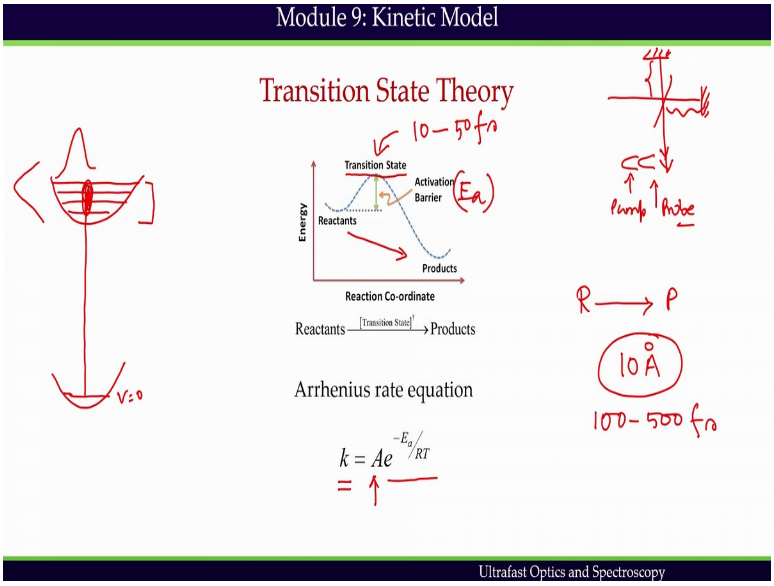
Ultrafast Optics and Spectroscopy
Dr. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru

Lecture - 26
Kinetic Model of Ultrafast Spectroscopy

Welcome to module 9 of the course, Ultrafast Optics and Spectroscopy. In this module we will study Kinetic Model of Ultrafast Spectroscopy.

(Refer Slide Time: 00:44)



Module 9: Kinetic Model

Transition State Theory

$$\text{Reactants} \xrightarrow{[\text{Transition State}]^{\ddagger}} \text{Products}$$

Arrhenius rate equation

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

Ultrafast Optics and Spectroscopy

In the field of reaction kinetics, transition state theory is an important theory which explains the rates of elementary chemical reactions. According to this, theory during chemical reaction the reactants approach a high energy activated state shown here. This state is called transition state, cross the activation barrier and then descent to products. So, reactant to product journey occurs through this transition state.

Before the development of transition state theory, the Arrhenius rate equation in which temperature dependent rate constant is expressed as k; rate constant equals pre exponential factor A multiplied by E to the power minus E a by RT where, k is the rate constant, A is the pre exponential factor and E a is activation barrier this activation barrier E a.

So, this Arrhenius equation was widely used to determine activation barrier to the reaction. Arrhenius equation was derived empirically from experimental observations and ignored mechanistic considerations. This why further development was necessary at that time to understand Arrhenius parameters A and E a at the fundamental level.

Transition state theory for the first time successfully provided analytical meaning of Arrhenius parameters. The whole trip from reactants to product, which often involves almost 10 angstrom nuclear configurational change in a particular molecule; takes typically, several 100 femtoseconds.

So, let us say it is 100 to 500 femtosecond; to undergo this 10 angstrom kind of configurationally change. Consequently the interference as at which one needs to record or observe the event in which nuclear configuration evolves through the transition state or at least in the range of 10 to 50 femtoseconds. If I want to observe transition state. Then, I have to record the experimental result in this time step 10 to 50 femtosecond time step.

The objective of the present module is to present early thinking of ultrafast transition state dynamics employing; a semi classical picture of ultrafast transition state dynamics. Although the kinetic model does not include coherence, which is quantum effects what does it mean? It means that let us say I have an excitation going on starting from V equals zero state vibrational state to the upper electronics vibrationally excitation this is called vibronic transition.

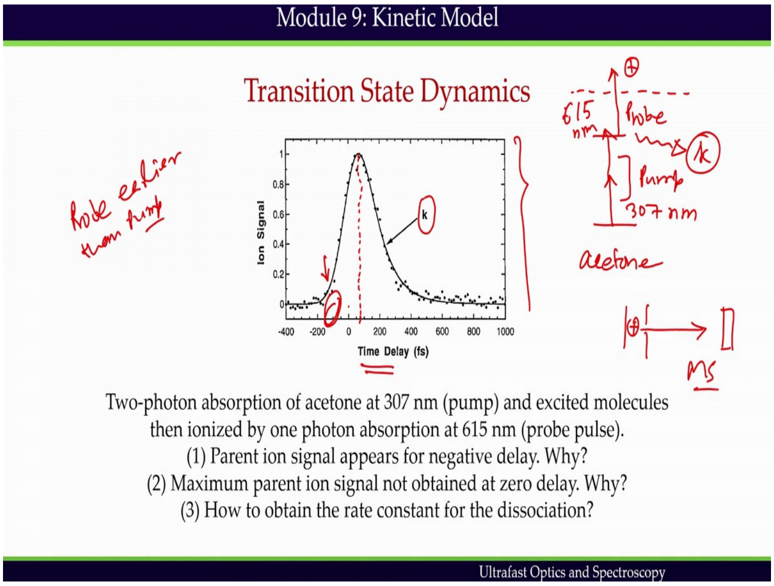
So, when I use an ultrafast pulse because of the broadband width it can simultaneously excite all these vibrational states and super position of all these vibrational states gives rise to the web packet. So, this is called quantum effect or coherence effect and in the kinetic model we will not use this coherence effect; in the kinetic model we will illustrate other aspects of observed femtosecond transition state dynamics; including nature of population change role of finite temporal with of the pulses cross section and etcetera.

In the study of transition state dynamics palm pro configuration can be employed in the palm pro configuration I can remind we use always a beam splitter to split the beam and then we have mirror to direct the beam and this two beam will be collinearly propagating along the along this directions.

So, basically the; if this path lengths are the same then we get two pulses overlapped and these two pulses one of them is called pump and another one is called probe.

So, there are many detection schemes, which can be used in the pump probe configuration such as fluorescence absorption, multi photon ionization, four wave mixing etcetera. However, here in this module, we will go for that detection technique related to ionization detection scheme.

(Refer Slide Time: 06:45)



Module 9: Kinetic Model

Transition State Dynamics

Two-photon absorption of acetone at 307 nm (pump) and excited molecules then ionized by one photon absorption at 615 nm (probe pulse).

(1) Parent ion signal appears for negative delay. Why?

(2) Maximum parent ion signal not obtained at zero delay. Why?

(3) How to obtain the rate constant for the dissociation?

Ultrafast Optics and Spectroscopy

So, we will go for the one interesting experimental result, this result is related to an electronically excited dissociative state of acetone molecule. This acetone molecule can be excited to an dissociative state with the help of two photon excitation and then from this excited state acetone molecule can be further ionized with the help of single photon excitation. So, this is the probe and this combined two photon is pump and this state is dissociative acetone molecule.

In the experiment gas phase acetone molecule where photo excited to the dissociative state more specifically a broad 4s mixed Rydberg state by two-photon absorption at 307 nanometer and the excited parent molecules, where then ionized by one photon absorption at 615 nanometer.

By changing the delay time between the pump and probe pulses the temporal behavior of the dissociative excited state prepared by the pump house was monitored using a mass spectrometer.

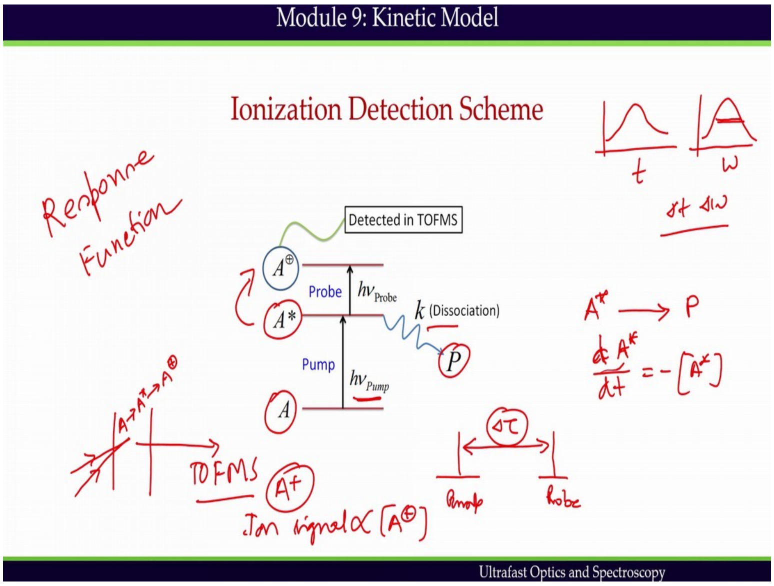
So, once we have created this positive ion that positive ion can be accelerated in a mass spectrometer and can be detected with MCP detector. So, this is mass detection scheme which has been used.

The pump probe transient as a function of delay time is given in this figure, this delay corresponds to the delay between pump and probe pulses. If you look at this figure there are number of questions which are obvious to us. If we look at the negative delay portion we see ion signal we can ask why we should see ion signal in the negative delay.

Negative delay corresponds to the fact that probe pulse coming earlier than pump pulse, which means probe cannot excite the molecule to the excited state it is only pump which can excite the molecule to the excited state.

In spite of this fact we are seeing some signal ion signal in the negative delay. On the other hand, if you look at the maximum of the signal it does not appear at the zero time delay question is why and from this transient profile will be able to extract dissociation constant k, question is how?

(Refer Slide Time: 10:14)



Module 9: Kinetic Model

Ionization Detection Scheme

So, with this questions we will start we will go for the ionization detects scheme before we begin thinking about electronic transition by a short optical pulse, which contents different frequency components.

Let us first understand the electronic transition by monochromatic photons. As we know that if I have a pulse this is in time domain then, in the frequency domain I will have on distribution of frequencies which means I have delta omega and this is unavoidable for a pulse. However, here we will begin with monochromatic excitation which means I have only single photon to excite or ionized and then we will extent this idea to the to the ultrafast spectroscopy.

Consider a molecule A; in an electronically ground state this is excited by monochromatic pump photon h nu pump from its ground state to an electronically excited state A star. So, A star is an electrically excited species.

A star dissociated to photo product P and we can say that first order kinetics is followed for an example. So, if A star is dissociated to P; then we can write down we can write down d A star d t equals minus of A star concentration that rate equation we can write down will go the this kind of rate equation soon.

To get a simplified picture let us not invoke other photo physical processes, when we excite the molecule to the excited state we can have florescence emission or many other processes internal conversion or intersystem crossing. We will just forget those processes we will just think of only dissociation process from the excited state.

After a time delay tau so, I have a pump pulse and then I have a probe, monochromatic, I have pump, I have probe and they are separated by delay delta tau. This is an very hypothetical experimental condition here we have assumed that we have monochromatic pulse, is an just an assumption in reality of no pulse can have can be monochromatic but it is an assumption and we are saying that these two monochromatic pulses are separated by delta t time. So, after a time delay another monochromatic probe photon ionizes A star. So, this A star is ionized to A plus.

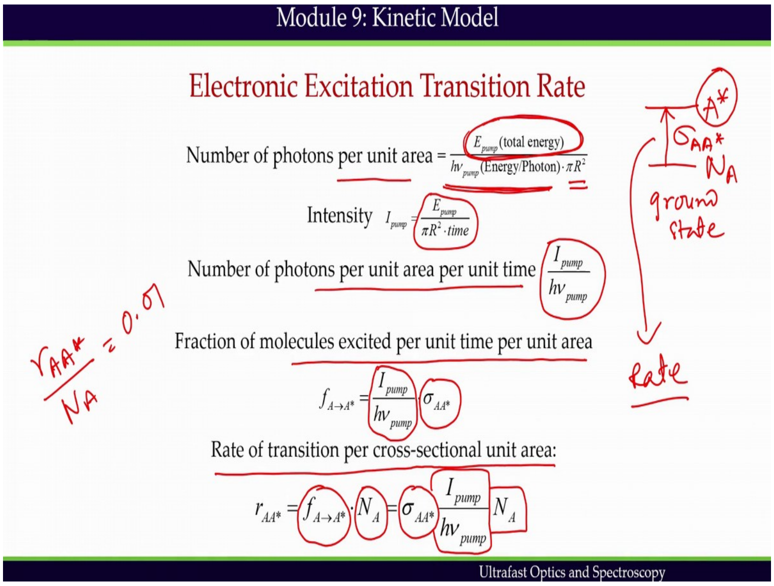
A time of flight mass spectrometer then detects the ion A plus the moment I create. So, I have two beams pump and probe and I am creating A going to A star then going to A plus. The moment I create this A plus this will be detected in time of flight mass spectrometer, this is one kind of mass spectrometer.

Mass spectrometer is sensitive to only A plus ions and it is quite clear that A plus can be generated by the joint action of the pump and probe photons which means, that the ion signal would be proportional to the A plus concentration or number of A plus we are creating.

If the excitation followed by ionization scheme is repeated for difference time delays and time varying ion signal can be recorded as a function of the time delay and so called transient profiled is obtained. The photo dissociation rate constant this k; can be estimated directly from the transient profile. In order to estimate k; however, we need to develop response function an important term response function.

So, we have to develop the response function for excitation followed by ionization scheme; response function is what we measure in the experiment and which contents all the dynamical information. Response function can be derived solving kinetic rate equation of the electronic transitions involved.

(Refer Slide Time: 16:15)



Module 9: Kinetic Model

Electronic Excitation Transition Rate

Number of photons per unit area = $\frac{E_{pump}\text{(total energy)}}{h\nu_{pump}\text{(Energy/Photon)}\cdot\pi R^2}$ =

Intensity $I_{pump} = \frac{E_{pump}}{\pi R^2 \cdot time}$

Number of photons per unit area per unit time $\frac{I_{pump}}{h\nu_{pump}}$

Fraction of molecules excited per unit time per unit area

$$f_{A\to A^*} = \frac{I_{pump}}{h\nu_{pump}}\sigma_{AA^*}$$

Rate of transition per cross-sectional unit area:

$$r_{AA^*} = f_{A\to A^*}\cdot N_A = \sigma_{AA^*}\frac{I_{pump}}{h\nu_{pump}}N_A$$

$\frac{r_{AA^*}}{N_A} = 0.01$

A*

σ_{AA^*}

N_A

ground state

Rate

Ultrafast Optics and Spectroscopy

So, let us look at how to represent electronic excitation transition rate? To understand the kinetic rate equation of electronic transition, let us first consider that the initial population of A in the ground electronic state is N A [N_A]; N A is the population in the ground state this is the ground state from where we are exciting the molecules.

Now if we have any number of molecules it is not possible that all the molecules are excited by the pump beam to A star because there is a probability of transition this pump induce excitation cannot be 100 percent. Instead a fraction of ground step molecule A; is excited by the pump beam.

The rate of this excitation is determined by two factors therefore. The cross section of absorption of a pump photon by a molecule so, this probability of transition is given by sigma A A star which features the probability of absorption of a photon by one molecule A; in the interaction energy and total number of photons impinging per unit cross section area per unit time.(Please look at the slides for mathematical expresions)

So, this is the two factors which will control how much population I will have in the excited step probability and how many photons I have and how many molecules I have. To estimate the rate of transition, we shall begin the discussion with Einstein's quantum theory of radiation. Based on this theory, number of photons can be calculated as follows. Number of photons is nothing but the total energy content divided by energy content of each photon.

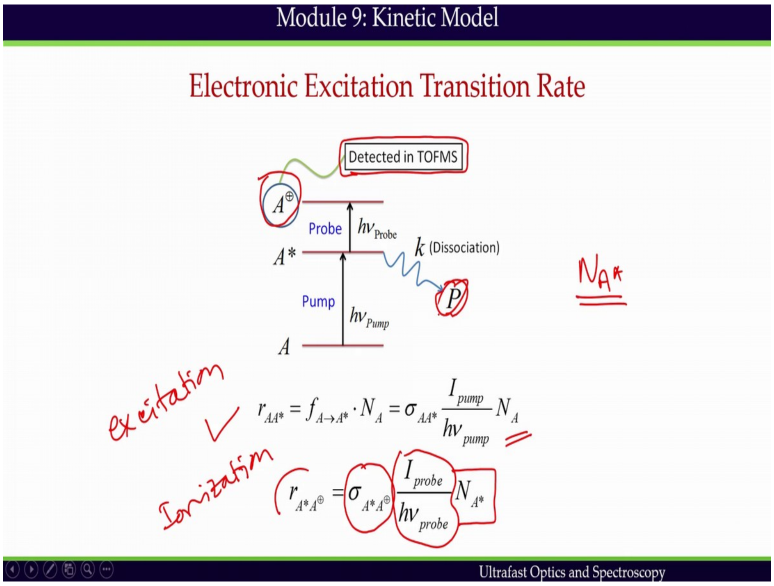
So, number of photons per unit area is again total number of total amount of energy divided by each photon energy divided by cross sectional area pi R square. Now by definition intensity is nothing but energy per time per cross sectional area. If we try to find out number of photons per unit area per unit time then that is given by intensity divided by h nu[hυ].

So, the fraction of molecules which are excited per unit time and per unit area that will be given by number of photons coming per unit area per unit time multiplied by the cross section. So, rate of transition per cross sectional unit area, will be given by this fraction multiplied by total number.

So, what we see is that, the rate of transition this rate depends on three components probability of transition, number of photons, number of molecules.

So, now question is; this r A A star what does it mean by this r A A star? This r A A star rate of transition is rate of transition per cross sectional unit area due to pump radiation. For an example if r A A star divided by N A for a particular process is 01 is 0.01; then it suggest that 10 in 1000 molecules is excited to the excited state per unit cross sectional area of the interaction region.(Please look at the slides for mathematical expresions)

(Refer Slide Time: 21:23)



Electronic Excitation Transition Rate

excitation ✓

$$r_{AA^*} = f_{A\to A^*}\cdot N_A = \sigma_{AA^*}\frac{I_{pump}}{h\nu_{pump}}N_A$$

Ionization

$$r_{A^*A^{\oplus}} = \sigma_{A^*A^{\oplus}}\frac{I_{probe}}{h\nu_{probe}}N_{A^*}$$

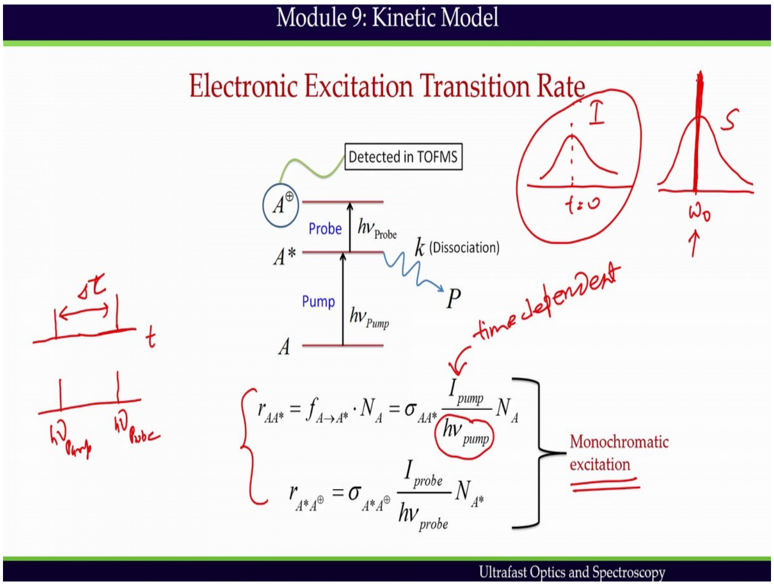
Similar rate equation can be derived for the sub sequent ionization process here ionization process. So, this rate is excitation and this rate is ionization and again it is it depends on probability of the ionization from the excited state number of photons in the probe because the probe is inducing the ionization and number of molecules which are in the excited state.

So, there are three components which will control this. Now here we note that N A star that is the population in the excited state depends on the time delay between pump and probe beams.

NA does not depend on the delay N A is number of molecules I have in the ground state, but number of molecules excited in the excited state depends on the time delay between pump and probe beams because if the probe beam comes too late by when all the A star molecules has dissociated all the A star molecules have dissociated to P probe beam will not see any A star population. (Please look at the slides for mathematical expresions)

And as a result I will not be able to prepare any ion consequently time of flight mass spectrometer will not detect any signal. So, in order to observe the signal pump and probe the delay between the pump and probe cannot be too long how long it could be it depends on the how quickly they are dissociating this excited step species are disassociating.

(Refer Slide Time: 23:22)



Module 9: Kinetic Model

Electronic Excitation Transition Rate

$$\left\{\begin{aligned} r_{AA^*} &= f_{A\to A^*}\cdot N_A = \sigma_{AA^*}\frac{I_{pump}}{\boxed{h\nu_{pump}}}N_A \\ r_{A^*A^{\oplus}} &= \sigma_{A^*A^{\oplus}}\frac{I_{probe}}{h\nu_{probe}}N_{A^*} \end{aligned}\right\}$$

Monochromatic excitation

Ultrafast Optics and Spectroscopy

So, in this derivation the pump and probe beams so treated as monochromatic beams as I told you they are like a pulse. So, is a hypothetical or imaginary experimental scheme, where their pulse is looks like this and they are frequencies are also like this which is impossible to get.

Shorter the pulse is broader the spectrum would beam. So, in time domain the difference is delta t delta tau and in frequency it is having h nu h nu this is pump and this is probe. So, that is that is an imaginary excitation process we have thought of. However, ultrafast pulses are not monochromatic light source. In fact, no optical pulse is monochromatic they have a finite bandwidth.

This feature of short pulse exhibits significant influence on the detective signal. If you want to extend his equations to the ultrafast spectroscopy we need to understand how to define h nu for an optical pulse; in addition pulse intensity is time dependent.

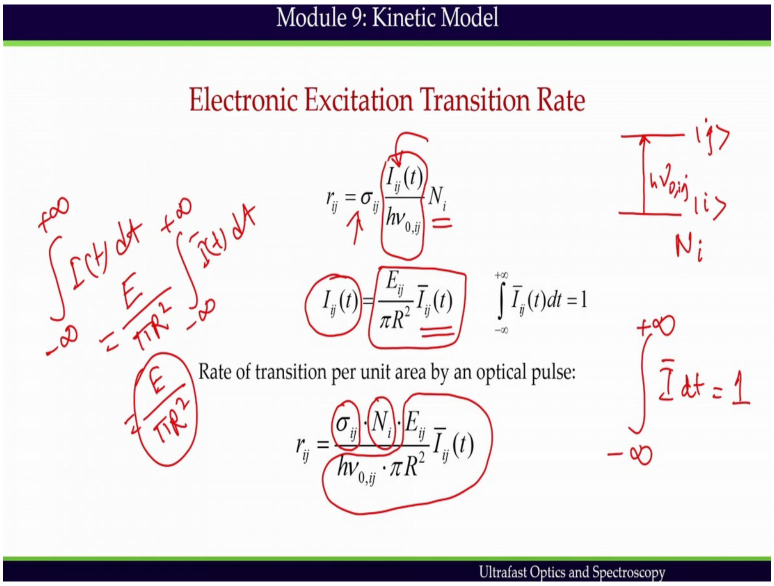
So, whatever I we are writing this would be time dependent for a pulse and question is how do I define this h nu for a pulse? Because, there will be many frequency components in a pulse to derive to get kinetic model of femtosecond dynamics.

We shall consider only centre frequency component of the pulse in spite of the fact that optical pulse contains a number of frequency components further mode finite temporal width of the pulse will be explicitly taken into account.

So, in order to extent this equation to the ultrafast spectroscopy what will do to develop this kinetic model? We will we will do one thing, this is the pulse temporal profile this I profile as a function of time let us see this is a Gaussian pulse. So, it will be center and t equal to 0 and corresponding spectrum is like this it is centered at omega naught[ω_0] this omega naught is center frequency.

So, we will consider full temporal profile of the pulse, but we will consider only the center frequency of the pulse. So, this is our strategy to develop the kinetic model.

(Refer Slide Time: 26:38)



Module 9: Kinetic Model

Electronic Excitation Transition Rate

$$r_{ij} = \sigma_{ij}\frac{I_{ij}(t)}{h\nu_{0,ij}}N_i$$

$$I_{ij}(t) = \frac{E_{ij}}{\pi R^2}\bar{I}_{ij}(t) \qquad \int_{-\infty}^{+\infty}\bar{I}_{ij}(t)dt = 1$$

Rate of transition per unit area by an optical pulse:

$$r_{ij} = \frac{\sigma_{ij}\cdot N_i\cdot E_{ij}}{h\nu_{0,ij}\cdot\pi R^2}\bar{I}_{ij}(t)$$

Ultrafast Optics and Spectroscopy

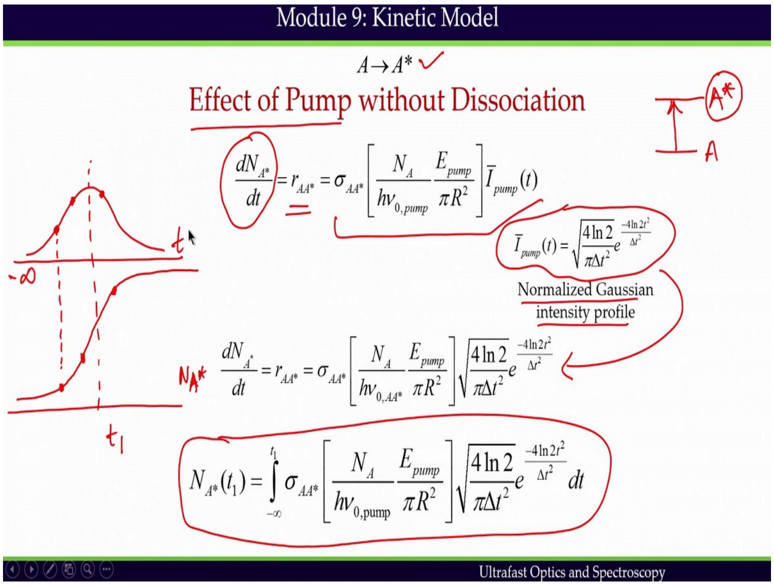
Thus the transition rate equation in the context of ultrafast spectroscopy may approximately written as r i j. Let us say I am undergoing transition from i th state to j th state and I have population N i. So, rate will depend on N i; I have excitation pulse many frequency components are present; however, I will consider only center frequency components which is h nu naught ij that is why it is number of photons and explicitly I am treating t as a function of time.

Explicitly I am treating intensity as a function of time and I have the probability of that transition. Now this ij this intensity profile how can I represent this intensity profile in terms of a normalized function intensity profile? I can do it with the help of this equation.

So, if I is the intensity profile normalize intensity profile then from minus infinity to plus infinity this intensity profile for integrate it will always give me 1. So, finally, if I integrate minus infinity to plus infinity any intensity profile we know that this equation is nothing but related to is related to the energy content which is E divided pi R square because, this integration minus infinity to plus infinity I bar t d t this is going to be 1. So, effectively we are getting an energy content in the pulse.

So, I will express intensity profile in terms of its normalized intensity profile. So, finally, what I get; I get rate of transition probability it depends on probability number of molecules and then rest is just number of photons is related to number of photons but it is expressed in terms of normalized intensity profile.

(Refer Slide Time: 29:40)


Module 9: Kinetic Model

$A \rightarrow A^*$ ✓

Effect of Pump without Dissociation

$$\frac{dN_{A^*}}{dt} = r_{AA^*} = \sigma_{AA^*}\left[\frac{N_A}{h\nu_{0,pump}}\frac{E_{pump}}{\pi R^2}\right]\bar{I}_{pump}(t)$$

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

Normalized Gaussian intensity profile

$$\frac{dN_{A^*}}{dt} = r_{AA^*} = \sigma_{AA^*}\left[\frac{N_A}{h\nu_{0,AA^*}}\frac{E_{pump}}{\pi R^2}\right]\sqrt{\frac{4\ln 2}{\pi \Delta t^2}}\, e^{\frac{-4\ln 2 t^2}{\Delta t^2}}$$

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

Ultrafast Optics and Spectroscopy

The excitation by the pump pulse alone results in build-up of A star population and if for now no photo dissociation of A star is invoked then the rate law for A to A star transition can be written as follows. So, what I have is that I am considering only photo excitation from A to A star by pump pulse. So, I am just looking at the effect of pump under the scheme we have already discussed.

And we are saying that this A star is not dissociating at all I am just preparing it. So, my ultimate target in this derivation current derivation is that I want to know how the buildup signal look like.

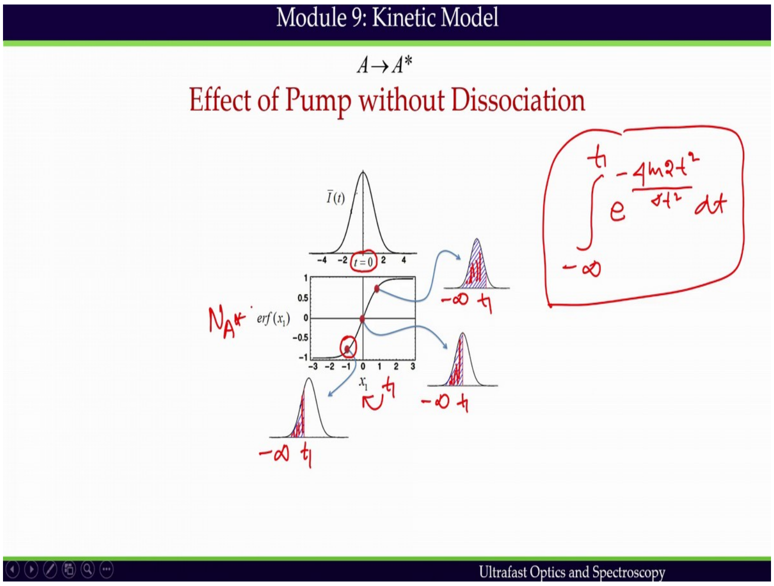
For that I have to prepare the kinetic equation which is nothing but rate of buildup of A star which is rate of transition which is given by this equation; where, I am considering normalized Gaussian intensity profile which is given by this is Gaussian in normalized Gaussian intensity profile.

So, I plug that in here I get this equation and then all we need to do is that integrate this from minus infinity to any time t 1.

What does it mean? I have a pulse here and it has intensity profile like this is minus infinity and I want to know at any time. From minus infinity to this time what would be my buildup signal N A; so, this is my N A signal how much would be N A as function of time will very soon will see that it follows like this. (Please look at the slides for mathematical expresions)

So, what I will get is that each point is the integration from minus infinity to that particular t 1; t 1 is the parameter yeah so, this is t.

(Refer Slide Time: 32:09)



Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

$$\int_{-\infty}^{t_1} e^{-\frac{4\ln 2 t^2}{\delta t^2}} dt$$

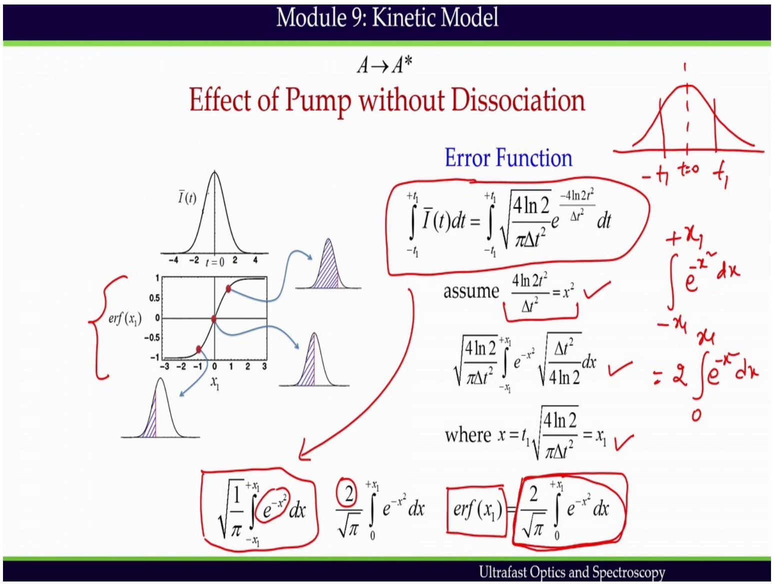
Ultrafast Optics and Spectroscopy

This is shown here again. So, each point here representing an integration from minus infinity to t 1; again this is minus infinity to t 1 this is minus infinity to t 1. So, t 1 is becoming a variable here this t 1 will be converted to x 1 very soon that is why it is shown in x 1, but the normalize intensity profile is shown in the time domain and the variable is here t.

So, effectively I am interested in this integration minus infinity to t 1, e to the power minus 4 l n 2 t square divided by delta t square d t. (Please look at the slides for mathematical expresions)

This integral is nothing but the area under the curve that is why each point corresponds to the area under the curve from minus infinity to a particular t 1 to get the buildup signal. So, this is the; this build-up signal is related to N A star.

(Refer Slide Time: 33:37)



Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

Error Function

$$\int_{-t_1}^{+t_1} \bar{I}(t)dt = \int_{-t_1}^{+t_1} \sqrt{\frac{4\ln 2}{\pi \Delta t^2}} e^{\frac{-4\ln 2 t^2}{\Delta t^2}} dt$$

assume $\frac{4\ln 2 t^2}{\Delta t^2} = x^2$ ✓

$$\sqrt{\frac{4\ln 2}{\pi \Delta t^2}} \int_{-x_1}^{+x_1} e^{-x^2} \sqrt{\frac{\Delta t^2}{4\ln 2}} dx \checkmark$$

where $x = t_1 \sqrt{\frac{4\ln 2}{\pi \Delta t^2}} = x_1$ ✓

$$\sqrt{\frac{1}{\pi}} \int_{-x_1}^{+x_1} e^{-x^2} dx \quad \frac{2}{\sqrt{\pi}} \int_0^{+x_1} e^{-x^2} dx \quad erf(x_1) = \frac{2}{\sqrt{\pi}} \int_0^{+x_1} e^{-x^2} dx$$

$$\int_{-x_1}^{+x_1} e^{-x^2} dx = 2 \int_0^{x_1} e^{-x^2} dx$$

Ultrafast Optics and Spectroscopy

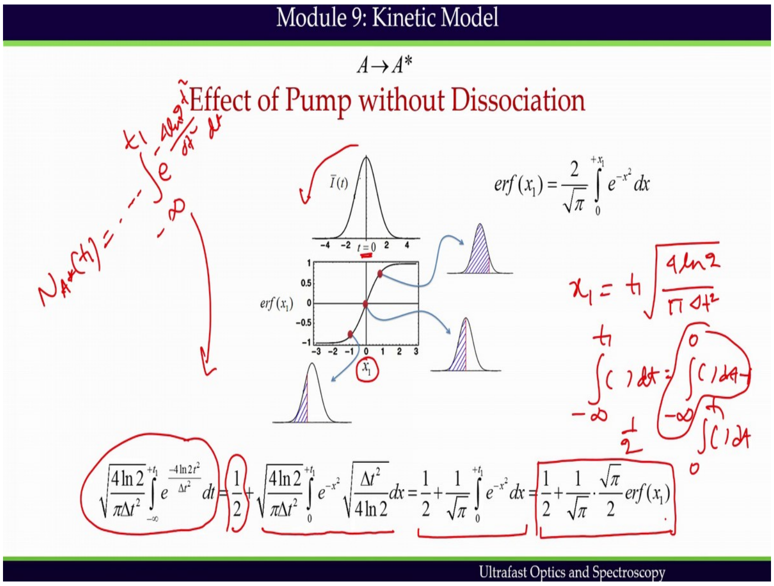
This is a direct connection there is a direct connection between the error function and normalized Gaussian function because the nature of this function is called error function and there is a direct connection between error function and the normalized Gaussian function and we get that connection if we take the integration of the normalized Gaussian function from minus t 1 to plus t 1.

So, I am just considering I let us say I have a Gaussian function normalized Gaussian function; and I have to take an integration from minus t 1 to plus t 1 and this is t equals 0. So, if we take that integration then how can I get this integration done first I will assume this very simple then I plug that in and we get the limit x 1 plus minus x 1.

So, finally, this integration after making this after inserting this we get we convert this integral to this and finally, we get an integral like this because it is a Gaussian function a to the power minus x square that is why we can write down this integral as minus x 1 to plus x 1 e to the power minus x square d x. This can be written as twice of 0 to x 1 because it is symmetric function.

And that is why it is 2 factor is coming in and finally, I get this integral this integral is called error function and error function is a function of x 1 which is the this limit.

(Refer Slide Time: 36:11)



Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

$$erf(x_1) = \frac{2}{\sqrt{\pi}} \int_0^{+x_1} e^{-x^2} dx$$

$$N_{A^*}(t_1) = \cdots \int_{-\infty}^{t_1} e^{-\frac{4\ln 2 t^2}{\Delta t^2}} dt$$

$$x_1 = t_1 \sqrt{\frac{4\ln 2}{\pi \Delta t^2}}$$

$$\int_{-\infty}^{t_1} (\ ) dt = \underbrace{\int_{-\infty}^{0} (\ ) dt}_{\frac{1}{2}} + \int_{0}^{t_1} (\ ) dt$$

$$\sqrt{\frac{4\ln 2}{\pi \Delta t^2}} \int_{-\infty}^{+t_1} e^{\frac{-4\ln 2 t^2}{\Delta t^2}} dt = \frac{1}{2} + \sqrt{\frac{4\ln 2}{\pi \Delta t^2}} \int_0^{+t_1} e^{-x^2} \sqrt{\frac{\Delta t^2}{4\ln 2}} dx = \frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^{+t_1} e^{-x^2} dx = \boxed{\frac{1}{2} + \frac{1}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} erf(x_1)}$$

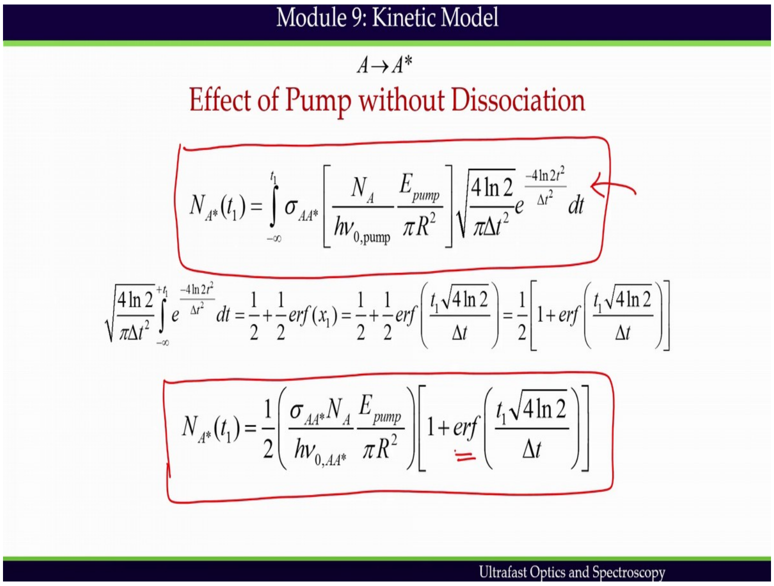
Ultrafast Optics and Spectroscopy

So, this so this figure shows the Gaussian function which is centered at x 1 x equals 0. This figure shows that this Gaussian function is centered at t equals 0. The error function which is obtained by integrating the normalize Gaussian distribution in the limit is 0 to x 1 is than plotted here and we know x 1 is related to t x 1 is nothing, but t 1 square root of four l n two by pi delta t square.

So, the integral of normalize Gaussian function can be written as this is what we want to know because our d A star d N A star d t that rate equation had this N A star population buildup signal N A star t 1 has an integral which was minus infinity to t 1 e to the power minus 4 l n 2 t square divided by delta t square d t. So, this integral was present in the buildup signal that is why we need to find out this integral.

And when you are trying to find out this integral, we have to because this is a normalize Gaussian function then, minus infinity to t 1 this integral can be written as minus infinity to 0 plus 0 to t 1 and because it is normalized this would be half and that is why this factor and then plus this integral which gives if we again substitute and finally, we get this function.

(Refer Slide Time: 39:56)



Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

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

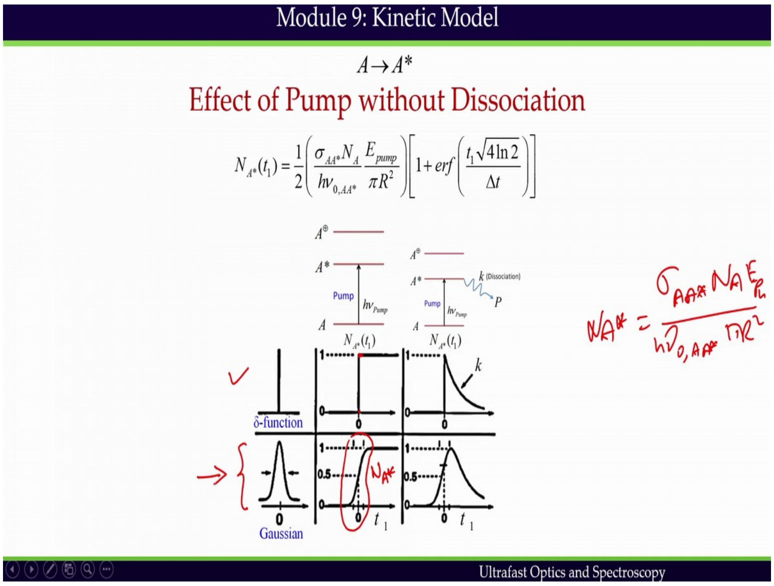
$$\sqrt{\frac{4\ln 2}{\pi \Delta t^2}} \int_{-\infty}^{+t_1} e^{\frac{-4\ln 2 t^2}{\Delta t^2}} dt = \frac{1}{2} + \frac{1}{2} erf(x_1) = \frac{1}{2} + \frac{1}{2} erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} \right) = \frac{1}{2}\left[1 + erf\left(\frac{t_1\sqrt{4\ln 2}}{\Delta t} \right) \right]$$

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

Ultrafast Optics and Spectroscopy

So, finally, we get the buildup signal which is nothing but this is which will depend on this integral and after doing this integration we get this is the buildup signal which depends on the error function.

(Refer Slide Time: 39:32)



Module 9: Kinetic Model

$A \rightarrow A^*$

Effect of Pump without Dissociation

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

$$N_{A^*} = \frac{\sigma_{AA^*} N_A E_p}{h\nu_{0,AA^*} \pi R^2}$$

Ultrafast Optics and Spectroscopy

Now, if we vary t 1 parametrically the normalized buildup of A star step population for a Gaussian pulse can be plotted here. So, this is the Gaussian pulse and this is the buildup signal we have plotted here which follows an error function which follows an error function behavior. It is interesting to consider the buildup of A star to another shape of the pump pulse.

If you considered now delta function then we will get N A star is nothing but sigma A A star N A E pump divided by h nu naught A A star square pi R square. So, the moment I come to this 0 point I get the maximum signal but in case of Gaussian pulse maximum signal does not appear at zero time it appears at some positive time due to involvement of this error function.

We will stop here we will meet again to continue this module.