# Ultrafast Optics and Spectroscopy
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## Lecture – 27
## Kinetic Model of Ultrafast Spectroscopy (Continued.)

Welcome again to module 9. In this module we are discussing Kinetic Model of Ultrafast Spectroscopy.

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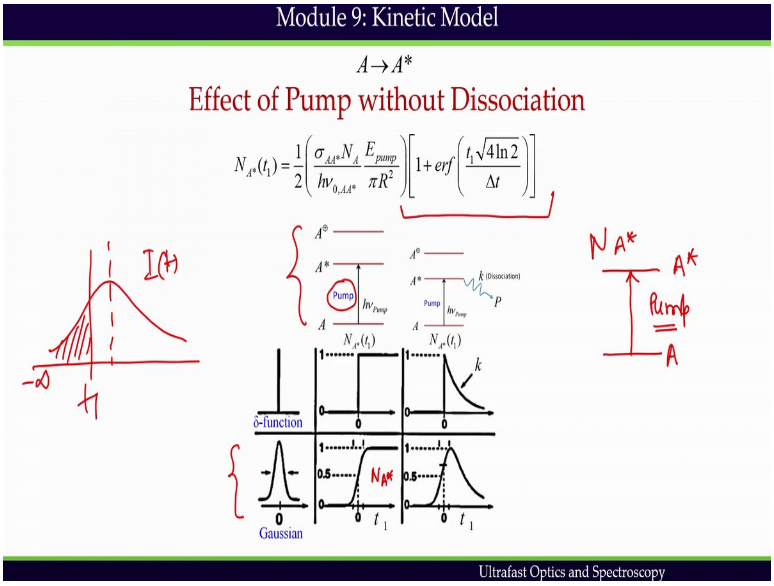

Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

$$N_{A^*}(t_1) = \frac{1}{2}\left(\frac{\sigma_{AA^*} N_A}{h\nu_{0,AA^*}} \frac{E_{pump}}{\pi R^2}\right)\underbrace{\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t}\right)\right]}$$

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So, far we have discussed the build up signal, the process which we are discussing is following we have excitation by pump from A to A star and we have only discussed the effect of pump in the build up signal N A star[$N_{A^*}$] is the population in the excited state.

So, due to a pulse we have seen that build up signal this is N A star build up signal depends on. So, this is the situation where we have only invoked the effect of pump and the build up signal depends on the error function, which is given by this equation as a function of t 1.

So, the basic idea is that I have a pulse time domain representation, this is the intensity profile of the pulse and this build up signal depends on the integration from minus infinity to any time t 1 and this area under the curve is contributing to this build up signal.

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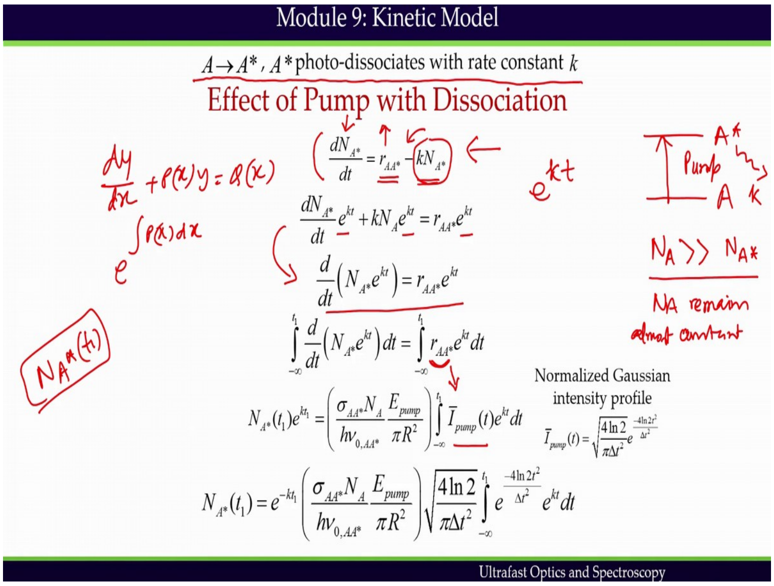

## Module 9: Kinetic Model

$A \rightarrow A^*$, $A^*$ photo-dissociates with rate constant $k$

### Effect of Pump with Dissociation

$$\frac{dN_{A^*}}{dt} = r_{AA^*} - kN_{A^*}$$

$$\frac{dN_{A^*}}{dt}e^{kt} + kN_{A}e^{kt} = r_{AA^*}e^{kt}$$

$$\frac{d}{dt}\left(N_{A^*}e^{kt}\right) = r_{AA^*}e^{kt}$$

$$\int_{-\infty}^{t_1}\frac{d}{dt}\left(N_{A^*}e^{kt}\right)dt = \int_{-\infty}^{t_1} r_{AA^*}e^{kt}dt$$

$$N_{A^*}(t_1)e^{kt_1} = \left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\int_{-\infty}^{t_1}\bar{I}_{pump}(t)e^{kt}dt$$

Normalized Gaussian intensity profile

$$\bar{I}_{pump}(t) = \sqrt{\frac{4\ln 2}{\pi\Delta t^2}}e^{\frac{-4\ln 2t^2}{\Delta t^2}}$$

$$N_{A^*}(t_1) = e^{-kt_1}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\sqrt{\frac{4\ln 2}{\pi\Delta t^2}}\int_{-\infty}^{t_1}e^{\frac{-4\ln 2t^2}{\Delta t^2}}e^{kt}dt$$

$$\frac{dy}{dx} + P(x)y = Q(x)$$

$$e^{\int P(x)dx}$$

$$e^{kt}$$

$N_{A^*}(t)$

$N_A >> N_{A*}$

NA remain almost constant

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Next we will discuss excitation of A to A star with the help of pump and subsequently A star photo dissociates with A rate constant k we are not considering probe pulse yet.

So, the process which we have the process which we are going to discuss here is A to A star excitation and then A star photo dissociates to the product with a rate constant k. So, for this process we will be able to write down the rate equation, rate equation depends on this dN A star dt rA A star minus kN A star this negative sign comes because that will decrease this process we will decrease the population of N A star that is why this negative sign. (Please look at the slides for mathematical expressions)

On the other hand r AA is star. This rate of excitation will increase the population of N A star. We can rewrite this equation this equation is strictly valid in the un saturation regime. Where we have assumed that N A number of population in a state is much greater than N A star; if this is valid then one can approximately say that N A star remains constant almost constant this is called unsaturation limit. Now, this equation this equation is the first order linear differential equation of the standard form d y d x plus p x y equals q x which can be solved using the integrating factor e to the power p x dx. (Please look at the slides for mathematical expressions)

So, for the given problem we get the integrating factor e to the power kt that is why we have multiplied e to the power kt and rearrangement of this equation we get this very easy to follow. Finally, we would like to integrate it from minus infinity to t 1 because we would like to know the build up signal ultimate motivation is to find out NA star t 1 how this population N A star population is responding?

So, this integration can be done, but we have inserted now this r AA star rate of excitation this expression is obtained before and this expression is related to this integration from minus infinity to t 1 for the normalized Gaussian function.

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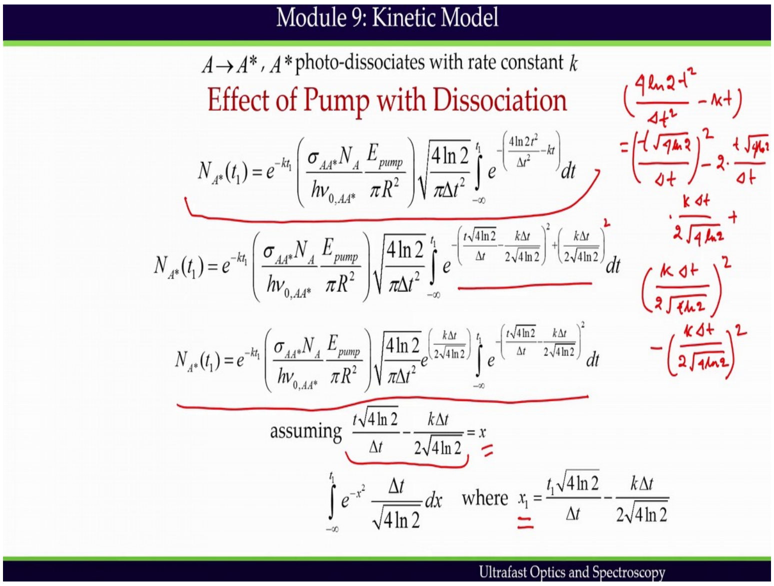

Module 9: Kinetic Model

$A \rightarrow A^*$, $A^*$ photo-dissociates with rate constant $k$

Effect of Pump with Dissociation

$$N_{A^*}(t_1) = e^{-kt_1}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\sqrt{\frac{4\ln 2}{\pi\Delta t^2}}\int_{-\infty}^{t_1} e^{-\left(\frac{4\ln 2t^2}{\Delta t^2}-kt\right)}dt$$

$$N_{A^*}(t_1) = e^{-kt_1}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\sqrt{\frac{4\ln 2}{\pi\Delta t^2}}\int_{-\infty}^{t_1} e^{-\left(\frac{t\sqrt{4\ln 2}}{\Delta t}-\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2+\left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2}dt$$

$$N_{A^*}(t_1) = e^{-kt_1}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\sqrt{\frac{4\ln 2}{\pi\Delta t^2}}e^{\left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2}\int_{-\infty}^{t_1} e^{-\left(\frac{t\sqrt{4\ln 2}}{\Delta t}-\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2}dt$$

assuming $\frac{t\sqrt{4\ln 2}}{\Delta t}-\frac{k\Delta t}{2\sqrt{4\ln 2}} = x$

$$\int_{-\infty}^{t_1} e^{-x^2}\frac{\Delta t}{\sqrt{4\ln 2}}dx \quad \text{where } x_1 = \frac{t_1\sqrt{4\ln 2}}{\Delta t}-\frac{k\Delta t}{2\sqrt{4\ln 2}}$$

$$\left(\frac{4\ln 2\, t^2}{\Delta t^2} - kt\right) = \left(\frac{t\sqrt{4\ln 2}}{\Delta t}\right)^2 - 2\cdot\frac{t\sqrt{4\ln 2}}{\Delta t}\cdot\frac{k\Delta t}{2\sqrt{4\ln 2}} + \left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2 - \left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2$$

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After integrating we get this expression and little bit of rearrangement this 4 ln 2 t square minus divided by delta t square minus kt, this can be written as t square root of 4 ln 2 divided by delta t whole square minus 2 multiplied by t square root of 4 ln 2 divided by delta t multiplied by k delta t divided by 2 4 ln 2 plus k delta t divided by 2 square root of 4 ln 2 whole square minus k delta t divided by 2 square root of 4 ln 2 whole square. (Please look at the slides for mathematical expressions)

So, this can be rewritten and in the end what I get is, this expression. So, this can be written and finally, we get this expression. In order to integrate it we will assume that this function is x. So, we will be able to get the x 1 limit corresponding to t 1. (Please look at the slides for mathematical expressions)

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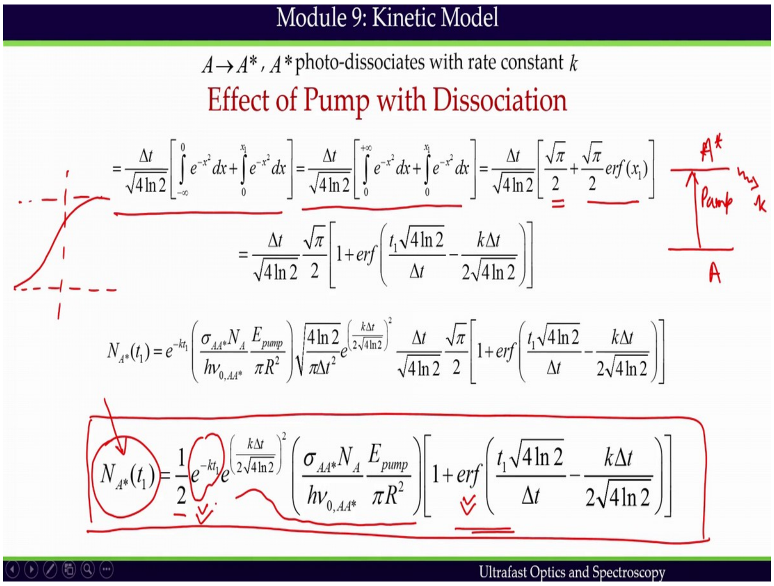

Module 9: Kinetic Model

$A \rightarrow A^*$, $A^*$ photo-dissociates with rate constant $k$

## Effect of Pump with Dissociation

$$= \frac{\Delta t}{\sqrt{4\ln 2}}\left[\int_{-\infty}^{0} e^{-x^2}dx + \int_{0}^{x_1} e^{-x^2}dx\right] = \frac{\Delta t}{\sqrt{4\ln 2}}\left[\int_{0}^{+\infty} e^{-x^2}dx + \int_{0}^{x_1} e^{-x^2}dx\right] = \frac{\Delta t}{\sqrt{4\ln 2}}\left[\frac{\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2}erf(x_1)\right]$$

$$= \frac{\Delta t}{\sqrt{4\ln 2}}\frac{\sqrt{\pi}}{2}\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} - \frac{k\Delta t}{2\sqrt{4\ln 2}}\right)\right]$$

$$N_{A^*}(t_1) = e^{-kt_1}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\sqrt{\frac{4\ln 2}{\pi\Delta t^2}}e^{\left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2}\frac{\Delta t}{\sqrt{4\ln 2}}\frac{\sqrt{\pi}}{2}\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} - \frac{k\Delta t}{2\sqrt{4\ln 2}}\right)\right]$$

$$N_{A^*}(t_1) = \frac{1}{2}e^{-kt_1}e^{\left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2}\left(\frac{\sigma_{AA^*}N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right)\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} - \frac{k\Delta t}{2\sqrt{4\ln 2}}\right)\right]$$

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And we get this expression for the integral and this expression is rewritten here and because it is a Gaussian standard Gaussian integral, we have written it here and this is nothing, but the error function.

So, finally, after doing this integrations we get an expression for the build up signal of N A star under the situation under the following situation I have pump exciting molecules from A to A star and this a star is dissociating and the dissociation rate constant is k. So, what we get is that the build up signal definitely depends on the error function which means, there should be some behaviour like this there will be behaviour like this.

But at the same time we have additional factor e to the power minus kt 1 these are all constants, these are all other components are other terms are constants. So, they will not they will not contribute to the shape overall shape of the of the build up signal N A star, but the shape will be controlled by the error function and this exponential decay function. This is now plotted. (Please look at the slides for mathematical expressions)

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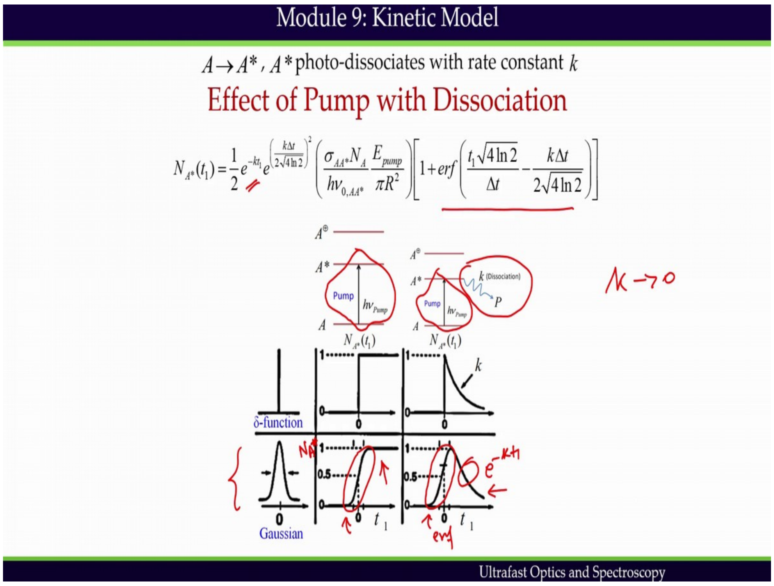

Module 9: Kinetic Model

$A \rightarrow A^*$, $A^*$ photo-dissociates with rate constant $k$

Effect of Pump with Dissociation

$$N_{A^*}(t_1) = \frac{1}{2} e^{-kt_1} e^{\left(\frac{k\Delta t}{2\sqrt{4\ln 2}}\right)^2} \left(\frac{\sigma_{AA^*} N_A}{h\nu_{0,AA^*}} \frac{E_{pump}}{\pi R^2}\right)\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} - \frac{k\Delta t}{2\sqrt{4\ln 2}}\right)\right]$$

$k \rightarrow 0$

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So, our previous situation was effect of pump now we are considering pump plus photo dissociation both are acting together. In that case if I have a pulse exciting the molecules to the excited state we see that the early part of the time is dominated by the error function just like the one which we have here, but then later part is dominated by the decaying that is the. So, this part is dominated by the error function and this part is dominated by the decay constant. Here there was no decay that is why we did not see our decay in the build up signal of the of N A star. So, this is N A star build up signal as a function of t 1.

And if we make it k 0 then we get back our earlier equation. So, it’s quite clear so, far is that excitation by a pulse when we undergo an excitation by a pulse build up signal in the excited state would be controlled by an error function of the kind shown here and if there is a decay or some other loss processes involved, then that would show up in the build up signal as well.

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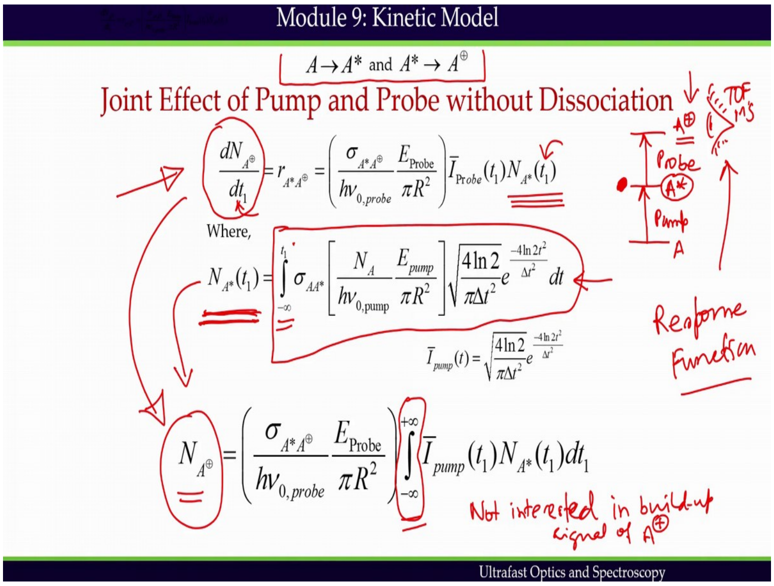

Module 9: Kinetic Model

$A \rightarrow A^*$ and $A^* \rightarrow A^{\oplus}$

Joint Effect of Pump and Probe without Dissociation

$$\frac{dN_{A^{\oplus}}}{dt_1} = r_{A^*A^{\oplus}} = \left(\frac{\sigma_{A^*A^{\oplus}}}{h\nu_{0,probe}} \frac{E_{\text{Probe}}}{\pi R^2}\right) \bar{I}_{\text{Probe}}(t_1) N_{A^*}(t_1)$$

Where,

$$N_{A^*}(t_1) = \int_{-\infty}^{t_1} \sigma_{AA^*} \left[\frac{N_A}{h\nu_{0,\text{pump}}} \frac{E_{pump}}{\pi R^2}\right] \sqrt{\frac{4\ln 2}{\pi \Delta t^2}} e^{\frac{-4\ln 2 t^2}{\Delta t^2}} dt$$

$$\bar{I}_{pump}(t) = \sqrt{\frac{4\ln 2}{\pi \Delta t^2}} e^{\frac{-4\ln 2 t^2}{\Delta t^2}}$$

$$N_{A^{\oplus}} = \left(\frac{\sigma_{A^*A^{\oplus}}}{h\nu_{0,probe}} \frac{E_{\text{Probe}}}{\pi R^2}\right) \int_{-\infty}^{+\infty} \bar{I}_{pump}(t_1) N_{A^*}(t_1) dt_1$$

Not interested in build-up signal of $A^{\oplus}$

Response Function

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Now, we will take a look at the joint action of pump and probe without invoking dissociation. So, our processes are following we have pump and then we have probe, we are creating positive ion, this is excited state and we want to find out if we monitor only ion signal by time of flight MS( mass spectrometer), time of flight mass spectrometer, then how the signal would look like and that is nothing, but the response function.

So, we would like to predict that response function when we look at the ion. Here we can remind ourselves that this ions would be absorbed only when I have population in the excited state which means if the delay between pump and probe is too long, then it may so, happen that A star we do not have anymore A star because it is decaying and we may not see A plus.

However, in this situation so, far we have not discussed we have not included the dissociation part we are saying that let us assume that molecules are excited to the excited state and the moment it is excited to the excited state it will stay there and then probe pulse can come and then ionize those excited molecules and produce A plus and we are going to observed A plus.

So, in this case we will be able to write down the rate equation the ionization rate equation which is dN A star d N A plus dt 1 we have to remind ourselves that this variable we have taken as dt 1 because N A star this will depend on the population of N A star and N A star we have seen so, far N A star population would depend on t 1. So, this equation has a variable t 1 where we have already seen that N A star t 1 can be represented by this integration.

And integration if we do this integration we get error function that we have seen already, but will not get the integration done immediately because we would like to convert the final expression for this dN A plus to some other form. So, this dN A this equation can be integrated and finally, we get N A plus population which is nothing, but an integration from minus infinity to plus infinity.

The idea behind pump probe configuration is that an ultra fast pulse is used to excite the molecules and the second probe pulse which arrives at a variable delay time is used to probe or interrogate the temporal evolution of the excited state prepared by the pump pulse by ionizing the excited molecules.

Thus in the ionization detection experiment the time integrated yield of the parent ion is monitored as a function of the variable time delay upon joint action of the pump and probe pulses. So, we have to clarify this point here, why we are taking an integration limit minus infinity to plus infinity for the ion signal? We are looking at the total ion signal produced due to joint the action of pump and probe. We are not interested in the build up signal; not interested in build up signal of A plus, we are interested in total ion signal at a particular delay between pump and probe pulses.

And that is why if we are interested in total ion signal produced at a particular delay between pump and probe, we have to integrate it from minus infinity to plus infinity. But here we are interested in the build up signal at a particular time how much population I have because that population will contribute to this population and that is why the integration here is taken from minus infinity to t 1 that particular time. (Please look at the slides for mathematical expressions)

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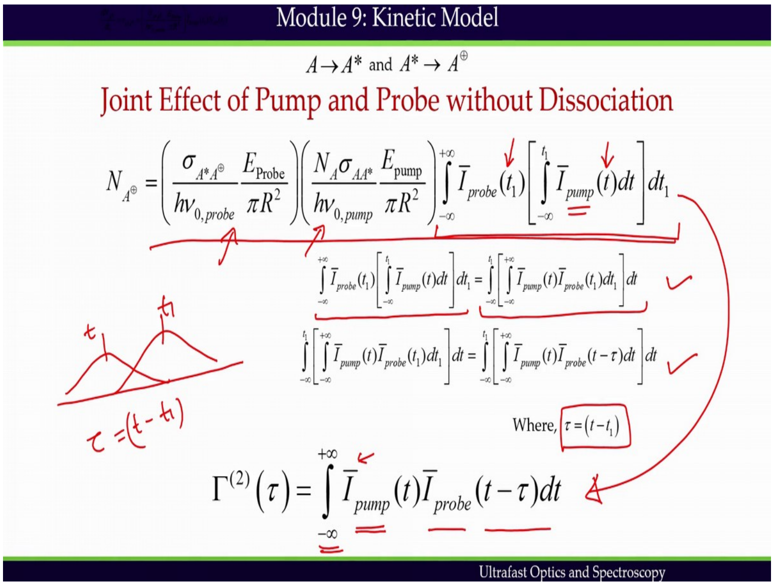

Module 9: Kinetic Model

$A \rightarrow A^{*}$ and $A^{*} \rightarrow A^{\oplus}$

Joint Effect of Pump and Probe without Dissociation

$$N_{A^{\oplus}} = \left(\frac{\sigma_{A^{*}A^{\oplus}}}{h\nu_{0,probe}}\frac{E_{\text{Probe}}}{\pi R^{2}}\right)\left(\frac{N_{A}\sigma_{AA^{*}}}{h\nu_{0,pump}}\frac{E_{\text{pump}}}{\pi R^{2}}\right)\int_{-\infty}^{+\infty}\overline{I}_{probe}(t_1)\left[\int_{-\infty}^{t_1}\overline{I}_{pump}(t)dt\right]dt_1$$

$$\int_{-\infty}^{+\infty}\overline{I}_{probe}(t_1)\left[\int_{-\infty}^{t_1}\overline{I}_{pump}(t)dt\right]dt_1 = \int_{-\infty}^{t_1}\left[\int_{-\infty}^{+\infty}\overline{I}_{pump}(t)\overline{I}_{probe}(t_1)dt_1\right]dt$$

$$\int_{-\infty}^{t_1}\left[\int_{-\infty}^{+\infty}\overline{I}_{pump}(t)\overline{I}_{probe}(t_1)dt_1\right]dt = \int_{-\infty}^{t_1}\left[\int_{-\infty}^{+\infty}\overline{I}_{pump}(t)\overline{I}_{probe}(t-\tau)dt\right]dt$$

Where, $\boxed{\tau = (t - t_1)}$

$$\Gamma^{(2)}(\tau) = \int_{-\infty}^{+\infty}\overline{I}_{pump}(t)\overline{I}_{probe}(t-\tau)dt$$

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So, this integration finally, N A plus integration can be rewritten as this these are the constants, we get for the pump and probe pulses and finally, integration we get this integration. And if we would be able to rearrange this integration because the variables which we have used remember pump pulse had a very had a variable a the pump pulse had a variable t and the probe pulse had a variable t 1 and they are related. But we can rewrite this integration as like this as t 1 and t are 2 independent variables the integral part of the above equation can be rewritten as this, which can be further rewritten as this where we are defining tau which is t minus t 1 that is the time delay we will say. (Please look at the slides for mathematical expressions)

So, finally, what we see is that, I have 2 pulses I have 2 pulses one of them variable t another one variable t 1. So, the difference delay between 2 pulses can be defined as tau equals t minus t 1 and in terms of tau the moment we express this expression we get this. This integral can be written as minus infinity to plus infinity integration I pump this is normalized that is why this sign and I probe t minus tau dt. This is a very familiar expression.

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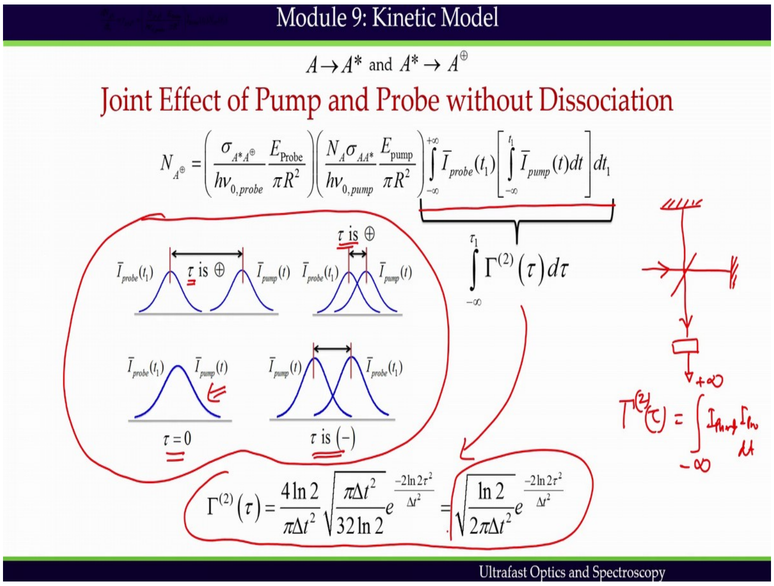

Module 9: Kinetic Model

$A \rightarrow A^*$ and $A^* \rightarrow A^{\oplus}$

Joint Effect of Pump and Probe without Dissociation

$$N_{A^{\oplus}} = \left(\frac{\sigma_{A^*A^{\oplus}}}{h\nu_{0,probe}}\frac{E_{\text{Probe}}}{\pi R^2}\right)\left(\frac{N_A\sigma_{AA^*}}{h\nu_{0,pump}}\frac{E_{\text{pump}}}{\pi R^2}\right)\underbrace{\int_{-\infty}^{+\infty}\bar{I}_{probe}(t_1)\left[\int_{-\infty}^{t_1}\bar{I}_{pump}(t)dt\right]dt_1}_{\int_{-\infty}^{\tau_1}\Gamma^{(2)}(\tau)d\tau}$$

$$\Gamma^{(2)}(\tau) = \frac{4\ln 2}{\pi\Delta t^2}\sqrt{\frac{\pi\Delta t^2}{32\ln 2}}e^{\frac{-2\ln 2\tau^2}{\Delta t^2}} = \sqrt{\frac{\ln 2}{2\pi\Delta t^2}}e^{\frac{-2\ln 2\tau^2}{\Delta t^2}}$$

$$\Gamma^{(2)}(\tau) = \int_{-\infty}^{+\infty} I_{Pump} I_{Pro}\, dt$$

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It is familiar because this expression is nothing, but autocorrelation expression. If we remind our self that this when we did an autocorrelation experiment we used fifty-fifty beam splitter and then we use this is Michelson interferometer and this is the way we got that. So, it was intensity autocorrelation that is why (Refer Time: 22:23) crystal was used and finally, this autocorrelation signal second order autocorrelation was written as a function of tau which is nothing, but minus infinity to plus infinity I pump I probe dt. (Please look at the slides for mathematical expressions)

And that is exactly what we are seeing. So, this expression can be written as an autocorrelation function and in this figures we have expressed the meaning of tau[τ]. If we look at these different figures given here, we are seeing that we are changing tau which means when they are completely overlapped tau equals 0, they are fully overlapped.

On the other hand tau can be negative, tau can be positive depending on when the pump and probe pulses are coming in time and from the pulse measurement from the discussion of pulse measurement we have also seen that, we have also seen that this the expression of the second order autocorrelation term is nothing, but this.

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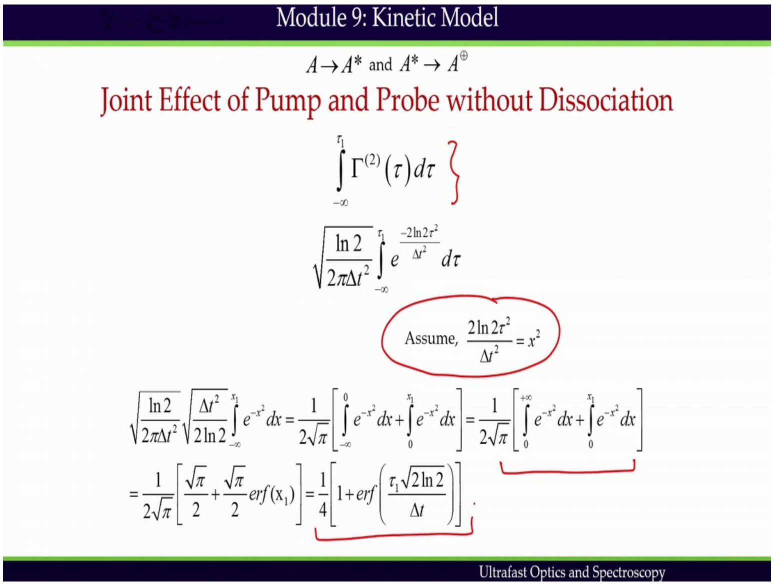

Module 9: Kinetic Model

$A \rightarrow A^*$ and $A^* \rightarrow A^{\oplus}$

Joint Effect of Pump and Probe without Dissociation

$$\int_{-\infty}^{\tau_1} \Gamma^{(2)}(\tau)\, d\tau \Big\}$$

$$\sqrt{\frac{\ln 2}{2\pi\Delta t^2}} \int_{-\infty}^{\tau_1} e^{\frac{-2\ln 2\tau^2}{\Delta t^2}}\, d\tau$$

Assume, $\frac{2\ln 2\tau^2}{\Delta t^2} = x^2$

$$\sqrt{\frac{\ln 2}{2\pi\Delta t^2}} \sqrt{\frac{\Delta t^2}{2\ln 2}} \int_{-\infty}^{x_1} e^{-x^2} dx = \frac{1}{2\sqrt{\pi}}\left[\int_{-\infty}^{0} e^{-x^2} dx + \int_{0}^{x_1} e^{-x^2} dx\right] = \frac{1}{2\sqrt{\pi}}\left[\underbrace{\int_{0}^{+\infty} e^{-x^2} dx + \int_{0}^{x_1} e^{-x^2} dx}\right]$$

$$= \frac{1}{2\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2} erf(x_1)\right] = \underbrace{\frac{1}{4}\left[1 + erf\left(\frac{\tau_1\sqrt{2\ln 2}}{\Delta t}\right)\right]}.$$

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So, the integral becomes minus infinity to tau 1 and here we will assume that this part to be x square following the same method which we have used previously to get the error function finally, we get the error function and if we plug that in then finally, we get this expression for the error function from this integration.

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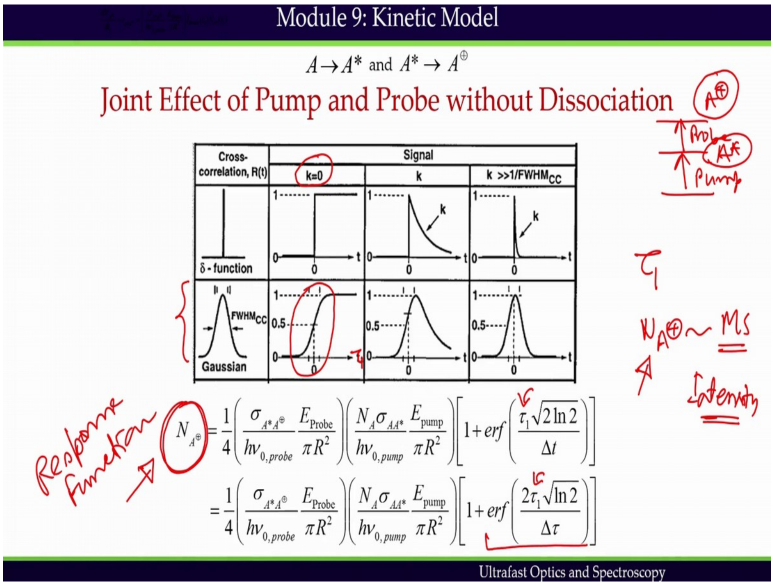

Module 9: Kinetic Model

$A \rightarrow A^*$ and $A^* \rightarrow A^{\oplus}$

Joint Effect of Pump and Probe without Dissociation

$\tau_1$

$N_{A^{\oplus}} \sim$ MS

Intensity

Response Function

$$N_{A^{\oplus}} = \frac{1}{4}\left(\frac{\sigma_{A^*A^{\oplus}}}{h\nu_{0,probe}} \frac{E_{\text{Probe}}}{\pi R^2}\right)\left(\frac{N_A \sigma_{AA^*}}{h\nu_{0,pump}} \frac{E_{\text{pump}}}{\pi R^2}\right)\left[1 + erf\left(\frac{\tau_1\sqrt{2\ln 2}}{\Delta t}\right)\right]$$

$$= \frac{1}{4}\left(\frac{\sigma_{A^*A^{\oplus}}}{h\nu_{0,probe}} \frac{E_{\text{Probe}}}{\pi R^2}\right)\left(\frac{N_A \sigma_{AA^*}}{h\nu_{0,pump}} \frac{E_{\text{pump}}}{\pi R^2}\right)\left[1 + erf\left(\frac{2\tau_1\sqrt{\ln 2}}{\Delta\tau}\right)\right]$$

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So, finally, we get N A plus dN A plus sorry N A plus ion signal total ion signal we get as a function of tau 1 this tau 1 tau 1 representing a particular delay between 2 pulses. So, at a particular tau 1 I will get a particular value for N A plus which will correlate to the ms mass spectrum intensity and if I change the delay between 2 pulses each for each delay we will be able to get different value of total ion yield and I will be able to plot it and again we are saying that that signal this is the response function that signal will depend on again the error function and the variable is tau 1.

So, let us look at this variation we have used the Gaussian pulse here and we have considered that we do not have k. So, A star is not dissociating, we have only pump and probe pulses and we are creating positive ion. The moment we create positive ion we can detect it and we are trying to find out total ion signal and when you plot the total ion signal as a function of time, what we get is that this is tau as a function of tau 1 then we see that total ion signal would look like this. So, if there is no photo-dissociation at all then total ion signal would be just like the build up signal which we have expected for the excited state.

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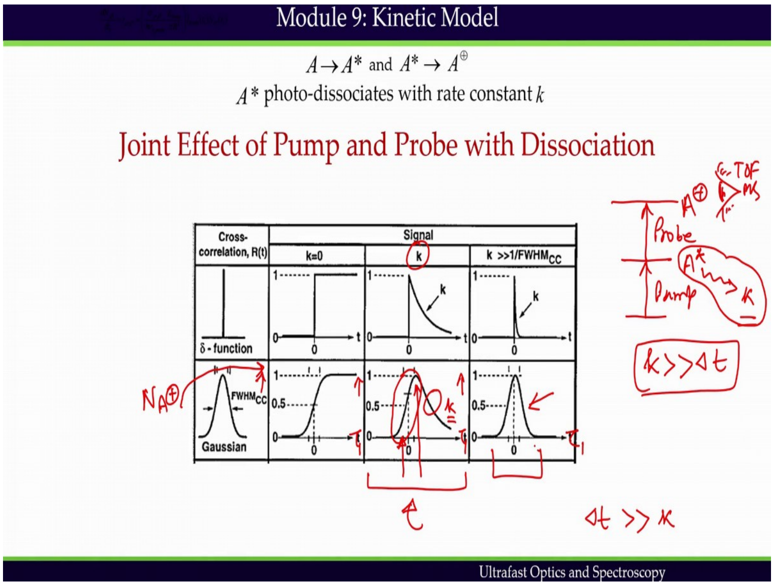

Module 9: Kinetic Model

$A \rightarrow A^*$ and $A^* \rightarrow A^{\oplus}$

$A^*$ photo-dissociates with rate constant $k$

Joint Effect of Pump and Probe with Dissociation

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But, what about if we have a dissociation? So, now, the now the process is following I have pump, I have probe, probe is creating positive ion pump is creating the excited state and this excited state is decaying to a photo product with a rate constant k.

So, I have a rate constant in that case this is going to be t tau 1 this is tau 1 this is also tau 1 it is a joint action of pump and probe. So, if we look at this then what will happen? We will see that in the early part the total ion signal.

So, we are looking at the total ion signal and if we look at total ion signal then it just behaves like an early part would be like an error function and the later part would be the dissociation. And if the dissociation is very very fast which means rate constant is very large, then what will happen will not be able to measure the pulse will not be able to measure the kinetics anymore, we will be able to measure we will end up with measuring the pulse.

So, if we open the photodissociation channel along with the joint action of pump and probe to model actual experimental observation under ionization scheme, details of the math are not shown here, but in this figure we show integrated yield. So, this yield is actually N A plus yield this y axis representing total integrated yield of A plus.

So, now this response function this particular response function explains all the questions we asked in the beginning of this module. It explains why we have a signal in negative delay. This is because of the error function. Maximum signal is not observed at 0 delay which is also obvious here and this is the consequence of this error function the behaviour of the error function which dominates the early part of the or the near zero delay part of the response signal.

And if we would like to know the k rate constant from this expression, we have to do the math and we will be able to get that expression. In addition to that if the process is very fast let us say this photo-dissociation is very very fast when I say very fast it means that k is much greater than the pulse with. If this is show then what will happen will not be able to measure the dissociation rate constant, we will end up with measuring the pulse and this is an important realization.

When I have pulses the pump and probe pulses longer than the rate constant which means the process is very slow and if the process is very slow, the dissociation process or some loss process is very slow, then only we will be able to measure the the process with the help of pump-probe configuration. If the process is itself very fast then we will not be able to measure the process we will be measuring the pulse duration and this looks like an autocorrelation signal.

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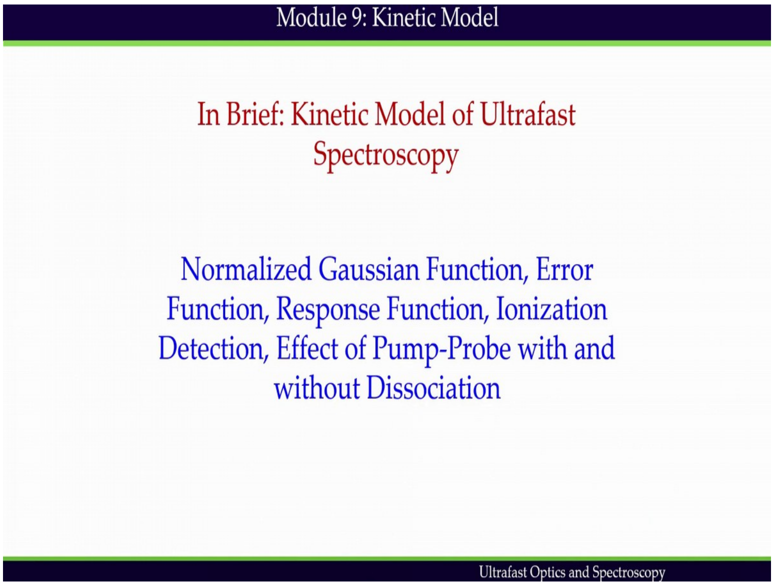

Module 9: Kinetic Model

## In Brief: Kinetic Model of Ultrafast Spectroscopy

Normalized Gaussian Function, Error Function, Response Function, Ionization Detection, Effect of Pump-Probe with and without Dissociation

Ultrafast Optics and Spectroscopy

With this we have come to the end of this present module, in this module we will we have discussed different aspects of kinetic model of ultra fast spectroscopy. We have discussed normal, we have discussed normalized Gaussian function, we have discussed error function, we have discussed response function ionization detection scheme, effect of pump and probe with and without dissociation. We will meet again for the next module.