by many scientists, like Charles Shank, Robin Hochstrasser, Graham Fleming and Ahmed Zewail, and there are many others. And Ahmed Zewail was given the Nobel prize in Chemistry for development of Femtochemistry in 1999. And I have here, a typical example how this spectroscopy works, and this was a work by Ahmed Zewail. And again remember that here the first thing is that I will initiate a photon process.

Now, what I have shown here is a diagram, it is called potential energy diagram will talk about it in details, in the later sections. Now, this is typically an energy level diagram of a diatomic molecule. And if you had studied a little bit of quantum mechanics, you know that diatomic vibrations are kind of like you can approximate it, as a harmonic motion and at the bottom of the holes, so this is the harmonic potential as you can see.

The in reality it will be an harmonic, and then this is the potential in the ground state. And the molecule is a diatomic molecule, which is sodium added. And this molecule was taken, in the gas phase, because sodium added you can actually heat and then it can form

a gas phase. So, then you have sodium atom and iridium atom and they are doing this vibration.

Now, it has an interesting energy. So, in the excited state when you excite this sample, so it can dissociate in two different ways; either actually you can dissociate it, in a ionic form where basically the it dissociate as N a plus and I minus or you could dissociate it as N a I, where you have N a atom and I atom. So, it is a kind of atomic dissociation versus ionic dissociation. Now if you follow this path, you will dissociate into our covalent way, and if you follow this path, you will dissociate in an ionic way, but these are just the details.

Now, what is done in femtosecond spectroscopy what Ahmed Zewail coracle state is to understand, how this dissociation process happens in the excited state. So, what they did is that initially you can think, when no light is present, the molecules are all in the ground state here, ground electronic state. And then, first from the laser we launched pulse, which will excite the molecules in the excited state. And the molecules will all come here, but in the excited state now they do this vibration.

Now, Vibration of the molecule means actually now that you have sodium atom, and the iridium atom and this is basically a stretching dynamics, which you just showed in the water molecule. The water was more complicated, because it has three vibrations; in this case, it is a diatomic molecule, it has only one vibration which is much more simpler system.

And then what happens after certain time, you can actually launch a probe pulse which is shown here. And then the second pulse actually excites, the dissociated sodium atoms which is shown here to some excited state. And you have seen sodium lamp on straight, and this is the same excitation, so you excite the sodium atom. And then you see the fluorescence from the sodium atom, which actually has a very typical wavelength, which is a he was detecting at 615 nanometre or something.

Now, what is this experiment, so I will excite the sodium iodide molecules in the excited state. And then once it stretches, some molecules actually stretch too much that the bond breaks, and it bond breaks as a sodium and iodine. And then the probe pulse comes, and it will excite the sodium atoms, to see the fluorescence. And the amount of the

fluorescence will be directly proportional to how many sodium atoms I have produced, during this dissociation process.

Now, what Ahmed Zewail work as state the he launched a pump pulse; and after certain time he launched a probe pulse. And this certain time, they could control just by using an interferometric setup, like you split the pump and the probe, and then you recombine; And then in one arm, when the probe pulse is going, so that mirror or some reflecting some reflector you just move. So, if you can actually move with a very very precise delay, that will translate to a temporal delay which is on the order of a fraction of a femtosecond. So, you are not initiating the process with a femtosecond pulse. And then you are launching, another femtosecond pulse which is time delayed with respect to the first pulse. And what I will do is that I will just measure this signal, which is the fluorescence from the sodium as a function of this time delay.

Now, let us see that animation it will be more clear. Suppose first the pump pulse comes, and this is basically the time delay, as I am showing in that green arrow. The green arrow is also shown here, it is basically the time delay between the blue pulse on the red pulse; blue is the pump pulse and red is the probe pulse. So, this technique is known as pump probe technique, because you are pumping the system, and then after certain time you are probing the system. And you are varying this time delay between the pump pulse and the probe pulse.

Now, what happens here let us see the animation. First, suppose the molecules are in the ground state, and then you launch a pump pulse that will excite the molecules in the excited state. And moment they go there, so then they move and some fraction as you can see has leaked here. So, this fraction means actually some fraction of molecules have dissociated, not all the molecules. And, because some molecules will actually come back from this well, and some molecules will leak. There are many details for this potential energy surface, I am not going into the details of that why some molecules why there is a fraction of the molecules; which are leaking or which are dissociating.

Now, then the probe pulse is very much tuned to the sodium absorption. So, it does not the probe pulse is not absorbed by the sodium added, like the pump pulse is observed only by the sodium added molecules; the probe pulse is only absorbed by the sodium atoms. And the probe pulse will come, and it will excite this sodium atom which is here.

And then you will see the fluorescence from the sodium. And, once you see this fluorescence, and then you record the fluorescence as a function of pump probe delay. So, what will happen here suppose at time 0, I launched the pump and probe together and then what will happen, the molecules are just in the excited sodium added, but they have not dissociated by that time.

So, you will have almost 0 signal at time at 0 time. So, here actually the 0 time is shifted, but originally the 0 will be here. So, here actually it is shifted according to the maximum of the signal. After certain time, if you just launch the probe pulse after some delay, you will see that you have some sodium which is building up.

Now, you will have a huge build up of sodium, and that build up will correspond to at what time it actually dissociated, at that time it will have a maximum number of sodium atoms. And then, if you repeat this process, you will see that these molecules, the sodium atom or fluorescence will have an oscillation which will directly correspond to this excited state of solution. Now, what is happening suppose again, in a very simpler word suppose you had started with 100 molecules each time, so you shine your light pulse, 100 molecules go into excited state; and suppose you started with 200 molecules and 100 molecules goes into the excited state. Now, all these molecules are doing vibrations.

Now, suppose 10 percent of them gets dissociated, so 10 molecules come out as N a plus I, those 10 molecules you probe with your probe pulse were actually instead of the molecules, you are probing the sodium atom which is a dissociated product. And then you see the characteristic fluorescence from the excited state that you measure. Now, what is happening here, after certain time these 90 molecules are left, there again doing vibration again. In the next vibration, 10 percent will dissociate. So, you see a 9 molecules coming out; and you are left with basically 81 molecules, and then in the next vibration, you get a 10 percent of 81 molecules something like that.

So, every vibration is making you a lesser and lesser number of dissociation, absolute amount of dissociation, that is why you see a decay in this dissociation. But the interesting thing is that this the sodium atom fluorescence, actually picks up right at a regular interval; and this interval directly corresponds to how the molecule was moving in the excited state. So, this is generally known as a pump-probe spectroscopic as I already have said.

And, this is a very advanced spectroscopy technique, but there are also other many other advanced spectroscopic techniques which are developed with a low time resolution as well as those which are developed with similar time resolution, but what actually you can; not only do the gas phase studies, but also work in corn in phase or in a solution phase, because most of the chemistry and almost all the biology happens in solution phase.

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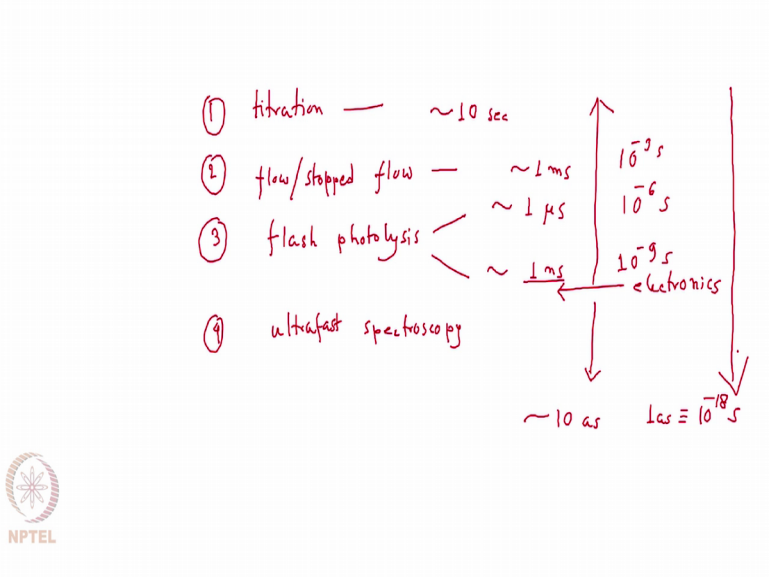

Now, I will conclude our discussion on this kinetic measurement here. So, to summarize what we said is that we first started with some traditional approach, where actually you can measure the kinetics, which often you do in the laboratory experiment, which is a part of your lab course, where actually do something like say titration based techniques, but that has a resolution on the order of say 1 minute or say a 10s of a second.

And then the next big achievement was basically flow and stopped flow method, and with these techniques you could achieve up to 1 millisecond time resolution something like that. And then can the era of flash photolysis, and the way to flash photolysis we described, how basically the developments in photographic techniques or which is known as a stroboscopic. It is a very typical them, stroboscopic means actually use a light pulse, flash light flash to capture fast events. And using these flash photolysis, initially it was achieved like with microsecond resolution; and subsequently people went to down to 1 nanosecond resolution.

And then came the era of ultrafast spectroscopy, where you cannot actually use electronics, because this is basically the limitation of electronics. You can initiate the very fast process with the nanosecond or femtosecond pulses, but you have to watch it over time. So, this is basically the window were electronics can participate, and electronics can actually work, but below this time window electronics does not work. And then there was a development of ultrafast spectroscopy, where actually you detect something, but the detection events is not a time result; but instead what you do is that, your time resolution comes from the delay between the two pulses, which you can very precisely give.

And you just look at the absolute signal. So, your detection you do not need a very fast electronics; so you need a slow electronics, where you are detecting the entire fluorescence, when the pump and probe pulses are say 100 frames femtosecond apart. Then you again change the direct to 200 femtosecond, again you collect the total fluorescence something like that was the experiment. So, the delay is entirely coming from this part, which is basically a mirror movement and which I as I said that you can achieve sub femtosecond delay step also.

So, right now, with the current status of ultra fast spectroscopy, we have down to few 10s of auto second resolution remember 1 auto second is 10 to the power minus 18 second. 1 nanosecond is 10 to the power of minus 9 second; 1 microsecond is 10 to the power of minus 6 second; and 1 millisecond is 10 to the power minus 3 second, as we see with the development of technology, how we started this discussion, and we said that this is basically mankind's attempt for this a race against time; so we want win our against time, so that we can actually observe, very very fast events in nature.

Now before I conclude, I would like to make one comment, so chemical reactions are biochemical reactions or physical processes have widely varying time skills, like if you think that all chemical reactions are out of us, it is not true, because we gave you examples like for example, generation of radicals or species are long lived triplets yet those are rather slow, and those who can actually study the microsecond dynamics, microsecond resolution.

And then there are many events, which for which you can a nanosecond spectroscopy will be good enough; or a picosecond spectroscope you will good enough. You do not

always need femtosecond spectroscopy for that, and there are extremely slow reactions also for example, say fossil formation, now fossil formation is a very much chemical process, but it is timescale size on the order of geological timescale, it millions of years.

So, and those processes you cannot actually study within your lifetime, because we also live for a certain time. So, you act for those cases you actually try to simulate the experiment, so that actually you see, try to actually, make this process happen very quickly, so that you can actually study it in real time. So, there are ultra slow processes; and there are difficulties with ultra slow processes to study, because you cannot just study there it in real time, because you would not live longer enough. And there are also ultrafast processes, and there are many challenges in ultrafast processes itself.

So, the bottom line here is that in chemical kinetics, you actually deal with various processes with widely varying timescales, but most of the processes which we will study is at the atomic or molecular level dynamics, which occur on the order of say picosecond to sub picosecond timescales. And, ultra fast spectroscopy is the life line for those processes. I will not further discuss, these kinetic measurements, and then but will come back, and discuss a little bit about how reactions work, when we discuss about the molecular reaction dynamics section.

Thank you.