# From nanosecond to femtosecond science

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Lasers have caused revolutionary changes in many fields of science and technology. A brief review is presented here of how lasers have provided access to measurements of short time intervals. Since 1960, six orders of magnitude, from $10^{-9}$ to $10^{-15}$ seconds, have been added to time-resolved observation of fast phenomena. New subfields of science, including femtochemistry and femtobiology, have been created. Some representative examples of transient Raman scattering and of impulsive and displacive excitations in molecules and crystals illustrate the usefulness of picosecond and femtosecond pulse techniques. In addition, the domain of power flux densities has been extended from $10^{12}$ to $10^{19}$ watts/cm$^2$ by the use of short focused pulses. This has given experimental access to new phenomena, including ultrafast phase transitions in electronic structure, above-threshold ionization of atoms, and high-order harmonic generation and acceleration of relativistic electrons by light pulses. [S0034-6861(99)01002-8]

## I. HISTORICAL INTRODUCTION

The measurement of short time intervals during the first half of this century was limited to intervals longer than one nanosecond. Before 1900 it was already known that electrical sparks and Kerr-cell shutters could have response times as short as $10^{-8}$ s. Abraham and Lemoine (1899) used a discharge from condenser plates which simultaneously activated a spark gap and a Kerr-cell shutter. The condenser plates were placed in a cell containing carbon disulfide between crossed polarizer and analyzer. The light path between the spark source and the Kerr cell was variable. If the delay path was longer than four meters, no light was transmitted. This proved that the Kerr-cell response was faster than $10^{-8}$ s. We now know that the response of the Kerr effect in $CS_2$ is about two picoseconds. Thus Abraham and Lemoine really measured the duration of light emitted by the spark. This experiment used the essential feature of a variation in light path length for the measurement of short time intervals. In most picosecond and femtosecond time-resolved experiments, the delay between a pump and a probe pulse is varied by changes in optical path length. Norrish and Porter (1950) used flash lamps to excite photochemical reactions and probed them spectroscopically with varying delays in the millisecond to microsecond range. This work in ''microchemistry'' was recognized by the Nobel prize for chemistry in 1967.

The advent of lasers in 1960 revolutionized the field of time-resolved spectroscopy. Shapiro (1977) has presented a historical overview and edited an early volume dedicated to ultrashort light pulses. During the past two decades the field has grown explosively and new scientific subfields, denoted by femtochemistry and femtobiology, have been created.

In Sec. II, the highlights in the experimental development are surveyed, leading from nanosecond to femtosecond light pulse generation and detection. In Sec. III, some paradigms of transient excitations, involving nuclear displacements and vibrations in molecules and in condensed matter, are presented.

A final section draws attention to the fact that the concentration of light in space and time, as achieved in focused femtosecond laser pulses, can reach power flux densities exceeding $10^{18}$ watts/cm$^2$. Some ultrahigh-field phenomena that are currently under intense investigation include ultrafast phase transitions in electronic structure and the creation of high-density, high-temperature plasmas. Other phenomena include above-threshold ionization of atoms, high-order harmonic generation, and the acceleration of relativistic electrons.

The vastness of the new orders of magnitude in time and in radiative density that have been opened up to experimental investigation by short light pulses may be illustrated by the following two observations: The minute is the geometric mean between the lifetime of the universe and the duration of a 10-fs pulse. The radiative density of blackbody radiation at ten million degrees, corresponding to star interiors, is $10^{17}$ watts/cm$^2$.

## II. HIGHLIGHTS IN SHORT-PULSE GENERATION AND DETECTION

The first laser, realized by Maiman (1960), was based on a ruby crystal, pumped by a xenon flash discharge. It created a laser pulse of fluctuating intensity lasting between a microsecond and a millisecond. Hellwarth (1961a, 1961b) proposed the concept of $Q$ switching at the second conference on quantum electronics, held in Berkeley, California, in March 1961. He reported $Q$ switching of a ruby laser by means of a Kerr-cell shutter at the APS Chicago meeting in November 1961. A ''giant'' pulse with a duration of about 10 nanoseconds was reported. Others achieved $Q$ switching by means of turbine-driven rapidly rotating reflecting prisms. The higher intensities available in $Q$-switched pulses aided in the detection and study of numerous nonlinear optical phenomena.

Mode locking of a large number of longitudinal modes all activated by the gain profile of the lasing medium was proposed to obtain shorter pulses. Active mode locking was first demonstrated for a helium-neon laser by Hargrove, Fork, and Pollack (1964). By modulating the index of refraction acoustically at the period of the round-trip time of the light in the laser cavity, they obtained an output from the He-Ne laser consisting

of a series of narrow pulses spaced by the cavity round-trip transit time. Since the gain profile of the active Ne atoms was narrow, the pulse duration remained well above one nanosecond.

Passive mode locking of a ruby laser by means of a saturable absorber was first demonstrated by Mocker and Collins (1965). Pulses shorter than a nanosecond were obtained by DeMaria *et al.* (1966) by passive mode locking of a Nd-glass laser, which has a broader gain profile. The generation of the short pulse may be qualitatively understood as follows: A stochastic peak in the amplified spontaneous emission output will bleach the dye absorber more and will consequently be preferentially amplified. Thus the emitted power will be concentrated in a short pulse with a duration determined by the gain bandwidth product of the laser. The broadband response of Nd-glass lasers, and later the Nd-Yag (yttrium aluminum garnet) lasers, made passive mode locking by a thin film of saturable absorbing dye in the laser cavity very effective. Pulses of 10-ps duration were readily obtained with such systems and utilized in many laboratories.

The first pulses shorter than 1 ps were obtained by Shank and Ippen (1974) with tunable broad-gain dye laser media in combination with a saturable dye absorber. An analysis by New (1972) showed that it is possible to obtain pulses shorter than the characteristic response time of either the absorbing or the emitting dye, as the pulse duration is determined by the balance of saturable gain and saturable absorption. Further developments include the use of counterpropagating pulses in a ring dye laser system. The two pulses cross each other in a thin film of saturable dye, with a thickness of a few $\mu$m. With compensation of group velocity dispersion by a configuration of glass prisms in the laser cavity, a repetitive train of six femtosecond pulses was reported by Fork *et al.* (1987). These systems, with pulse durations between 10 and 100 fs, required delicate adjustments, but were used by many investigators during the decade of the eighties.

In the current decade they are rapidly being replaced by Ti-sapphire lasers. Spence, Kean, and Sibbett (1991) discovered that these lasers may show "spontaneous" dynamic mode locking without the use of a saturable absorber. The effect is based on the occurrence of self-focusing by the intensity-dependent index of refraction in the Ti-sapphire crystal. In combination with a suitable aperture, the round-trip gain is increased at higher intensities, as more light is focused to pass through the aperture inside the optical resonator. Again, compensation of group velocity dispersion is essential to obtain very short pulses. Zhou *et al.* (1994) obtained a pulse of 8-fs duration from a Ti-sapphire laser. An all-solid-state system based on pumping the Ti-sapphire with a semiconductor array to emit a continuous train of short pulses is feasible. Thus femtosecond pulse generators are rapidly becoming a standard laboratory tool.

The measurement of the duration of picosecond pulses was first carried out by fast photoelectronic streak cameras, but soon autocorrelation and cross-correlation techniques were introduced. In a typical arrangement one divides a pulse by a beam splitter. The two pulses are recombined with a variable delay in one path. The state of polarization may also be changed. When the two pulses travel in opposite directions in a fluorescent medium, two-photon-induced fluorescence may be observed at right angles. This fluorescence is enhanced in a narrow strip where the two pulses overlap. The two pulses may also be recombined traveling in different directions in a thin sliver of a nonlinear material. Second-harmonic generation in the phase-matched directions occurs only when the two pulses are simultaneously present. Note that a picosecond differential corresponds to a delay in optical path length of 0.3 mm, and a femtosecond differential to 0.3 $\mu$m. A picosecond traveling-wave Kerr-cell shutter activated by an intense pump pulse traveling in the same direction was realized rather early. The change in index of refraction or birefringence is proportional to the intensity of the pump pulse. These detection methods are all based on the nonlinear response of an optical medium. The temporal response of the amplitude or the intensity of the probe pulse is readily measured.

Important information about the temporal behavior of the phase of the pulsed field may be obtained by spectrally analyzing the second-harmonic or sum frequency signal produced by the two pulses as a function of delay time. This technique was first introduced by Trebino and Kane (1993) and is called FROG (frequency-resolved optical gating). The time variations in the observed spectrum of the combination signal give the temporal variations in phase. Thus a complete picture of the pulsed field was obtained for a Ti-sapphire laser by Taft *et al.* (1995).

Conversely, it is also possible to generate a pulse with prescribed amplitude and phase. To achieve complete pulse shaping one obtains a spectrum of the collimated pulse from a grating and a lens combination. In the focal plane one has separated the various Fourier components spatially. In this focal plane one can insert an amplitude and phase filter. The various frequency components are then recombined by a second lens and grating. The results of this pulse-shaping technique may be verified by FROG analysis.

A detailed pedagogical survey of short-pulse techniques by Glezer (1997) has recently been published. Ippen (1994) has written a review of theory and experiment of passive mode locking. This section has extracted much information from these papers.

## III. SOME HIGHLIGHTS OF ULTRAFAST SPECTROSCOPY

Transient Raman scattering was one of the phenomena extensively investigated early on with picosecond pulses. Carman *et al.* (1970) presented a detailed description of how stimulated Raman scattering changes its characteristics when the pulse duration $t_p$ is shorter than the characteristic damping times of the Raman-active vibration. A paradigm experiment was carried out by Laubereau, von der Linde, and Kaiser (1972). A pi-

cosecond laser pulse was partially converted to a second-harmonic pulse. The two pulses were separated by a dichroic mirror. The strong fundamental pulse triggered a coherent vibrational excitation, by stimulated Raman scattering. The vibration continued to ring after the exciting pulse had passed. The second-harmonic pulse probed the vibrational excitation with a variable time delay.

Stokes and anti-Stokes components in the forward direction of the second-harmonic pulse are created as the sum and difference frequencies of the incident light and the coherent vibration. These signals decay with a characteristic phase coherence relaxation time $T_2$ of the vibrational excitation. Spontaneous emission of anti-Stokes light in arbitrary directions measures the population in the excited vibrational state. This light decays with a different characteristic time $T_1$ for vibrational energy relaxation. Many molecular liquids and mixtures have been analyzed by this system. Heavily damped rotational excitations can also be investigated by stimulated Rayleigh wing scattering with short pulses. Time-resolved and frequency-resolved spectroscopic measurements are complementary. Time-resolved observation is especially useful to detect very fast phenomena hidden in the weak far wings of frequency-resolved spectra.

An entirely new regime occurs when the pulse duration $t_p$ is short compared to the vibrational period itself, $\omega_{\mathrm{vib}} t_p \ll 1$. In this case the vibrational mode is impulsively excited. The pulse contains many pairs of Fourier components with a difference in frequency equal to the vibrational resonance. In experiments by Ruhman, Joly, and Nelson (1988) the very short pulse is split into two parts of equal intensity which are recombined spatially to form a diffraction pattern in a Raman-active liquid. Thus a grating of impulsively excited vibrations is established. This grating is probed by the diffraction of a weak pulse with a variable delay. Alternatively one may detect the impulsively excited coherent vibration by sending a probe pulse along the same path as the first pulse. If the delay of the probe is an integral number of vibrational periods, the probe will enhance the excitation. As it loses energy from Fourier components of higher energy to those of lower energy, a redshift occurs. When the delay is an odd number of half vibrational periods, a blueshift is detected, as the vibrational energy is shifted back from the vibrational excitation to the probe in an anti-Stokes scattering process.

Impulsive Raman scattering has also been observed in a single crystal of germanium by Kutt, Albrecht, and Kurz (1992). The Raman-active vibration can be probed in reflection, as it produces a small modulation in the effective index of refraction.

Impulsive excitations must be sharply distinguished from displacive excitations, which can be induced by the absorption of short pulses in many crystalline materials, including semiconductors, high-temperature superconductors, and metals. A sudden change in carrier density or in electron temperature causes a change in equilibrium internuclear separations. Zeiger *et al.* (1992) describe the excitation of totally symmetric vibrations in Bi, Sb, $Ti_2O_3$, and high-temperature superconductors. Kutt *et al.* (1992) observe excitations of longitudinal phonons in GaAs, as the sudden creation of carriers changes the internal space-charge field near the surface. The excitation is detected by probing the oscillations in reflectivity which occur following the pump pulse.

A displacive type of vibrational excitation occurs during an optical transition in a molecule. The Franck-Condon principle states that the internuclear distance coordinates do not change during the transition to an electronically excited state. The equilibrium nuclear distances in this excited state are different from those in the electronic ground-state configuration. A short optical pulse, absorbed in a molecular gas, excites a rotational vibrational wave packet. The time evolution of this wave packet has been observed by Dantus, Bowman, and Zewail (1990) in an $I_2$ molecule by probing the excited configuration with a second absorption process to a still higher configuration from which fluorescence can be served. Oscillations in the fluorescent intensity as a function of pump-probe delay demonstrate the temporal evolution of the ro-vibrational wave packet in a time-resolved manner.

A paradigm of femtochemistry is the excitation of the NaI molecule to a predissociative state. The evolution of the wave packet following femtosecond optical excitation shows periodic Landau-Zener tunneling to separated atoms. This time dependence can be observed by resonant fluorescence of the Na atom induced by a probe pulse. Zewail (1993) has presented an overview of the rich field of femtochemistry.

As a final example, the *cis-trans* configurational change of the 11-*cis* retinal molecule should be mentioned. The absorption of a photon to an excited electronic state induces this transition. It is the first step in the vision process. The *trans* configuration has a different absorption spectrum. Thus the temporal evolution of this configurational change may again be probed by a femtosecond pump-probe technique. Matthies *et al.* (1994) established that the configurational change takes place in less than 200 fs. It is a prototypical example of the new field of femtobiology.

## IV. PHENOMENA AT HIGH FLUX DENSITIES

The development of femtosecond pulses has led to very high instantaneous power levels attainable with a relatively small table-top laser configuration. Diffraction-limited laser pulses may be focused to a spot size of an optical wavelength. The concentration of light in space and time has opened up new regimes of high-intensity radiation to experimental investigation.

A pulse of 1 $\mu$J of 100-fs duration is readily available from a Ti-sapphire laser system. When such a pulse is focused onto a surface of an absorbing medium with a spot size of $10^{-5}$ cm$^2$, the fluence is 0.1 J/cm$^2$. A large number of electron-hole pairs exceeding $10^{22}$ cm$^3$ is created in the absorption depth. This carrier density, created in $10^{-13}$ s, will change the band structure of gallium

arsenide. Huang *et al.* (1998) have shown that the effective indirect band gap decreases to zero by measuring the complex dielectric function by reflection of a time-delayed white-light probe pulse. When more than about 10 percent of the valence-band electrons have been promoted to the conduction band, the tetrahedral lattice structure becomes unstable and the second-order nonlinear susceptibility, observed by reflected second-harmonic light in reflection, vanishes within 100 fs, before significant lattice heating occurs.

On time scales longer than several picoseconds the energy transfer to the lattice causes melting and evaporation, both of which may be verified by post-pulse inspection. A well-defined damage threshold for the 001 surface of a gallium arsenide crystal irradiated by a 70-fs pulse at 635-nm wavelength is 0.1 J/cm$^2$.

The peak power flux density of a 1-$\mu$J pulse of 100-fs duration, focused onto an area of $10^{-5}$ cm$^2$ is one terawatt/cm$^2$. In a transparent medium, dielectric breakdown is initiated by multiphoton absorption and enhanced by avalanche ionization. Glezer *et al.* (1996) have proposed the use of damage spots with submicron dimensions inside transparent materials, such as glass, silica, or sapphire, for three-dimensional optical storage.

Pulsed irradiation of metallic targets at fluences exceeding 1 J/cm$^2$ creates very hot, high-density plasmas, which can serve as pulsed x-ray sources.

A special technique, first introduced by Strickland and Mourou (1985) is required to amplify short pulses to attain higher flux densities. An unfocused 10-fs beam of 1 cm$^2$ cross section with 1 $\mu$J energy has a power flux density of $10^8$ watts/cm$^2$. At this power level the beam becomes susceptible to self-focusing and filamentation in solid-state amplifier media with good energy storage characteristics such as Ti-sapphire, Nd-Yag, and alexandrite. The technique of chirped pulse amplification permits amplification by a factor of 10 000 or more. For this purpose the pulse is first stretched in time. Different frequencies have different optical path lengths, if diffracted between a pair of antiparallel gratings. A stretched pulse, chirped in frequency, is amplified and then recompressed by a matched combination of gratings. A pulse is also stretched by group velocity dispersion in an optical medium, but the recompression by a combination of gratings or optical prisms is more difficult in this case. Champaret *et al.* (1996) have amplified a 10-fs pulse with subnanojoule energy to a level near one joule, after stretching by a factor of $10^5$ and recompression close to the initial pulse duration.

When a one-joule 10-fs pulse is focused, power flux densities in the range of $10^{18}$ to $10^{20}$ watts/cm$^2$ are attained. Previously such power levels were only available in an assembly of many Nd-glass laser beams of large cross sections, as operated at the Lawrence Livermore National Laboratories and a few other large installations. These pulses with energies of 1–100 kJ have been used in the study of inertially confined fusion plasmas.

New physical regimes of exploration have been opened up by the use of one-joule femtosecond pulses. The Coulomb field responsible for the binding of valence electrons in atoms and molecules is on the order of $e/a_0^2$, where $a_0$ is the Bohr radius. According to Poynting's formula, the light field amplitude equals this Coulomb field of about $10^9$ volts/cm at a power level of about $10^{15}$ watts/cm$^2$. In this regime the light field can no longer be considered as a small perturbation. At this power level harmonics of more than one hundred times the laser frequency are created. The phenomenon of above-threshold ionization is related to the quiver energy of a free electron in an intense oscillating field.

The quiver motion of the electron becomes dominant at higher power levels. Here one should first solve for the motion of the free electron in the strong pulse, and the Coulomb atomic field becomes a perturbation.

A low-energy free electron will start to oscillate parallel to the transverse electron field. The Lorentz force due to the transverse magnetic field will cause an oscillation at twice the light frequency in the longitudinal direction. Classically and nonrelativistically the quiver energy $e^2E^2/2m\omega^2$ at $10^{19}$ watts/cm$^2$ at 1 $\mu$m wavelength would be three times $m_0c^2$, where $m_0$ is the rest mass of the electron. The electron reaches relativistic velocities and the Lorentz force attains the same magnitude as the electric force. A Lorentz-invariant formulation is indicated and detailed solutions have recently been given by Startsev and McKinstrie (1997).

In short, focused pulses with very large spatial and temporal gradients in intensity give rise to ponderomotive forces, related to the gradient in quiver energy. In a plasma the positive heavy ions will not be displaced much, but the electrons may oscillate with large amplitude. Huge internal longitudinal electric fields may be generated in the wake of a short light pulse. Tajima and Dawson (1979) have proposed the acceleration of electrons traveling in synchrony with the wake field of a light pulse. Recent papers by Umstadter, Kim, and Dodd (1996) and by Siders *et al.* (1996) provide many references to the extensive literature. ''Table top'' electron accelerators using femtosecond pulses may become a reality.

The scattering of femtosecond pulses with highly relativistic electrons, produced by a LINAC accelerator, has been studied. Burke *et al.* (1997) have observed nonlinear Compton scattering and electron-positron pair production. The field of ultrahigh-intensity laser physics has recently been reviewed by Mourou, Barty, and Perry (1998).

In conclusion, ultrashort laser pulses have opened up not only the field of femtosecond time-resolved spectroscopy, but also the study of relativistic electrons and plasmas at ultrahigh intensities.

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