

**Ultrafast Optics and Spectroscopy**  
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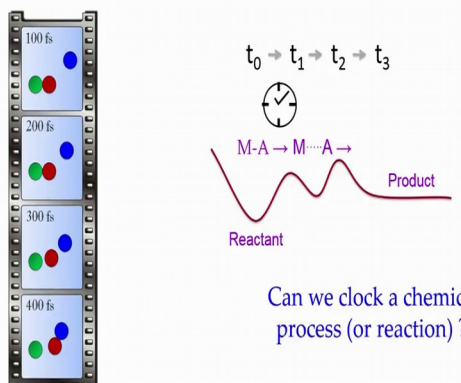
**Lecture - 01**

Welcome to module 1 of the course Ultrafast Optics and Spectroscopy. As this course has been designed primarily keeping physical chemistry students in mind we shall introduce the subject ultrafast optics and spectroscopy from a chemist point of view. Chemistry has both static and dynamic aspects.

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Module 1: Introduction (Part 1)

Dynamic Aspect of Chemistry:  
Chemical Dynamics



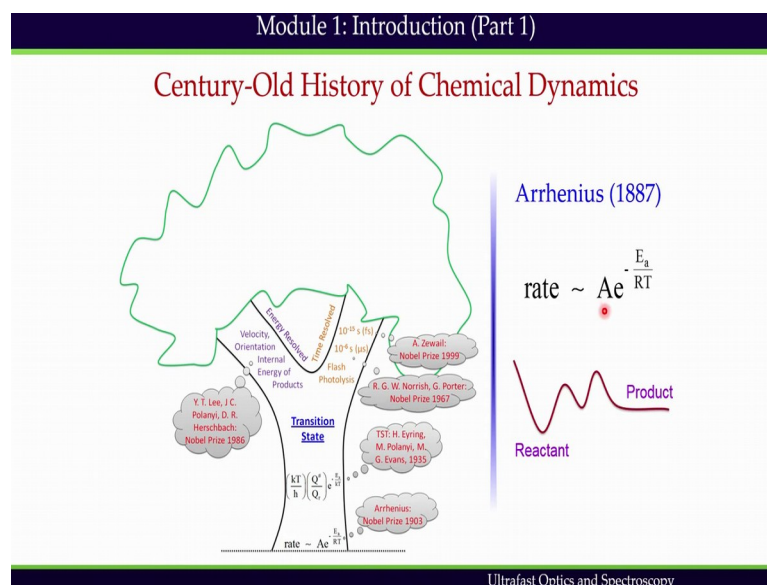
Can we clock a chemical  
process (or reaction) ?

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Ultrafast Optics and Spectroscopy

Static aspect of chemistry deals with the structure and dynamic aspect of chemistry deals with the evolution of the structure which includes both the mechanisms and the rates of the structural evolution.

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Over the past century we have come to understand significant details of dynamic aspects of chemistry, which is often called chemical dynamics or chemical kinetics. This figure depicts a tree which represents the milestones of the historical development of the chemical dynamics field.

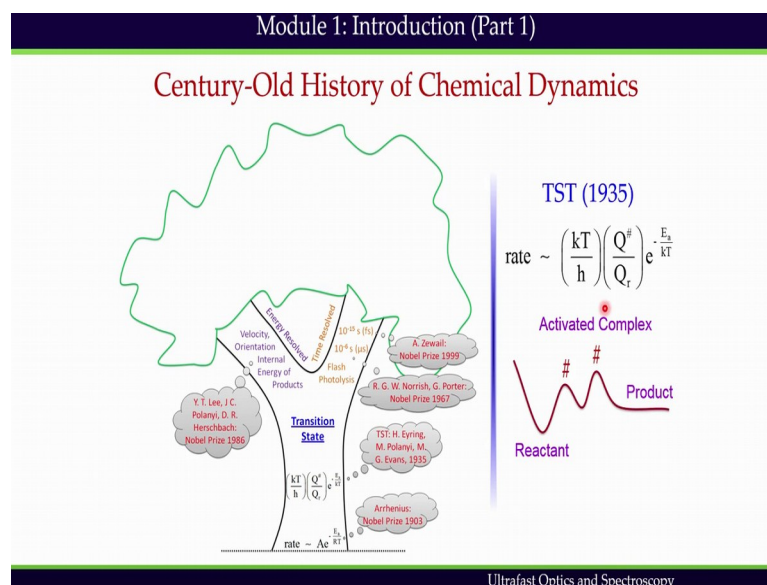
Though history has no beginning the field of chemical dynamics was born without perhaps anybody noticing it in 1887. In 1887, Arrhenius proposed an equation for reaction rate which is today well known as the Arrhenius equation. Reaction rate depends on exponential factor A and exponential function e to the power minus  $E_a$  by RT where RT represents the mean collision energy at absolute temperature T and  $E_a$  is the activation energy which was conceived by Arrhenius for the first time as being the height of the energy barrier.

One simple interpretation of Arrhenius equation which was given based on the earlier kinetic theory of gases of Maxwell and Boltzmann was the was that the reaction rate was equal to the number of collisions in unit time having energy greater than the barrier to the reaction  $E_a$ .

This A in the Arrhenius equation was related to the collision number. Since it was often true that  $E_a$  is much greater than RT, reaction on the thermal collisions must involve the timely fraction of molecular collisions at a particular temperature that have sufficient energy to cross the barrier of height  $E_a$ . The century old Arrhenius equations systemized

a large body of experimental data expressing a reaction rate in terms of the activation energy  $E_a$  this  $E_a$  and the pre exponential factor  $A$ ; however, many details of molecular picture of the reaction were missing in the Arrhenius equation, this is why for the development of a more elementary theory of chemical dynamics was demanded. The transition state theory fulfils this demand at least for the uni molecular reactions.

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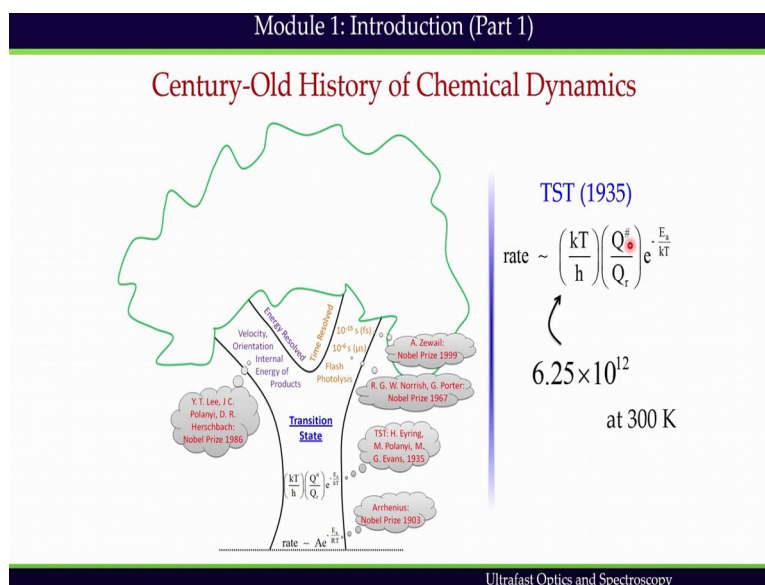


In 1935 Eyring Polanyi and Evans developed the transition state theory or activated complex theory. In this theory  $E_a$  this  $E_a$  in the Arrhenius equation was identified as the energy of the activated complex. The state of the activated complex is called transition state which was assumed to be in thermodynamic equilibrium with the reactants. So, this is reactant and the transition state which is shown by this hash they are in thermodynamic equilibrium.

The reaction rate in transition state theory was calculated based on the partition functions of the concerned molecule undergoing reaction assigning one coordinate to the reaction path. So, the reaction rate was represented by this equation where  $Q_r$  this  $Q_r$  is the product of partition functions for the reactants,  $Q^\ddagger$  is the product of the partition functions for the activated complex excluding the partition function assigned to the reaction coordinate.

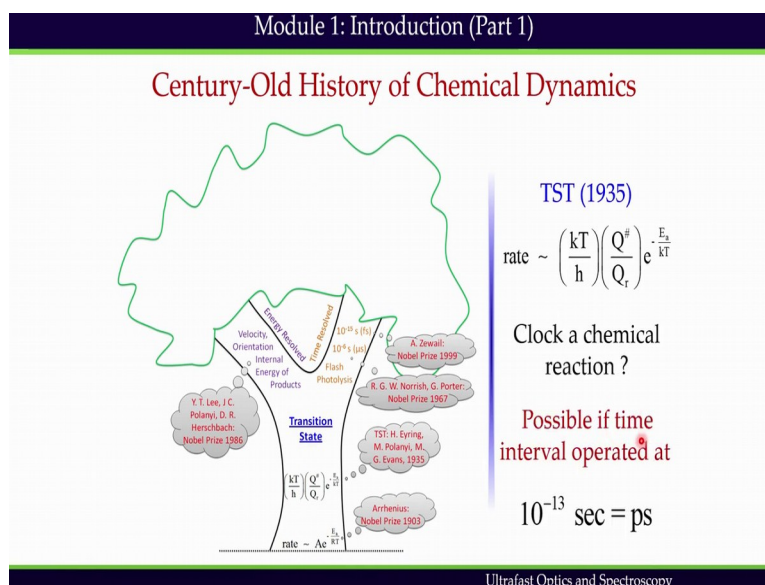
Transition state theory was capable of predicting reasonable values for the reaction rates of elementary reactions in its various refined forms transition state theory is the basis of most of the chemical dynamics till today.

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The pre exponential factor which is  $kT/h$  in transition state theory equals to  $6.25 \times 10^{12}$  at 300 Kelvin temperature.

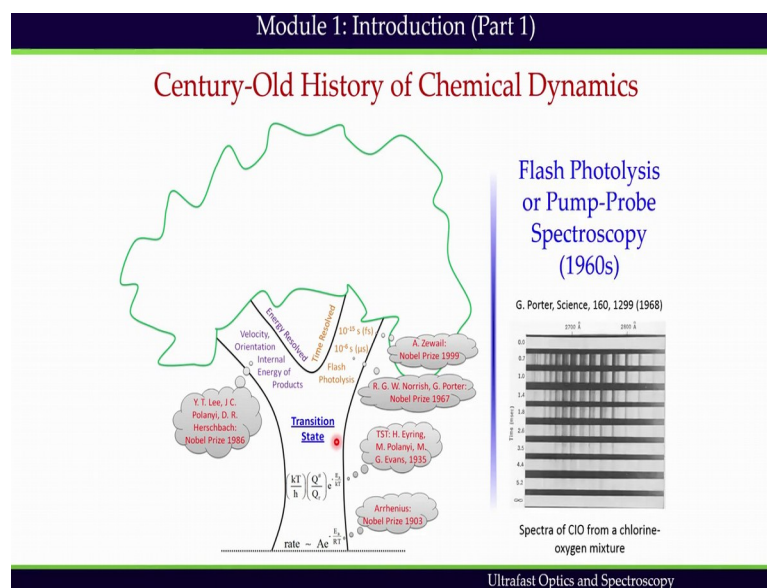
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This mandates that if you want to observe the passage of a chemical transformation through the transition state we must operate the experiment in the time intervals of 10 to

the power minus 13 seconds or pico seconds. This is an important realization for all time resolved chemical dynamics studies. In addition the importance of transient intermediate the activated complex in the interpretation of the chemical dynamics was also revealed by the same theory, transition state theory. The transition state theory became the heart of chemical dynamics.

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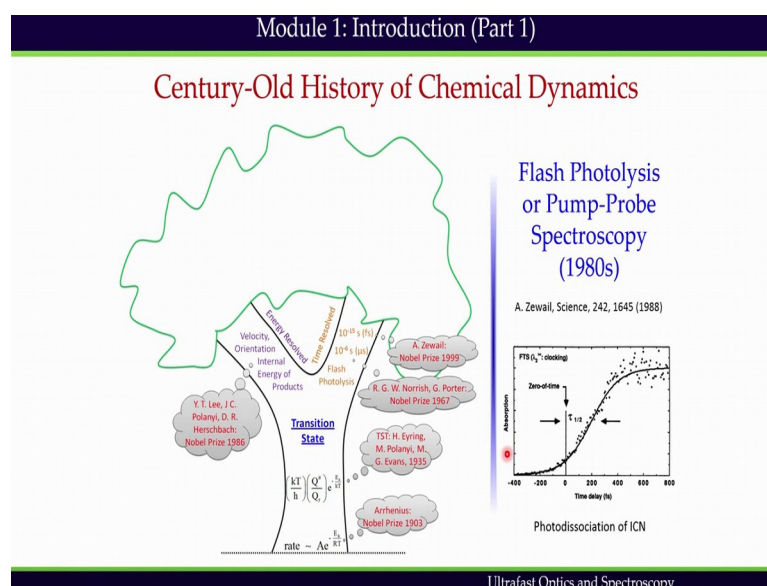
By 1945, X ray crystallography made it possible to see atoms in the molecular framework; however, due to lack of appropriate physical method direct experimental evidence for transient intermediate was lacking due to their very short life time or in other words to see atoms moving in the course of chemical change was impossible in 1940s. Flash photolysis or pump probe spectroscopy was developed for the first time in early 1960s for the study of very fast reactions or to capture very short lived transient intermediate. In the flash photolysis approach chemical dynamics is studied by initiating the reaction as well as recording it with the help of flashes of light.

The fast flash photolysis apparatus employed two flashes the pump to initiate the reaction and the probe to record the situation a short time interval later. By repeating this at increasing time intervals movie of the molecular change was recorded. The ultimate time resolution in the flash photolysis study of chemical dynamics depends on the duration of the flash and the time interval between pump and probe flashes. Here in this slide we have taken an example of the flash photolysis of the fast flash photolysis study

which recorded absorption spectrum of diatomic radical ClO from a mixture of chlorine and oxygen. This was done with micro second time resolution this time change this change in time is micro second.

Further extension of the pump probe spectroscopy into the nanosecond picosecond and femtosecond time regimes enabled us to study the life time of the electronically excited state species such as singlet and triplet states of several organic molecules to understand photochemical mechanisms, orientational and vibrational relaxation and energy and electron transfer mechanisms.

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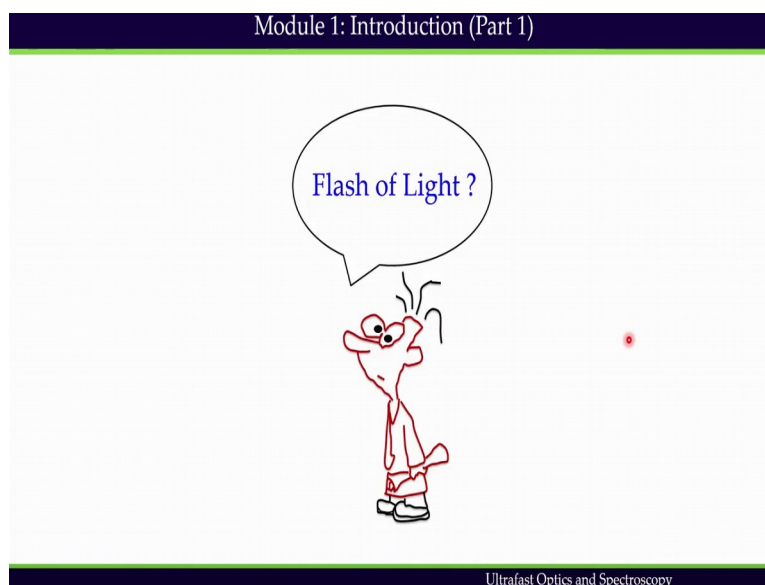


The extension of the pump probe spectroscopy into the femtosecond regime resulted in capturing the transition state directly. As an example photo dissociation dynamics of ICN molecule is shown here in this figure.

Here we must note that in conjunction with the time resolved studies another method which separates the product molecules by velocity and orientation and internal energy distribution such as rotational, vibrational and translational became also popular to study chemical dynamics. However, as our focus in this course is only on the point of view of flash photolysis which is time resolved studies, we will skip this energy resolved way of investigating chemical dynamics.

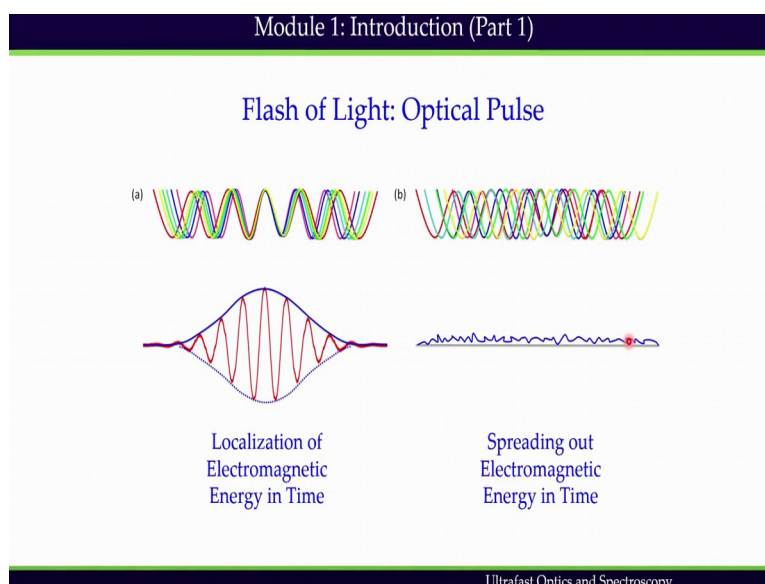
We shall stay focused on the time resolved aspects of the chemical dynamics its experimental schemes and related optics. So, from this very rich historical perspective of the century old time resolved chemical dynamics field we get an important information.

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Pump probe spectroscopy requires flash of light. What is flash of light by the way?

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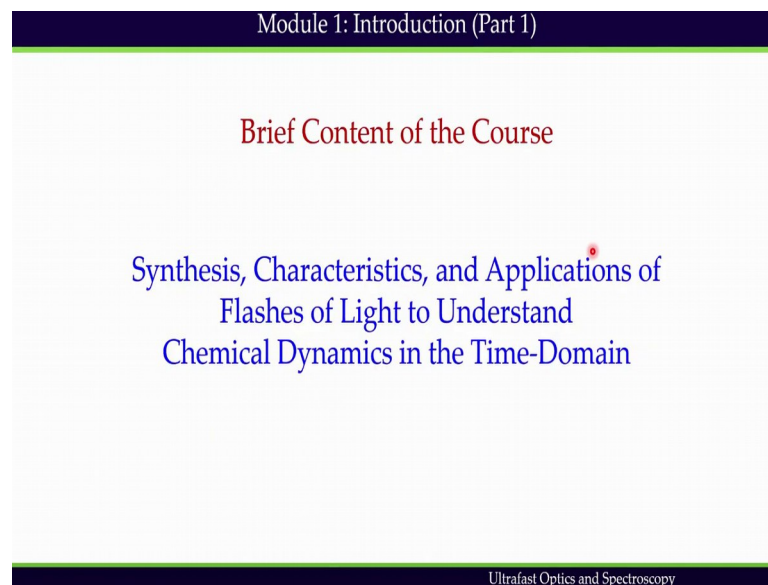


Flash of light is nothing, but localization of electromagnetic energy for a very short time. Synthesis of flash of light requires a large number of plane waves or colour components which are represented here by different colours. Each colour is representing a plane

wave. The temporal duration of the flash of light this duration depends on the colour components that constitute the flash and the phase relationship between the colour components. In this figure a we show that a flash of light with very short duration can be synthesized with different coloured plane waves with fixed phase relationship here this all the phases are locked.

Figure b in this figure it shows that if the phase relationship is random, all the phases are randomly changing electromagnetic energy spreads out in time as a result no flash is created.

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What factors govern this spread out? The content of this course will revolve around synthesis, characteristics and applications of flashes of light to understand chemical dynamics in the time domain.