Ultrafast laser clocks*

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Within the microscopic world of matter, the atoms and molecules are moving rapidly about. These molecular motions are about a trillion times faster than the everyday events we usually experience. In order to study these motions and energy transfer processes, we must be able to time the events that occur in the molecular world. Just as we use a watch to time events which occur in our daily lives, we need a specialized clock to measure the events which occur in the microscopic world. The appropriate time scale to probe most processes in the molecular world is the picosecond – a picosecond is 10^{-12} sec.

In order to time these events the new clock must have the capability of measuring events on a picosecond time scale. Such ultrafast clocks are now available to us! The light pulse emitted from a mode-locked laser is the key element required for the operation of the ultrafast clocks. The smallest divisional marking on its time scale – comparable to the seconds on an ordinary clock – is the duration of the light pulse, typically a few picoseconds. The basic "gear" mechanism which turns the "hour and minute hands" of the laser clock is the light pulse traveling at a constant speed, c, over a known distance. To adjust the time of this clock, one changes the distance over which the light pulse travels; it takes a light pulse 33 psec to transverse a distance of 1 cm in air. The interval of time is determined by varying the separation between two light pulses. The various types of "gears" used to delay the arrival time of the light pulse are displayed in Fig. 1.

Ultrafast laser clock technology has become as important and revolutionary in giving fundamental information by time measurements as the spectral measurement of light scattering and fluorescence.[1-3] The purpose of this article is to introduce the reader to this new field and to give an indication of the current progress and direction it is taking. We hope to demonstrate the wide scope and versatility of these laser clocks to tackle fundamental problems in science. In this article we will briefly describe the operation of the mode-locked laser, the different types of laser clocks, and some of the recent advances in measuring rapid phenomena in biology, chemistry, and physics.

Mode-locked lasers

The theory of stimulated emission of radiation was first described by Einstein and Planck in the early 1900s. The feasibility of laser action was considered in the 1950s but it was not until the 1960s that the first working laser was built. Even though the laser has been available for 16 years, it is still a relatively new tool and more applications for its use are constantly being found.

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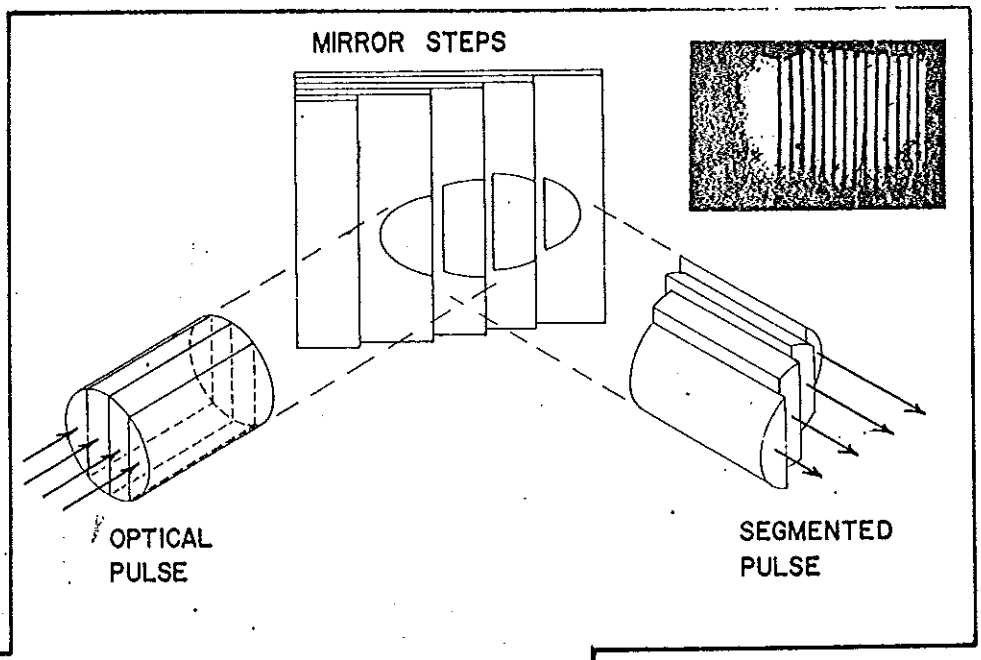
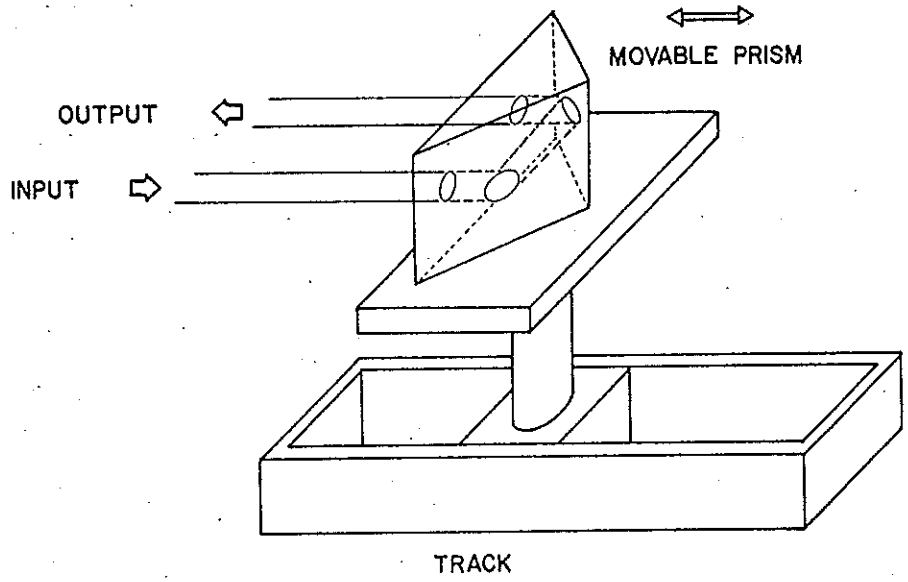
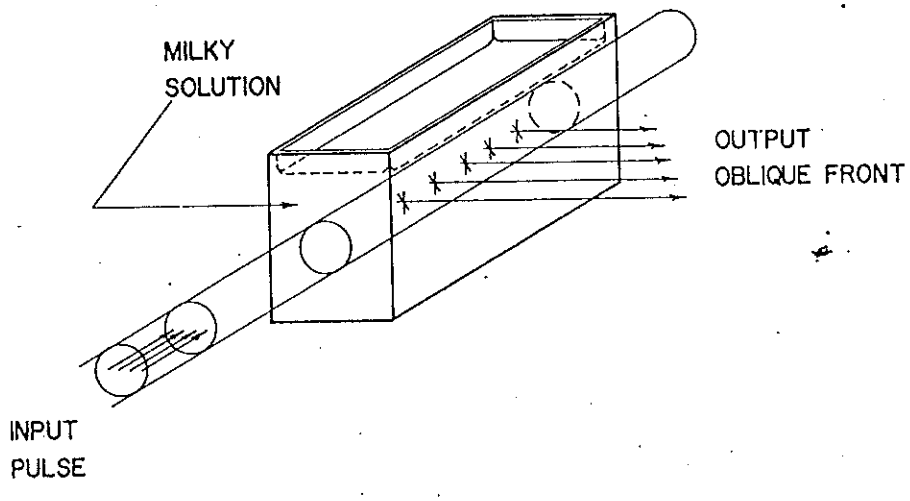


Fig. 1. a) The input beam is incident on the stepped portion of the mirror plates. The output is delayed in steps proportional to the thickness of the plates. The insert is a photograph of the image of the array using a 560-nm pico-second pulse.



b) By moving the prism to different positions, the distance the input beam must travel is changed; thereby increasing (or decreasing) its arrival time at the sample.



c) As the input beam passes through a solution, the scattered light leaves the cell in an oblique front.

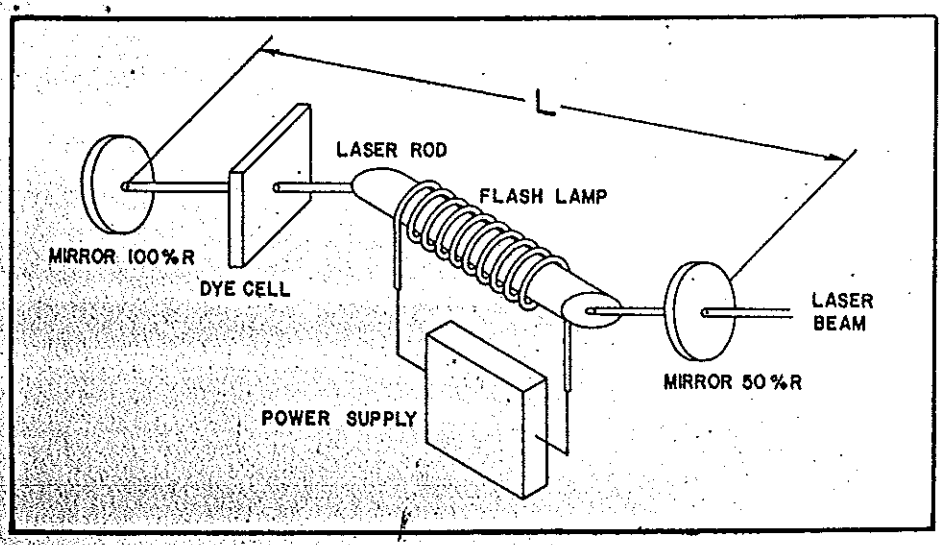


Fig. 2. A mode-locked solid-state laser consists of two mirrors, a dye cell and a laser rod (ruby or glass) surrounded by a flash lamp.

A particular class of lasers called mode-locked lasers[4] has proved invaluable in the study of ultrafast phenomena. A schematic representation of a solid state mode-locked laser cavity is shown in Fig. 2. It consists of a neodymium-doped glass rod with its ends polished optically flat to 1/10 wave and cut at Brewster's angle* and a bleachable dye; both are situated between two dielectric coated mirrors†,—one 100% reflective and the other 50-60% reflective with their surfaces wedged at approximately 1°. The cavity has an overall optical length L. The dye cell and laser rod are set at Brewster's angle to the optical path. The reasons for the angles are to prevent feedback and reflection losses from the surfaces when the light reflects back and forth within the cavity.

The flashlamp surrounding the laser rod provides the optical energy to pump the laser medium. The absorption of a sufficient amount of the light by the laser rod causes a population inversion of the energy states in the laser medium which first produces fluorescence upon relaxation. Unlike the common gas lasers, many different frequencies, are emitted. The fluorescence is emitted in all directions with various phases. Some of this fluorescent light travels along the cavity axis, bouncing back and forth between the mirrors, stimulating other excited states in the medium to emit light with the same phase and in the same direction as the original light. In this manner a potent chain reaction is initiated until a massive amplification takes place as the light bounces back and forth through the laser medium. The cavity also acts as a frequency filter, allowing only certain frequencies of the light to reproduce themselves after a round trip. In order to get constructive interference between the waves in the cavity, the phase shift of a light wave over a round trip must be an integral number times 2π, i.e., $2kL = 2\pi$ where k, the propagation constant is equal to $2\pi/\lambda$. Therefore, only particular discrete frequencies called modes can oscillate and be supported in the cavity. The frequency separation between the modes is $c/2L$; this is also the reciprocal of the time for a light pulse to travel the length of the cavity and return. These modes, however, are more or less independent of each other, being generally uncoupled and having no fixed phase relationship with one another.

To generate an ultrafast pulse, several of the laser modes must be coupled together and forced to oscillate with a definite phase relationship between them. An element which can lock the modes in phase is a bleachable dye. The absorption characteristic of this dye is nonlinear; that is, the absorption at laser frequency decreases with light intensity above a critical intensity. (The dye is bleached.) The light in the cavity initially consists of a messy noiselike signal with random amplitude and phase fluctuations. These fluctuations are produced with respect to the cavity round-trip time. The fast pulse is built up out of this random distribution of noise pulses by the bleachable dye. The largest fluctuation in the initial fluorescence intensity pattern of the laser medium is selected out and preferentially amplified. As the light bounces back and forth in the cavity, the bleachable dye acts as a time-varying attenuator, opening and closing (transmitting and absorbing) at a frequency equal to the difference in frequency of two adjacent modes. Through this action the fields of the oscillating modes interfere, thereby coupling each of two adjacent modes together, and a definite relationship among the oscillating modes is achieved. The dye is used to absorb the smaller-amplitude pulses and acts as a pulse-sharpener on the most intense pulse, attenuating the wings of the pulse and producing a much sharper pulse.

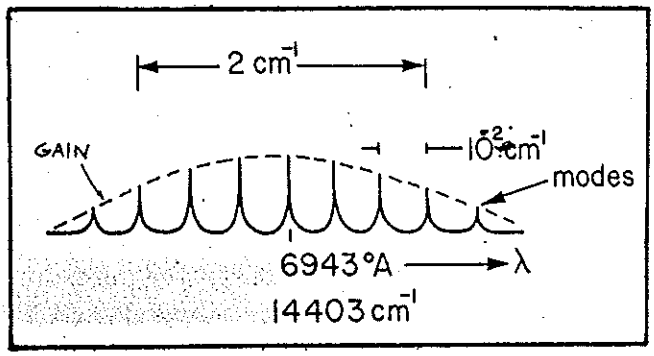


Fig. 3. Schematic of the spectral profile of an ultrafast pulse from a mode-locked Ruby laser (nL = 50 cm).

*For light polarized in the plane of incidence, the intensity of the reflected light is zero when the surface is oriented at this angle.

†A substrate, usually glass, coated with various thin film layers of dielectric material such as Magnesium Fluoride, and Zinc Sulfide. The thickness of the layers, multiples of 1/4λ, determines the reflectivity of the mirror.

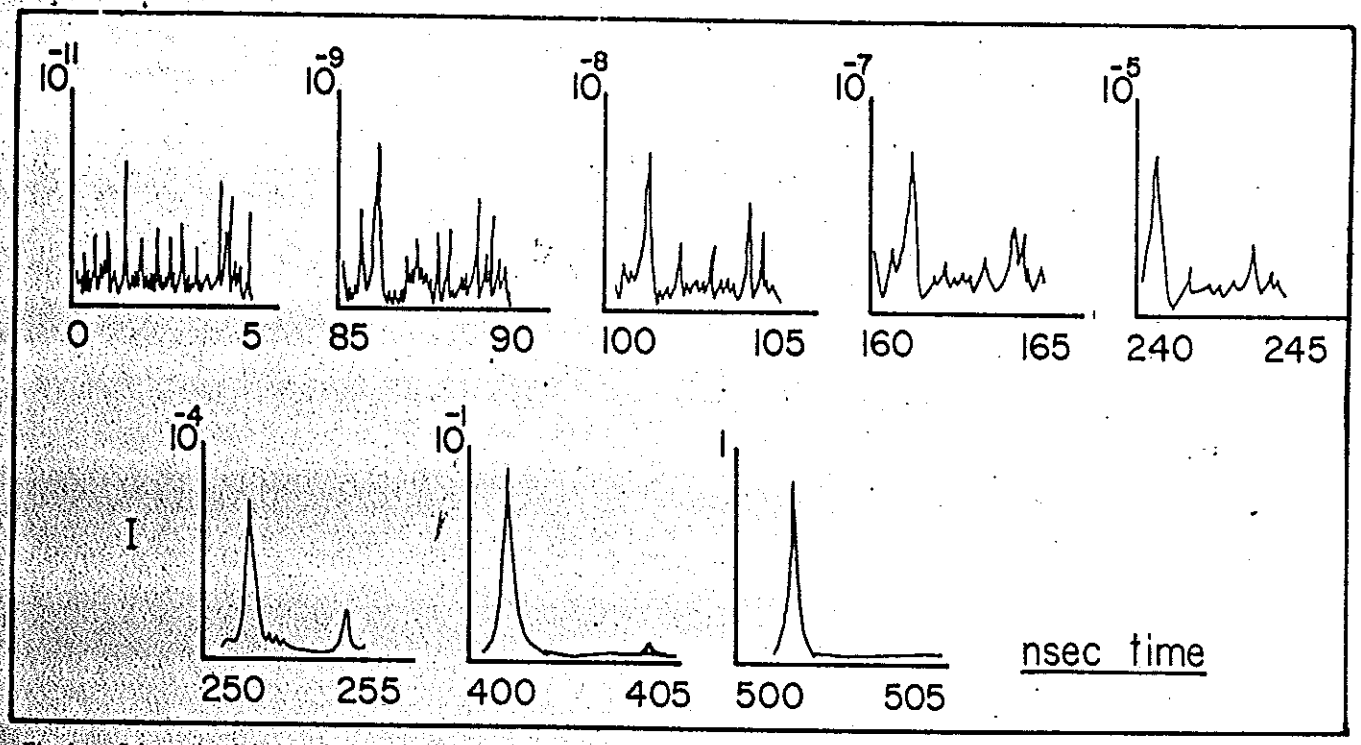


Fig. 4. Schematic of time evolution of an ultrafast pulse from the spontaneous emission (Round trip time is 5 nsec.)

This pulse sharpening proceeds until the maximum number of modes are coupled together, typically 10^3 modes (see Fig. 3). After hundreds of passes through the laser activity, the combination of the nonlinear absorption of the dye and amplification by the laser medium results in an intense pulse circulating in the cavity (see Fig. 4). Upon each pass onto the semireflective mirror, about 50% of the light escapes through this mirror, resulting in a periodic train of ultrafast pulses. These pulses are separated by the round trip time in the laser cavity, $2L/c$, typically 7 nsec. The characteristics of typical ultrafast lasers is shown in Table I. The emission from a mode-locked laser detected by a fast photodetector and displayed on an oscilloscope is shown in Fig. 5.

TABLE I:

Typical characteristics of mode-locked lasers

Laser	Pulsewidth (PS)	Wavelength (microns)	Energy/pulse (mj)
Ruby	10-40	0.6943	1
Nd: Glass	6-10	1.06	1
Nd: Yag	30-100	1.064	10^{-1}
Dye (c.w.)	0.3-2	0.61	10^{-6}
Dye (pulse)	2-10	0.5-0.8	10^{-2}

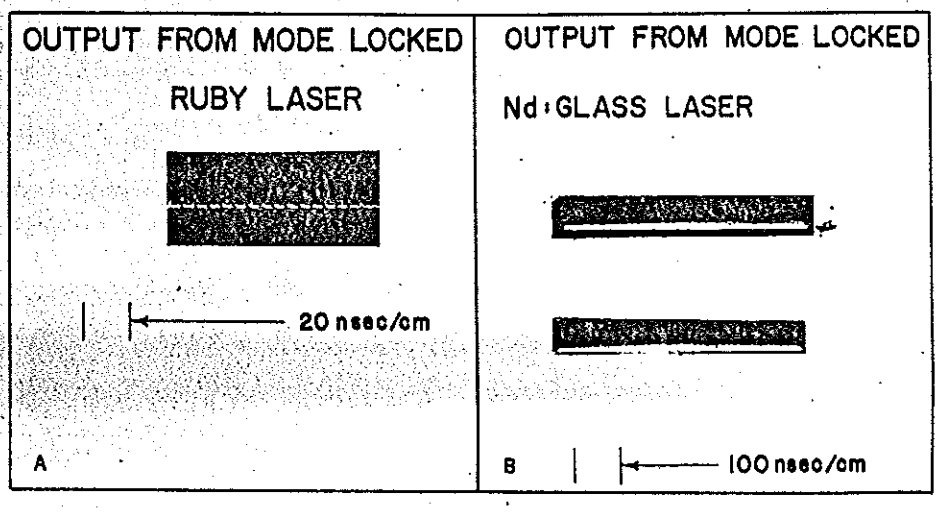


Fig. 5. Photographs of the laser pulse emission from a) Ruby laser and b) Nd: glass laser, measured by a fast photo detector and displayed on an oscilloscope. The photograph consists of an array of pulses, each pulse is separated by the time it takes a pulse to travel back and forth in the cavity (~5 nsec).

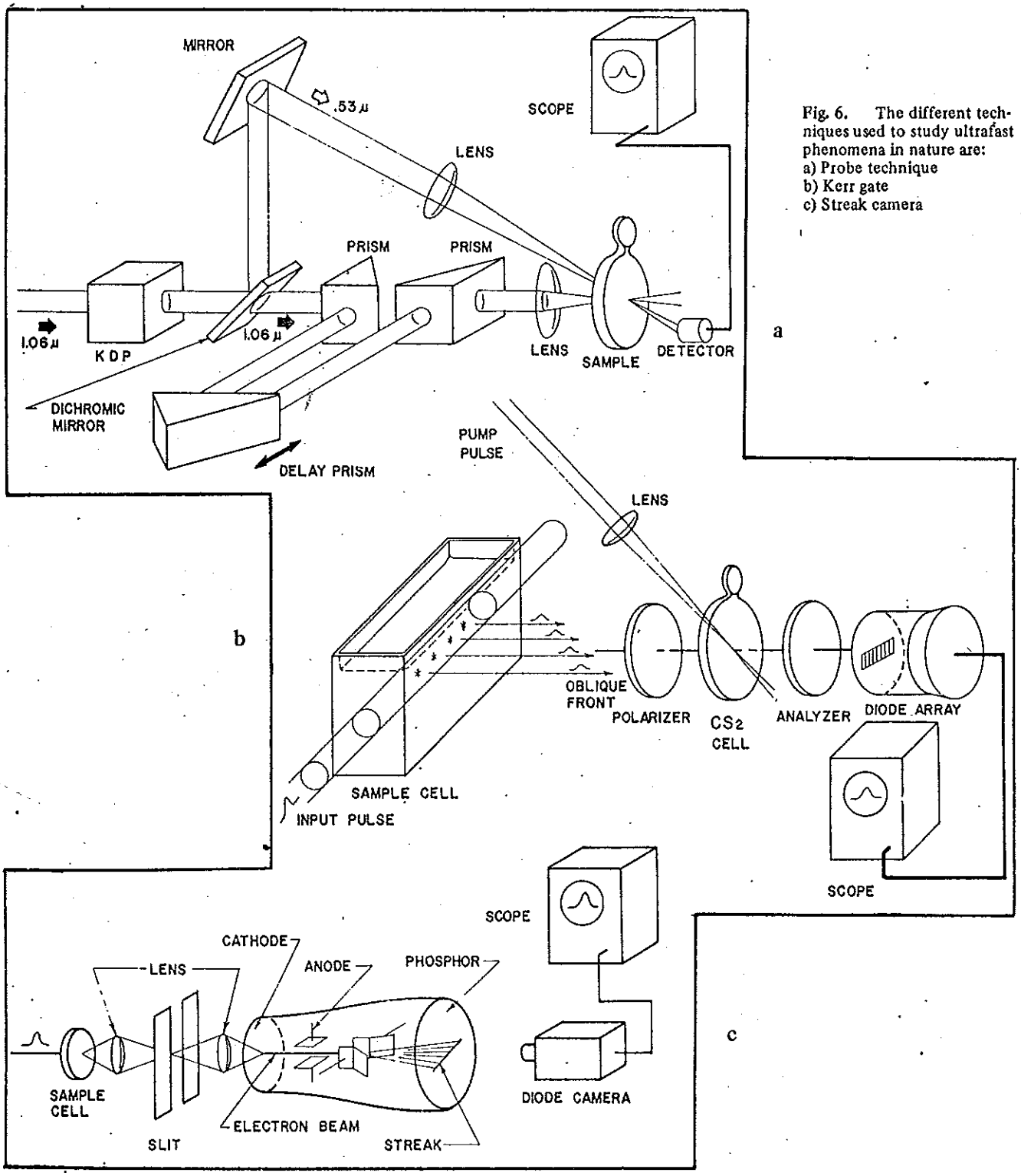


Fig. 6. The different techniques used to study ultrafast phenomena in nature are:
a) Probe technique
b) Kerr gate
c) Streak camera

Clock techniques

There are three basic laser clocks used for measuring picosecond events. They are the probe technique, optical Kerr gate, and the streak camera which are shown schematically in Fig. 6. In these techniques the material of the sample is first disrupted from equilibrium by optical excitation using a picosecond laser pulse, and then the rate of return to equilibrium is studied by one of these clocks.

A. Probe technique (Fig. 6a) In this technique the laser pulse is divided into two beams by a dielectric mirror—an intense pump pulse and a weak probe pulse. The more intense pump pulse is directed to the sample and the weaker probe pulse is directed along a variable optical delay path to arrive at the sample later than the pump pulse. The pump pulse excites the molecules in the sample. The probe pulse is used to examine one of the parameters of the system, such as light absorption, as a function of time subsequent to excitation. By moving the prism in the delay path, one can vary the time between the pump and probe pulses.

TABLE II: Nonlinear optical processes used to change wavelengths of light pulses

PROCESS	INPUT Wavelength	OUTPUT Wavelength	Typical Amount converted*
Second Harmonic	1.06μ	0.53μ	10%
Second Harmonic	1.06μ and 0.53μ	0.35μ	1%
Fourth Harmonic (Second harmonic twice)	0.53μ	0.265μ	1%
Picosecond continuum:[5]			
Frequency broadening and parametric processes	0.53μ 1.06μ	0.4-0.8μ 0.4-3μ	1%
Stimulated Raman scattering		large number of discrete lines	1%

*Input power above 10^9 W/cm^2

Depending on the sample to be investigated, picosecond laser pulses of differing wavelengths are used to excite and probe the sample. The easiest way to produce new wavelengths in the visible and uv region is by nonlinear optical methods such as harmonic generation. An intense wave induces a nonlinear polarization in a crystal such as KDP, this polarization in turn radiates a wave at the harmonic frequency. This process can double or triple the frequency of the input pulse. For example, by passing the 1.06μ-pulse from a Nd:glass laser through a KDP crystal, 10% of the pulse can easily be converted to a 0.53μ pulse. Table II lists some of the different nonlinear optical processes which can be used to convert an intense picosecond laser pulse to different wavelengths.

To measure an entire absorption spectrum on a picosecond time scale in a single shot, a picosecond probe pulse with a broad spectral width is required. A light source containing all frequencies in the visible spectrum can be generated by an intense monochromatic picosecond pulse passing through certain materials. This light source is called a picosecond continuum, because it is of six-picosecond duration and contains all the colors of the visible spectrum. The nonlinear response of material is believed to be responsible for the generation of the continuum. Numerous substances, such as glass and water, have been used to generate a continuum.[5] A number of experiments on various dynamic processes have been investigated using the continuum by monitoring the absorption spectra of transient species.[5,6]

An innovative absorption probe technique uses a stack of thin mirror plates arranged in step sequences.[6] The probe laser beam's cross-section is magnified and the central spatially uniform portion is selected to cover many mirror steps. Upon reflection off the mirror stacks, the probe pulse is split up into a number of delay pulses with a step progression of time delays (see Fig. 1). A mirror step introduces approximately 4 psec of delay per millimeter at an angle of incidence of 45°. The probe beam can then be directed to the sample to interrogate the sample's kinetics on a single shot. A range of 100 psec is easily covered.

B. Optical Kerr gate (Fig. 6b) In this technique the light emitted from a sample which has been excited by a laser pulse is passed through an optical camera-like shutter composed of a cell filled with CS_2 liquid situated between a crossed polarizer and analyzer. Because of the crossed polarizers this shutter is naturally closed, preventing the light from being transmitted. When an intense laser pulse is directed through the CS_2 cell, the electric field of the laser beam causes a short-lived birefringence in the CS_2 liquid which opens the shutter.[7] Note that this technique is different from the traditional one of imposing an external dc electric field on the cell. In this case, one part of the laser beam opens the Kerr gate while another starts the action to be observed. The birefringence is caused by rotation of the CS_2 molecules in the liquid through the interaction of the optical electric field of the laser pulse with the induced dipole moment of the molecules. The decay of the induced birefringence determines the resolution time of the shutter. Using the emission from a Nd:glass laser and CS_2 liquid the shutter opening time is about 10 psec. Therefore, a 10 psec section of a fluorescence temporal profile can be carved out and detected. By moving a prism to vary the arrival time of the fluorescence pulse different sections of the time history of a fluorescence signal can be measured. This technique is useful over a range from 10 psec to 1 nsec. The fluorescence kinetics from a spinach

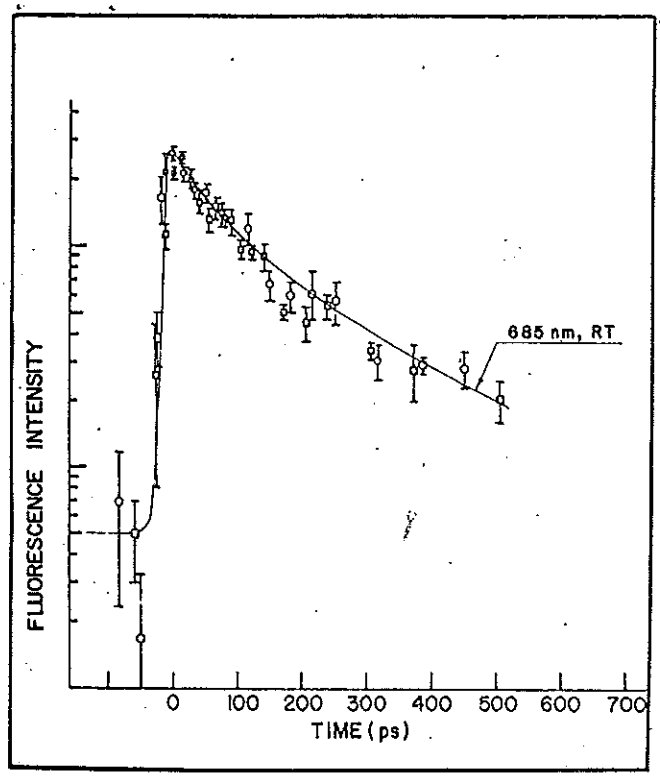


Fig. 7. The time dependence of the fluorescence emission of a spinach leaf (o) and of chloroplast preparation (o). The solid curve represents the sum of two exponentials with decay times of 56 and 220 picoseconds.

leaf is shown in the graph in Fig. 7. Using a subpicosecond pulse[8] the resolution can be improved to 0.3 psec.

C. Streak camera technique[9] (Fig. 6c) In this technique, the light emitted from a sample which has been excited by a laser pulse is focused onto a photocathode. Here electrons are released in proportion to the light intensity and are accelerated through an anode. They are deflected by an applied voltage ramp which increases with time and streaks the electrons onto a phosphor screen. Thus the electrons released at different times strike the screen at different positions and the resulting phosphorescent track is photographed or electronically detected by a photo diode array, giving a picture of the lifetime of the fluorescence.

Typically the streak rate is about 2 cm per nsec with a resolution of a few picoseconds. This technique can measure the fluorescence kinetics from low yield quantum dyes of $\phi \sim 10^{-3}$ on a single laser shot.

Some recent advances in research

In this section we will discuss some of the recent advances in measuring rapid phenomena in biology, chemistry, and physics. It is difficult to give complete coverage of all the recent breakthroughs in this expanding field but we have chosen illustrative examples which give the direction in which the various fields are heading. We apologize in advance to those scientists whose research we have omitted. No attempt has been made to give a comprehensive coverage.

A) Biology

Three very important biological areas have been studied by picosecond techniques: photosynthesis, vision, and hemoglobin.

Photosynthesis is being extensively studied by scientists[10-13] with a view to understanding the extremely efficient primary energy-transfer process. In green plants, chlorophyll *a* and other pigment molecules absorb light and rapidly transfer the energy to a few specialized molecules called traps. Thereafter, a sequence of chemical steps is slowly initiated to bring about photosynthesis. Fluorescence lifetimes are a direct measure of the rate of energy-transfers from the light collecting units to the chemical traps. The fluorescence and energy-transfer times are very rapid events and in order to obtain information about these fundamental processes in photosynthetic kinetics, picosecond clock techniques are used.

Using the optical Kerr gate[10] physicists have measured and studied the time dependence of fluorescence emission from chlorophyll in plants (see Fig. 7). They found that the rise time of the fluorescence was extremely fast ($<$ 10 psec) and the time-decay profile was nonexponential with an overall decay profile of 250 psec. Using the streak camera, scientists[12] showed that the technique of using intense picosecond pulses to excite photosynthesis is complicated by the intensity dependence of the fluorescence lifetime. Absorption probe studies[13] have been done to estimate time limits in transferring energy from one pigment to another in photosynthetic bacteria and an upper limit of 7 psec was found for the transfer.

Over the years experiments have been performed on the visual process to try to determine how the initial energy is ultimately transformed into pulses to the brain. Dramatic results on the detection and identification of the first event in vision are being obtained using ultrafast laser clocks. It is believed that the first step in vision is initiated when light falls upon the pigment molecules responsible for sensing light in the eye; the pigments are photo-induced to change their conformation. Using the absorption-probe method scientists[14] have studied the kinetics of the primary step and have observed the appearance and decay of a transient intermediate called bathorhodopsin, the first photochemical product of rhodopsin. Bathorhodopsin appears almost instantaneously, within 6 psec after light is absorbed by rhodopsin and decays with a lifetime of ~30 nsec. This is consistent with the conclusion that bathorhodopsin is probably a geometric transformation of a small part of the entire rhodopsin pigment molecule rather than a structural change of the complete molecule.

Hemoglobin plays an essential role in the blood, binding and transporting oxygen from the lungs to various parts of the body. Myoglobin is a simpler molecule than hemoglobin having one chain of amino acids and one heme group (see Fig. 8). Hemoglobin has four heme groups attached to two different protein chains. Myoglobin stores and transports oxygen in muscles. Most recently the photodissociation of complexes of hemoglobin was investigated by absorption-probe techniques using subpicosecond laser pulses[15] to obtain information on the binding kinetics. The ligands of hemoglobin, O_2 and CO, are thought to be bonded to an iron atom in a globin cage. By dissociating O_2 and CO from the iron atom, one can study the escape dynamics of CO or O_2 from the iron in the cage of hemoglobin. When the ligand escapes, the iron atom moves caus-

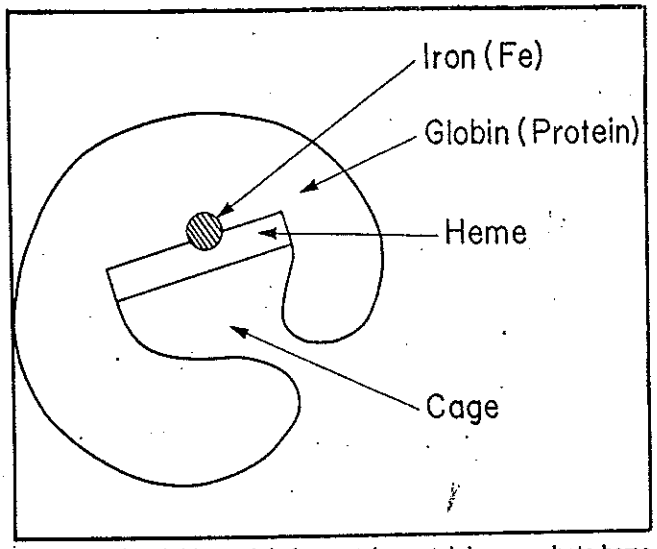


Fig. 8. Myoglobin, a globular protein containing one photo heme and iron, plays an important role in transporting and storing oxygen in muscles. Ligand molecules such as 0_2 and CO bind to iron which is located near the center of the heme group.

ing a spectral shift in the absorption spectrum of the hemoglobin. Monitoring the absorption band of the hemoglobin complex following photodissociation provides a means of observing the recombination of CO and O_2 to the hemoglobin. It was found that dissociation of CO occurs in a time less than ½ psec and no recombination of CO was observed back to the hemoglobin up to a time of 20 psec. This experiment indicates a lack of caging of CO to hemoglobin subsequent to photodissociation. The subnanosecond time scale should be investigated to see if caging is slower than 20 psec.

Further studies are being undertaken to determine how light energy is transmitted in these biological systems.

B) Chemistry

Studies have been done to probe the dynamics of molecular motions, particularly those which deal with the motions in liquids. In a collision involving molecules, energy is exchanged during the redistribution of translational, rotational, and vibrational degrees of freedom. Picosecond laser clock techniques have enabled scientists to measure some of these relaxation phenomena. We shall briefly describe research on the vibrational and rotational motion of molecules and on the nonradiative processes in the liquid state.

Some of the latest studies done on liquids use the optical Kerr gate to measure relaxation times by probing the time evolution of the induced transitory birefringence in mixed liquids. Using nitrobenzene in various mixed solutions of molecules of comparable size, it has been found that the relaxation time decreases with decreasing concentration, even with increasing viscosity.[16] This does not agree with the Debye theory, which is applicable to single isolated molecules, but the effect is probably due to a local viscosity and correlation effects among the molecules. Other studies have measured the rotational relaxation of pure CS_2 liquid and have shown definitely that this is the predominant mechanism for the observed induced birefringence in CS_2.[8]

A large effort in picosecond spectroscopy has been devoted to studies of nonradiative transition[1] – transition involving no light emission – in organic dye and solvent molecules. Studying the dynamics of electrons and ions localized in solvents has yielded information on electron–solvent interactions.[17] Within 6 psec the interaction between a "free" electron and solvent is completed; that is, the electron becomes caged by the potential well formed by its interaction with the surrounding solvent molecules. Absorption probe measurements have also been used to obtain information on vibrational relaxation in dye molecules in excited and ground states. Typical vibrational decay times of a few picoseconds have been measured in various dyes.[8] The fluorescence kinetics from low quantum yield dyes (quantum yield, $\phi \sim 10^{-4}$ at pump density of 10^{13} photons/cm^2) have been measured at CCNY using a Hamamatsu Streak camera.[18]

A large number of experiments have been performed to measure the vibrational relaxation in liquids and solids.[19,20] It has also been possible to study the direct decay routes of a vibration into other vibrational modes in the liquid state.[19,20] The technique[2] commonly used is to excite the vibration with an intense laser pulse by either Raman scattering or infrared absorption, and then monitor the relaxation of the vibration at different times with a weak probe pulse by watching the decay of the Raman signal.

C) Physics

Much of the research done in solid state physics using picosecond laser techniques has been to investigate semiconductor properties. The absorption of picosecond laser pulses in silicon and germanium can produce a quasi-metallic photoconducting state.[21] It has been demonstrated that electron-hole plasma in excess of 10^{20}/cm^3 can be generated.[21] The time evolution of generated plasma in the solid was shown to be consistent with the electrons and holes diffusing into the medium. This has been used to form the basis of ultrafast electronic switches and gates, which turn on and off in a few picoseconds. This provides a capability for measuring and generating picosecond electric pulses.

Recently, studies on germanium show the relaxation of a nonequilibrium distribution of electrons and holes created by an optical pulse may relax via phonon emission in about 60 psec. Other research in physics using picosecond lasers has been done to study the temporal behavior of excitons (an electron and a hole bound together) and to study exciton-exciton interactions.[22]

Future

We may look forward to the development of *intense* subpicosecond lasers in the not too far distant future, which will enable scientists to probe the microscopic world even further. With the refinement of ultrafast gates, electronic measuring devices will have the capability of subpicosecond measurement. The most tangible results of using laser clock techniques is to study the basic mechanisms of energy transfer.

Within a decade, picosecond clock techniques will have been used to unravel most of the mysteries of nature that occur within the time region between a 1 psec to

1 nsec. In particular, the primary steps in photosynthesis and vision most likely will be completely understood. These picosecond techniques will become as routine to study of the primary processes in biology, chemistry, and physics as using a spectrophotometer to obtain the absorption spectra of a material.

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