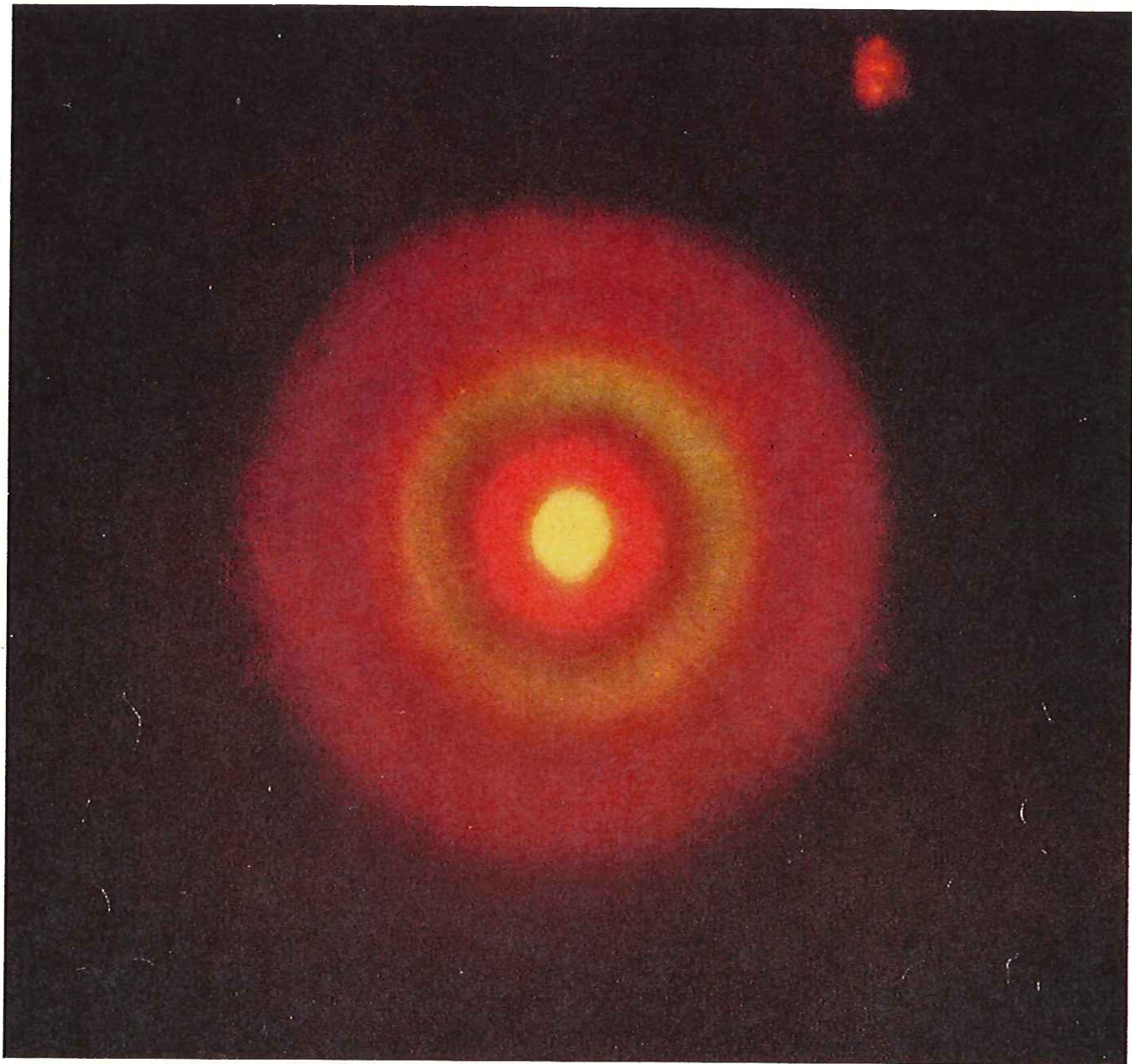


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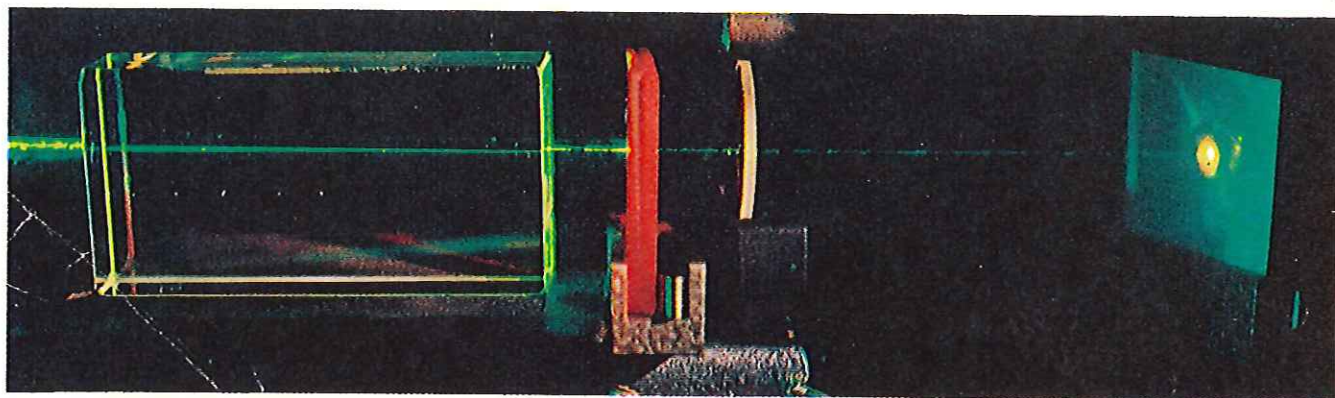
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EXTREME INTENSITY of the ultrashort laser pulses used in the authors' experiments to explore the atomic and molecular properties of materials is demonstrated by the colorful effect captured in this photograph. A pulse of green light derived from a "mode-

locked" solid-state laser was directed through a transparent piece of glass, distorting the refractive index of the glass in the path of the beam. The altered refractive index in turn reacted back on the light pulse to produce this circular pattern of spectral colors.



EXPERIMENTAL SETUP of the type employed to make the photograph at the top of the page was photographed in the laboratory of one of the authors (Alfano) at the City College of New York.

Outside the glass block the laser beam was made visible with the aid of smoke. The reddish objects are filters. For this picture the image at right was formed on paper instead of photographic film.

Ultrafast Phenomena in Liquids and Solids

Intense laser pulses a trillionth of a second in duration are harnessed to probe the extremely rapid energy-transfer times characteristic of events in the submicroscopic world

by R. R. Alfano and S. L. Shapiro

At the submicroscopic level even the quietest, most peaceful scene in nature is in fact a riot of activity. Within every substance, no matter how passive its outward appearance, atoms and molecules are in continuous motion: rotating, vibrating, rocking back and forth, colliding with their neighbors—all in times measured in picoseconds (trillionths of a second). Until recently it has not been possible to observe such atomic and molecular motions on a time scale of less than about a nanosecond (a billionth of a second) because of the inherent limitations of the available experimental techniques. As a consequence nearly all our knowledge about these extremely rapid events has been derived somewhat indirectly from an analysis of the characteristic frequencies of the radiation they cause to be absorbed or emitted.

The recent development of the "mode-locked" laser, a solid-state device capable of generating extremely intense light pulses with a duration on the order of a picosecond, has in effect opened up this hitherto inaccessible world of ultrafast phenomena to direct exploration. The light pulses from such a laser can be so intense that they tear an atom or a molecule apart into its basic building blocks (protons, neutrons and electrons). The laser pulses can also alter the way an atom or a molecule behaves by disturbing its structure.

A dramatic example of the power of this new research tool is provided by the photograph at the top of the opposite page. The picture shows a novel effect observed when a sufficiently intense pulse of green light from a mode-locked laser is directed through a piece of transparent glass. The laser pulse significantly

changes the refractive index of the glass, causing the altered refractive index in turn to react back on the light pulse in such a way as to generate a brilliant array of colors spanning the entire visible spectrum.

In this article we shall discuss techniques for using such ultrashort laser pulses to probe rapid energy-transfer processes in various materials. Historically this effort has evolved from two different directions. In one approach the experimenter studies the characteristic frequency spectrum of a material in order to derive information about its structure and its internal processes; in the other approach he subjects the material to some outside shock and then measures the material's characteristic "relaxation time," that is, the time it takes for the atoms or molecules of the material to return to their normal states.

Measuring Frequency Spectra

The frequency spectra of the light emitted and absorbed by materials have been the subject of investigation ever since man first noticed that objects have color. The first systematic scientific study of the interaction of light with matter was carried out by Isaac Newton, who in 1666 succeeded in splitting the white light of the sun into different colors with a prism. Newton reported these results in his first scientific paper, which appeared in 1672. His theory that "ordinary white light is a mixture of rays of every variety and colour" was vigorously attacked by such eminent contemporaries as Robert Hooke and Christiaan Huygens, causing Newton to consider giving up natural philosophy altogether. Newton also believed that light

consisted of tiny corpuscles. When in 1803 Thomas Young demonstrated that light consisted of waves, he too was vehemently assailed, because it was felt that he was undermining the corpuscular theory of Newton.

In 1873 James Clerk Maxwell published his general wave theory of electromagnetism, explaining light propagation in terms of waves that could be of any frequency. Thus the colors observed by Newton correspond to frequencies that can be detected by molecules sensitive to visible light and interpreted in the eye-brain system. In 1905 Albert Einstein, trying to explain the ejection of electrons from metallic surfaces by light, introduced (with the aid of Max Planck's quantum principle) the concept that the energy in a light beam travels through space concentrated in the bundles called photons. By the end of the 19th century many materials had been shown to emit and absorb well-defined spectral frequencies. The origin of these mysterious discrete spectral frequencies was firmly established in the 1920's with the development of the theory of quantum mechanics, which united the corpuscular and wave theories of light.

According to quantum theory, atoms and molecules have distinct energy states corresponding to different configurations of the electrons around nuclei. Discrete spectral lines appear when a transition from one energy state to another occurs in the atomic or molecular system and the excess energy is emitted or absorbed in the form of a light wave. Spectral lines yield information about atomic and molecular structure by telling us where the allowed energy states lie and which transitions between these

energy states are possible. Different frequency regions yield information on the various types of molecular motion that occur in matter.

Additional information about the structure of materials from their spectra became accessible after an important effect was discovered experimentally by C. V. Raman in 1928. This phenomenon, now commonly called the Raman effect, occurs whenever monochromatic light passes through any transparent material. The emerging light is somewhat less monochromatic than the incident light; new frequencies are added to the original beam as "side bands" but are so weak that a sensitive apparatus is required for their detection. Some of the new frequencies are discrete and well separated from the original frequency and are attributable to the vibrational motion of atoms within molecules; these vibrational frequencies were the ones first observed by Raman. Vibrational frequencies are low compared with visible-light frequencies because they arise from the motion of the massive nuclei, whereas the visible frequencies arise from the motion of the much lighter electrons.

In the 1930's new, lower Raman frequencies were discovered. These frequencies are associated with rotational

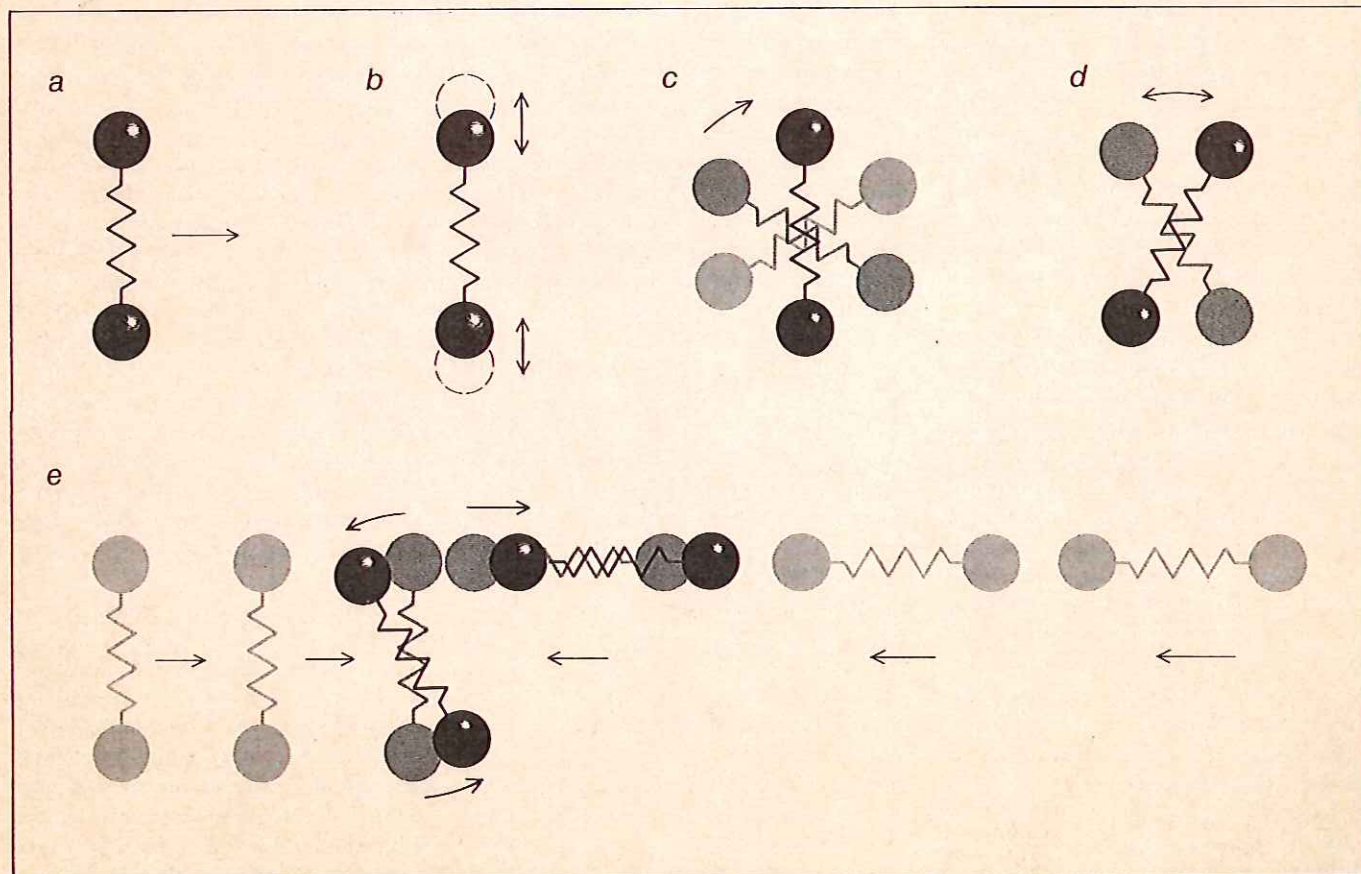
motions of molecules and with acoustic waves in liquids and solids. A subsequent discovery revealed a frequency band that clusters around the original light frequency and is slightly broader than the spectrum of the monochromatic light; this spectrum is caused by the disordered thermal motion of the individual atoms or molecules. Within the past decade light-scattering research has had a rebirth because of the invention of the laser and of new tools for examining the frequency spectrum. As a result the frequency-analysis approach has furnished a wealth of new information on molecular and atomic behavior. It is possible to obtain an estimate of the lifetime of a particular energy transition using the frequency-analysis approach (by computing the reciprocal of the frequency bandwidth of the transition); this indirect method of investigation is rarely employed, however, because it often leads to large errors.

Measuring Rapid Relaxation

Rapid molecular-energy-transfer relaxation times were first measured with mechanical devices, because advanced electronic techniques did not yet exist. In 1859 Edmond Becquerel devised a

spinning-disk technique capable of resolving times as short as a ten-thousandth of a second [see top illustration on opposite page]. The property most important for measuring a short time interval with any mechanical device is either a rapid rotational velocity or a rapid translational velocity. In Becquerel's scheme two slotted disks are mounted on a shaft with the luminescent sample placed between the two disks. As the disks spin, light from a light source passes through the first disk, exciting the sample and causing it to luminesce. The luminescence is observed by the experimenter behind the second slot at a time determined in part by the angle formed by the slots in the two disks and in part by the angular velocity. By varying the velocity of rotation or the angular displacement of the second disk one can measure the duration of the luminescence.

In 1905 Robert W. Wood devised a technique similar to Becquerel's that demonstrated a lifetime as short as five hundred-thousandths of a second for the luminescence of zinc sulfide bombarded with radiation emitted by radium [see middle illustration on opposite page]. Wood coated the rim of a wooden disk with zinc sulfide and placed a speck



VARIETIES OF MOLECULAR MOTION are represented schematically by the spring-coupled two-atom systems in this drawing.

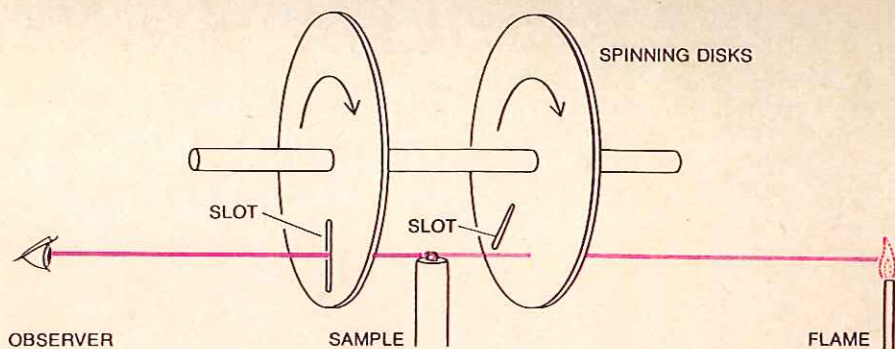
Sample molecular motions shown include a translation (a), a vibration (b), a rotation (c), a libration (d) and a collision (e).

of radium above the disk on the point of a needle. The disk was mounted on the shaft of an electric motor. He viewed the apparatus in a dark room and found that the luminescence came from a sharp point when the disk was stationary or rotating slowly but was drawn out into a streak when the disk was rotating rapidly. The length of the streak divided by the velocity of the rim of the wheel then yielded the lifetime of the luminescence. In 1921 Wood, using a spark to excite the sample on a disk, was able to measure times as short as two millionths of a second.

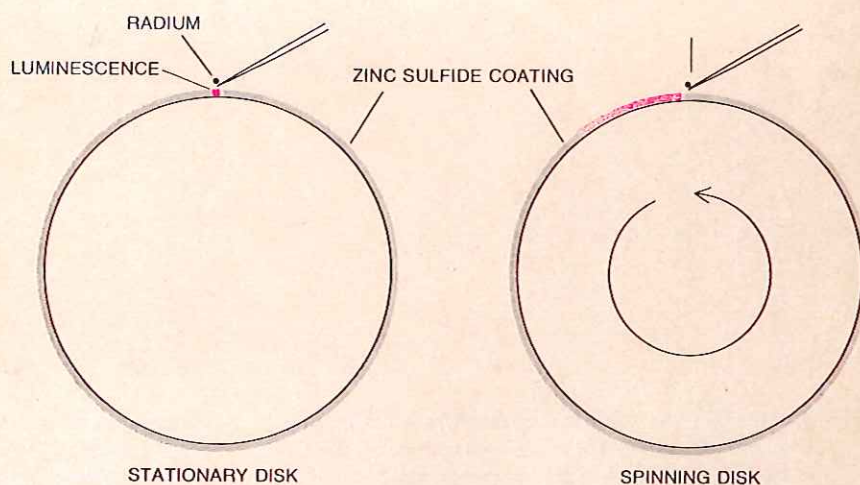
Wood and his colleague Charles E. Mendenhall later found that liquids could be investigated by another mechanical technique. They used a high-pressure pump to force a liquid containing a fluorescent dye through a nozzle at high velocity [see bottom illustration at right]. A tiny hole was made at the end of the nozzle for sunlight to enter and excite the dye. The fluorescent tracks they observed were less than a tenth of a millimeter long; from this observation they concluded that the fluorescent lifetime for the dye in water was less than four ten-millionths of a second.

Another ingenious mechanical device for measuring rapid relaxation times was the streak camera invented by S. I. Vavilov and V. L. Levshin in 1926 [see top illustration on next page]. In this scheme a spark of short duration excites a sample; luminescence from the sample then passes through a slit, is collected by a lens, bounces off a mirror and is imaged onto a photographic plate. If the mirror is rotated at high velocity, the luminescence is recorded as a streak on the photographic plate, indicating by its length the luminescent lifetime of the sample.

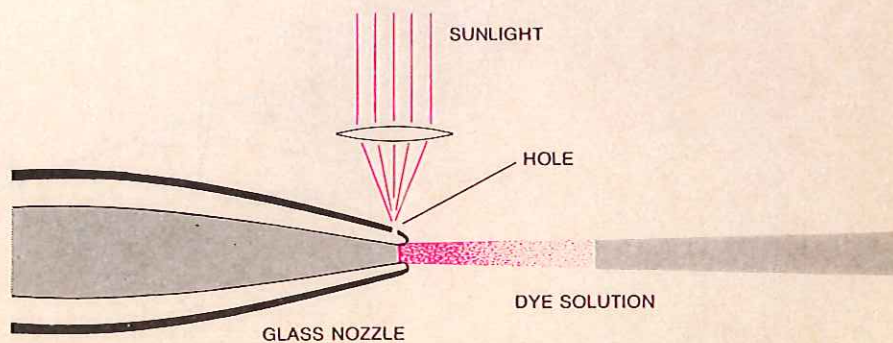
About 1925 electronic techniques began to replace mechanical devices for measuring rapid relaxation times. The first of these techniques made use of a shutter that was based on electro-optic effects discovered by John Kerr in 1875. The thought that led to Kerr's investigation was in his own words "that if a transparent and optically isotropic insulator were subjected properly to intense electrostatic force, it should act no longer as an isotropic body upon light sent through it." (An isotropic body is a body whose properties are the same in all directions.) Kerr found that when a direct-current electric field is applied across a piece of glass, the index of refraction of the glass is different in the direction of the field. In technical terms, a birefringence is said to be induced.



PHOSPHOROSCOPE, an ingenious mechanical device invented by Edmond Becquerel in 1859, was capable of resolving luminescent lifetimes as short as a ten-thousandth of a second. The sample was placed between two spinning disks. Light from a flame source passed through a slot in the first disk, exciting the sample and causing it to luminesce. The luminescence observed through the slot in the second spinning disk enabled the experimenter to determine the luminescent lifetime of the sample. In Becquerel's original apparatus a complicated set of gears was attached to the disks and the device was cranked by hand.



SIMILAR TECHNIQUE, devised by Robert W. Wood in 1905, was employed to demonstrate that the luminescence stimulated from zinc sulfide by radiation from radium has a lifetime of only five hundred-thousandths of a second. Wood coated the rim of a wooden disk with zinc sulfide and caused it to luminesce by placing a speck of radium above the disk on the point of a needle. When the disk was stationary or was rotated slowly (left), the luminescence came from a small point; when the disk was rotated rapidly (right), the luminescence was drawn out into a streak. The lifetime of the luminescence was obtained by dividing the length of the streak by the velocity of the rim of the disk.



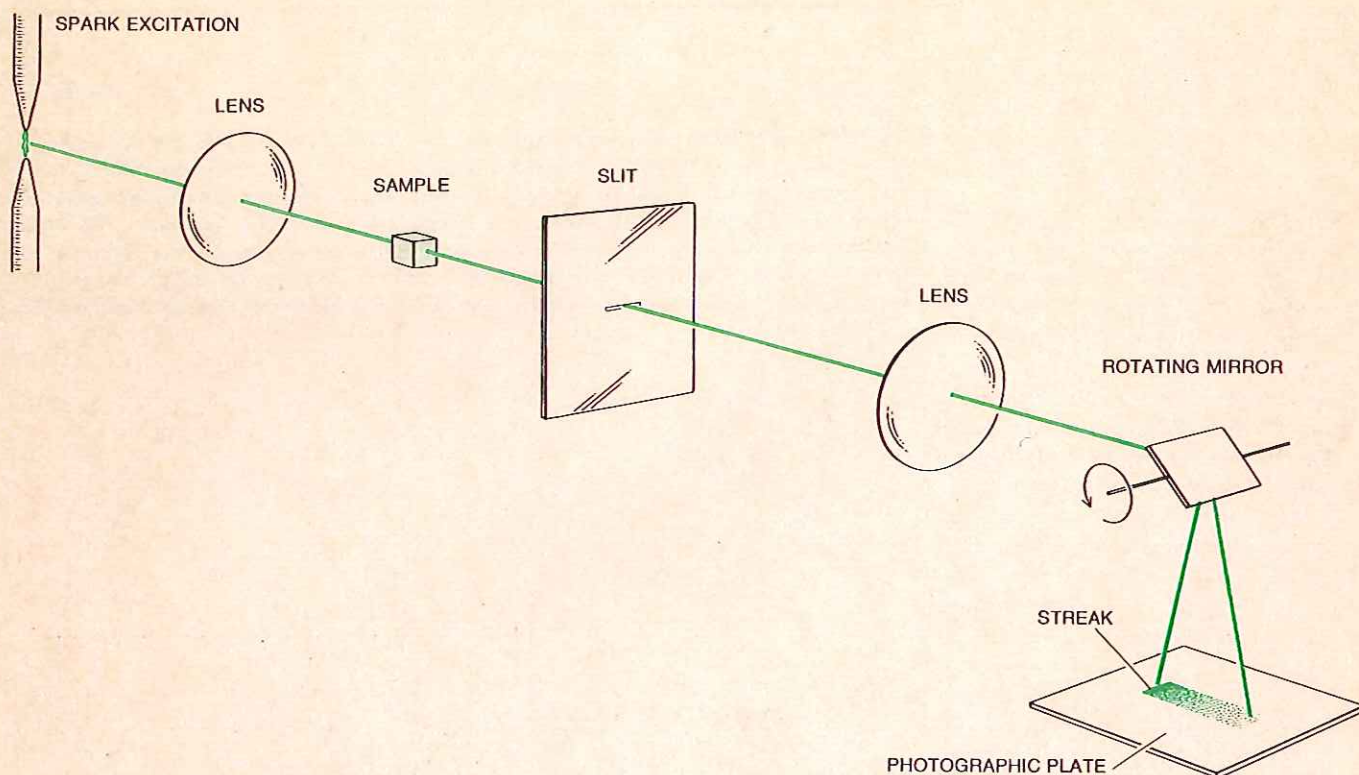
FLUORESCENIN DYE was found by Wood and his colleague Charles E. Mendenhall to have a fluorescent lifetime of less than four ten-millionths of a second with the aid of the mechanical technique depicted here. The solution of fluorescein in water was forced through a glass nozzle at high velocity by means of a high-pressure pump. Fluorescence was excited in the dye solution by sunlight entering through a small hole near the end of the nozzle. The fluorescent lifetime was measured by dividing the length of the fluorescent streak (typically less than a tenth of a centimeter long) by the velocity of the liquid.

According to Kerr, the birefringence is caused by dielectric particles that become polarized and tend to align themselves along the direction of the electric field. The particles subsequently attract one another, which leads to a compression and to an increase in the refractive

index along the lines of electric force. Based on principles discovered by Kerr, a direct-current optical shutter, or Kerr gate, was built by Henri Abraham and J. Lemoine in 1899. Although these two investigators succeeded in demonstrating that Kerr's device was capable of

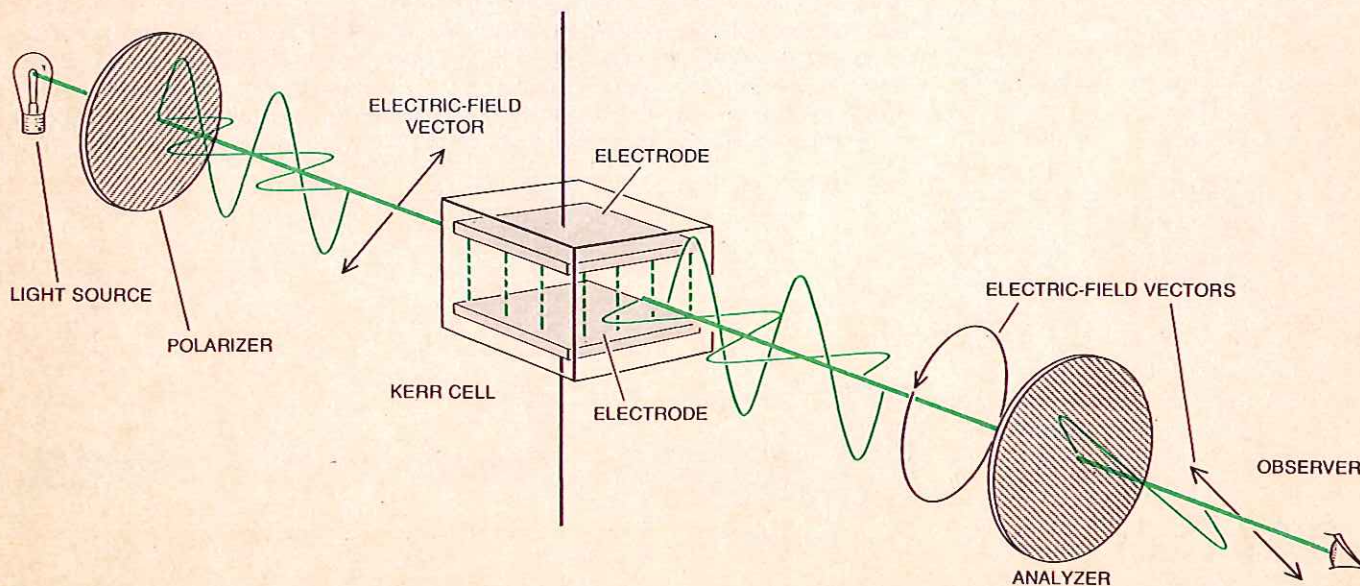
measuring rapid time intervals, a quarter-century was to pass before it was used systematically for that purpose.

The direct-current Kerr gate consists of two metal electrodes immersed in a cell of liquid situated between crossed polarizer and analyzer filters [see bot-



MECHANICAL STREAK CAMERA, invented by S. I. Vavilov and V. L. Levshin in 1926, was capable of measuring even shorter luminescent lifetimes. Light from a spark discharge was focused on a sample, causing it to luminesce. The luminescence from the sample then passed through a slit, was collected by a lens, bounced off a

rotating mirror and was imaged on a photographic plate. The rapid rotation of the mirror "smeared" the luminescence across the plate, forming a streak whose length indicated the luminescent lifetime of the sample. Electronic techniques subsequently replaced such mechanical devices for measuring rapid molecular-relaxation times.



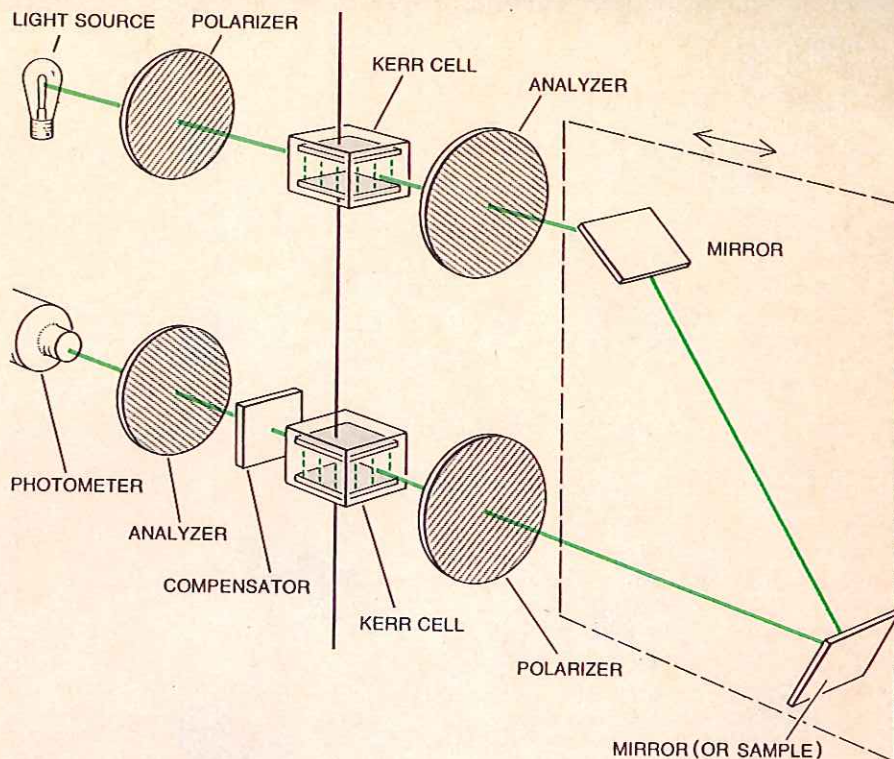
DIRECT-CURRENT KERR GATE, an early electronic device for measuring rapid molecular-relaxation times, was based on electro-optic effects discovered by John Kerr in 1875. The device consisted essentially of two electrodes immersed in a liquid cell situated between crossed polarizer and analyzer filters oriented at $+45$ degrees and -45 degrees with respect to the axis of the applied

electric field. When no voltage is applied to the Kerr cell, none of the incident light, which is linearly polarized by the polarizer, passes through the analyzer. When a high voltage is applied, however, the light becomes elliptically polarized on passing through the Kerr cell, with the result that the polarization component of the light parallel to the axis of the analyzer is transmitted.

tom illustration on opposite page]. The polarizer is oriented at an angle of $+45$ degrees with respect to an axis perpendicular to the metal plates and the analyzer at -45 degrees. A light beam passing through the polarizer is therefore polarized at an angle of 45 degrees. The polarization of the light remains unchanged when the beam passes through the cell because there is no preferable new direction in the isotropic liquid. The gate remains closed (that is, no light is transmitted through the system), because the light has no component in the analyzer direction if the analyzer is oriented at 90 degrees with respect to the direction of polarization. When a strong direct-current electric field is applied across the liquid, however, the gate transmits light, because the light beam becomes elliptically polarized on passing through the liquid cell; as a result the component of light polarized along the analyzer axis is transmitted. The elliptical polarization arises from the fact that the light wave can be split into two components; the one that is polarized along the electric-field axis slows down or speeds up with respect to the one that is polarized at right angles to the electric-field axis, because of the change in refractive index due to the field.

If an electric-field pulse of short duration is applied to the electrodes of the liquid cell, only the portion of light coincident with the electric-field pulse passes through the analyzer of the gate. The resolution time, or fastest shutter time, of this type of gate is determined by the shortest duration provided by an electrical voltage pulser: about a nanosecond. Even though the time resolution of the shutter is about a nanosecond, however, experimenters through the early 1940's had to resort to an additional bit of craftiness to measure short lifetimes with it. Electronic devices such as the high-speed oscilloscope and the fast photomultiplier were unavailable at that time, and rapid relaxation times had to be measured with complicated shutter schemes.

One such scheme, an improved version of a design devised originally by Enrique Gaviola in 1926, was used by W. Szymanowski in 1935 to measure lifetimes as short as a nanosecond with an accuracy of a few percent [see illustration on this page]. The apparatus works as follows. Two Kerr cells are electrically connected to some voltage source, which is varied synchronously and sinusoidally at a characteristic frequency. Light from a light source passes through the first Kerr cell and is modulated at this frequency. The light is re-



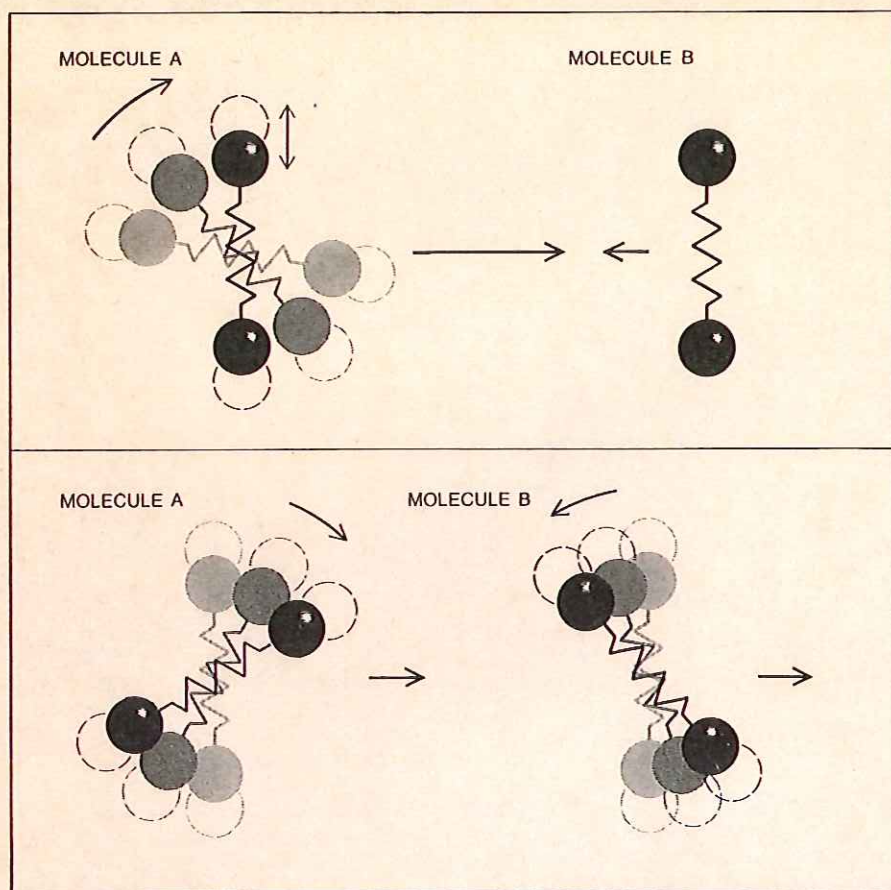
COMPLICATED SHUTTER SCHEME based on the principle of the direct-current Kerr gate was designed by Enrique Gaviola in 1926; an improved version of this scheme was later used to measure fluorescent lifetimes as short as a nanosecond (a billionth of a second) with an accuracy of a few percent. The apparatus consists of two Kerr cells hooked up in series with the voltage across them varying synchronously and sinusoidally at a characteristic frequency. Light from a light source is modulated electronically in the first Kerr cell. After being reflected by a system of mirrors the light passes through the second Kerr cell only if it arrives in phase with the modulation. If a fluorescent sample is placed at the position of one of the mirrors, the induced fluorescence from the sample will be delayed with respect to the frequency of the second Kerr cell by an amount that depends on the relaxation lifetime of the fluorescence. Phase differences can be adjusted by moving the part of the apparatus within the broken line, by varying the ellipticity of the polarization with a compensator or by changing the frequency. A plot of the intensity of the light received as a function of frequency enables one to derive fluorescent lifetime of the sample.

flected from a system of mirrors and arrives either in phase or out of phase at the second Kerr cell, depending on the length of the light path between the cells. The phase difference can be adjusted by adding a compensator in the second Kerr cell.

If one of the mirrors is replaced by a fluorescent substance, the fluorescent light will no longer arrive in phase at the second Kerr cell because of the time delay attributable to the relaxation lifetime of the fluorescence. The light that passes through the second Kerr cell is detected by a photometer and depends on that lifetime. By varying the frequency at rates comparable to the lifetime one can obtain a curve of the intensity at the photometer as a function of frequency, and from this curve one can derive the fluorescent lifetime. This "phase shift" technique was developed because the photometers could measure only the average intensity of the light and were not yet fast enough to respond to rapid variations in light intensity.

The first use of high-speed photomultipliers capable of responding to rapid lifetimes was made as recently as 1948. At that time nuclear physicists were very interested in determining the lifetime of certain phosphors used in scintillation counters. The method by which a scintillation counter monitors the decay of nuclei is based on the fact that particles released by a nuclear event can cause ionization in liquids or solids with the consequent emission of light. The light waves can then be detected by high-speed coincidence-counting circuits, and the decay time of the nuclear event can be inferred from a measurement of the decay of the light intensity. Since some nuclear decays are of exceedingly short duration, the characteristic lifetime of the scintillator must be rapid indeed.

In 1948 George B. Collins measured fluorescent lifetimes by allowing the emission from a sample of radium to impinge on a phosphorescent substance and then detecting the light emission from the phosphor as a function of time



ENERGY IS EXCHANGED between different types of motion in a collision involving molecules. Before the collision depicted in this drawing, for example, molecule *A* is translating, rotating and vibrating, whereas molecule *B* is just translating (*top*). After the collision the distribution of translational, rotational and vibrational modes is altered (*bottom*).

with a high-speed photomultiplier connected to an oscilloscope. He found that the passage of a single million-electron-volt electron produced enough light in the phosphor for observing both the rapid rise of the fluorescence determined by the minimum response time of the photomultiplier circuit and the decay of the fluorescence, which yielded the fluorescent lifetime. Later, bursts of X rays were used to excite scintillating samples for the measurement of lifetimes in conjunction with photomultipliers and oscilloscopes.

Using an ionized particle is probably not the most accurate way of measuring fluorescent lifetimes, however, because the lifetime depends on the means of excitation. Excitation with a gamma ray, for example, may yield a different decay time than excitation with a neutron or a beta ray. This difference in decay time enables the experimenter to discriminate between emission of different particles but would not necessarily determine the true fluorescent lifetime of the material.

A more conventional scheme for measuring fluorescent lifetimes, not subject to such a drawback, is to excite a sample with a pulse of ultraviolet radiation ob-

tained from a hydrogen flashtube and to detect the fluorescence with a photomultiplier connected to an oscilloscope. Such a technique has been used by I. Beriman and his co-workers at the Argonne National Laboratory to measure fluorescent lifetimes in a variety of materials, with the times measured being as short as a nanosecond.

Harnessing the Picosecond Laser

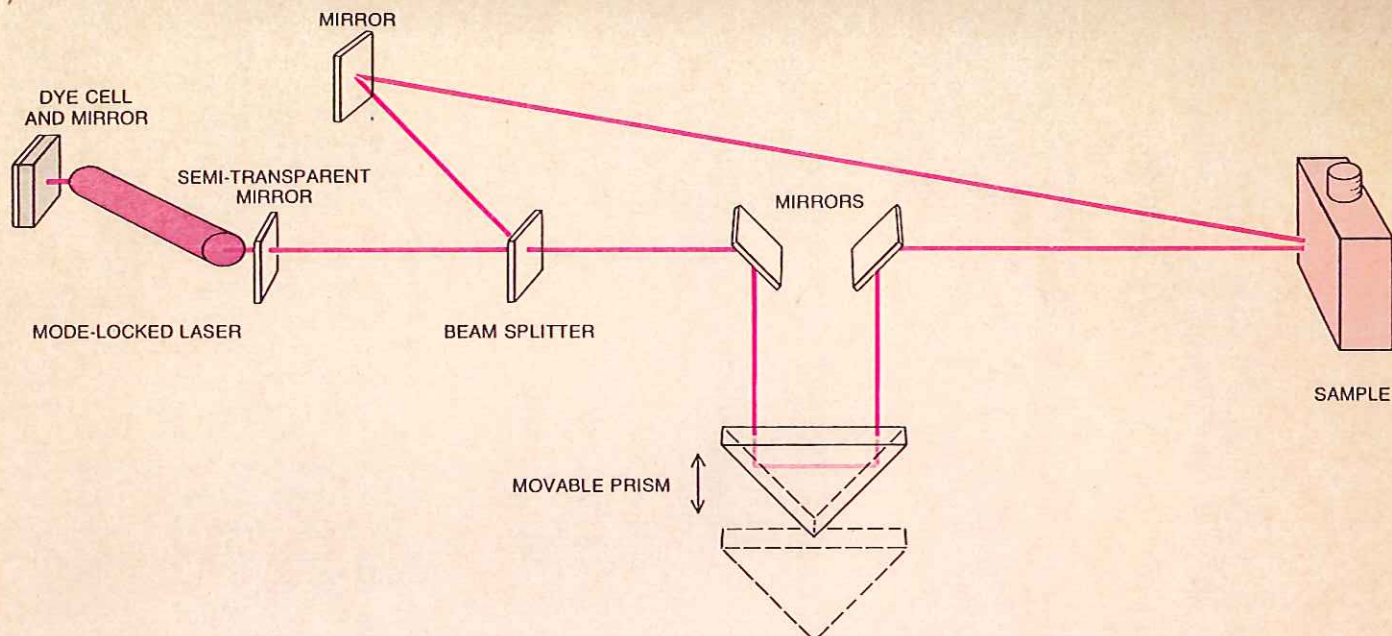
With the advent of ultrashort laser pulses one can now study, in addition to rapid fluorescent processes, the dynamics of energy transformation between the different types of motion that occur in solids, liquids and gases. For example, a molecule moving in a liquid with a particular velocity and vibrating and rotating at a well-defined rate can collide with another molecule at rest and transfer some or all of its kinetic, vibrational and rotational energy. In a real material one has a collection of colliding molecules that interact, exchange energy and come to equilibrium between the various types of motion. If one particular vibration or rotation is selectively excited in a molecule by a light beam, this mo-

tion will decay by transforming its energy into other vibrations, rotations and molecular motion by means of collisions in an interval of about a picosecond in a liquid or a solid.

In crystals, where atoms are interconnected in a regular periodic array, the atoms are in collective vibration. Depending on the complexity of the crystal and the constituent molecules, the lattice can have many vibrational modes. The frequencies of these vibrations extend from the audible to the optical, and their modes are called acoustical and optical phonons. The energy of lattice vibrations is quantized in analogy with the photon, which is the quantum of energy of a light wave. The complexity of the forces between the molecules results in a coupling between these different vibrations, or phonons, so that a single vibration excited by a laser pulse can readily decay into other vibrational motion or heat.

To measure fast decay times and to determine routes of energy transfer between molecules, one needs a clock with a time-scale index of a picosecond. Just as a kitchen clock cannot accurately measure events that take place in less than a second (such as the explosion of a firecracker or the rapid blink of an eye), so a fast-decay-time clock cannot perform its function unless it has a time-measuring capability faster than the event to be measured. Such a clock with the necessary time-scale index is available; it uses the light pulse emitted from a mode-locked laser. The duration of the light pulse (about a picosecond) denotes the smallest divisional marking on the clock's time scale, corresponding to the markings for seconds on an ordinary clock.

In the laser clock the constant speed of light traveling over a known distance provides the basis of the time-measuring mechanism. It takes a light beam one nanosecond to travel a foot in space. An interval of time on the clock is determined by the separation between two light pulses, which can be varied by arbitrarily spacing the two pulses in a manner analogous to the setting of the hour and minute hands on an ordinary clock. As an example, consider two light pulses traveling toward a target on the same line and separated by a distance of a foot. The second pulse will obviously arrive a nanosecond after the first. The clock is calibrated by knowing the coincident position of the two light pulses. Then the two pulses can be separated by any known distance. Coincidence is accomplished by a process that is accentuated when the two light pulses



TWO SYNCHRONOUS ULTRASHORT LIGHT PULSES suitable for calibrating a fast-decay-time clock to an accuracy on the order of a picosecond (a trillionth of a second) can be produced by taking the emission from a mode-locked laser and reflecting part of the beam with a semitransparent mirror while allowing the rest

of the beam to pass through the mirror. The separation of the two pulses is then adjusted by means of a scheme that directs the pulses along different paths to a target. In this scheme a movable prism delays one pulse with respect to the other by changing the length of one optical path between the source and the target.

intersect; any "nonlinear" optical effect (such as "frequency-doubling" in a suitable crystal) will do. Various nonlinear processes used in picosecond-pulse clocks will be discussed below.

Two synchronous ultrashort light pulses can be produced by taking the emission from a mode-locked laser, reflecting part of the beam with a semitransparent mirror and allowing the rest of the beam to pass through the mirror and then adjusting the separation of the two pulses by means of a scheme that directs the pulses along separate paths to a target [see illustration above]. To probe the time evolution within the microscopic world (the creation and annihilation of vibrations, rotations and so on) the first picosecond light pulse ini-

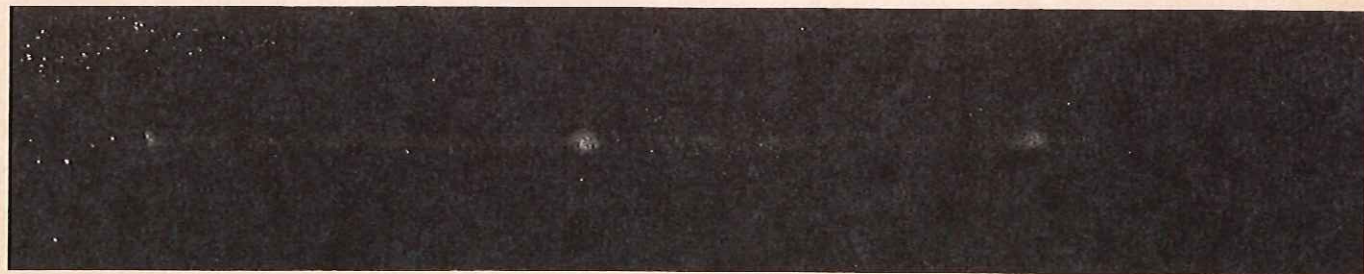
tiates the physical process to be studied and the second picosecond light pulse probes the time evolution of the process at different delay times.

For example, a laser pulse excites the system of molecules into a vibrational state, a rotational state or an electronic state by inducing a change of state on absorption of the light pulse. If the molecules are excited with a pulse longer than the decay time one is interested in, the molecules would be excited and would decay within the pulse width of the laser pulse, so that the measurement of time evolution would be difficult or impossible. For such a measurement one needs an ultrashort pulse that will excite the particular type of molecular motion abruptly, leaving the molecules to decay

freely under the influence of the forces within the microscopic world. The molecular decay can then be observed either by probing the number of remaining excited molecules with the second pulse or, if the excited molecule emits light, by observing the light decay with an ultrafast camera that is opened with the second pulse.

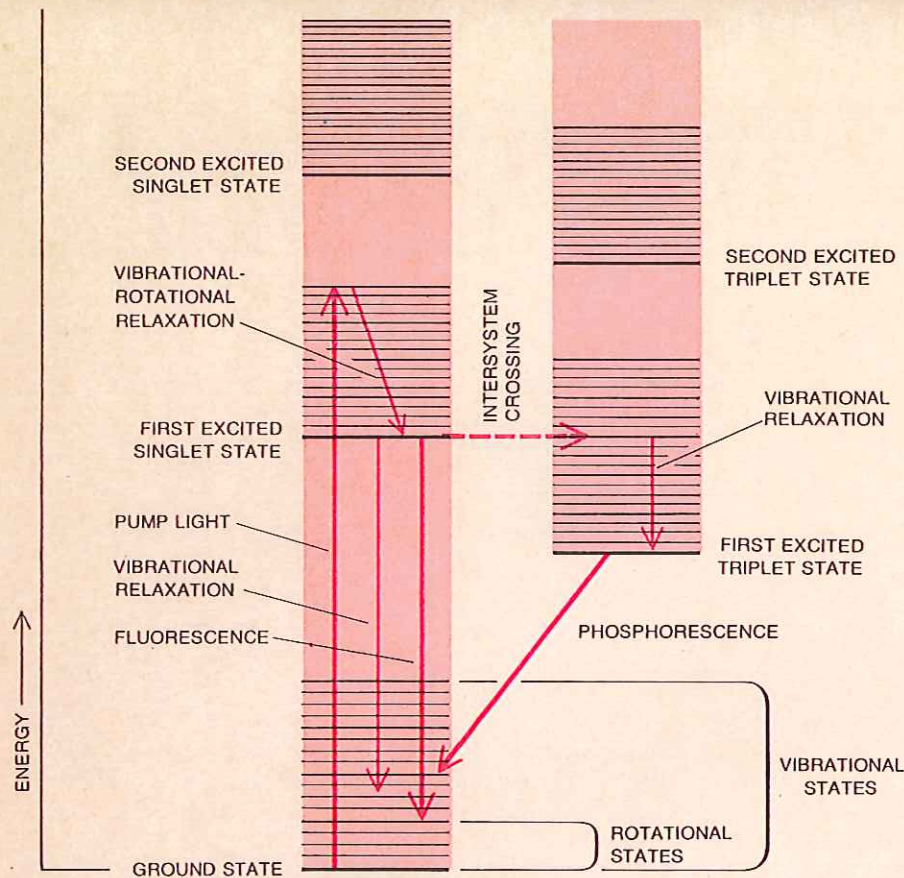
Let us now discuss how picosecond laser pulses are generated by a mode-locked laser, how the duration of these pulses is determined and how the pulses are used to measure ultrafast processes in liquids and solids.

The active medium of the mode-locked lasers used to generate high-power ultrashort light pulses must have a wide fluorescent bandwidth in order to

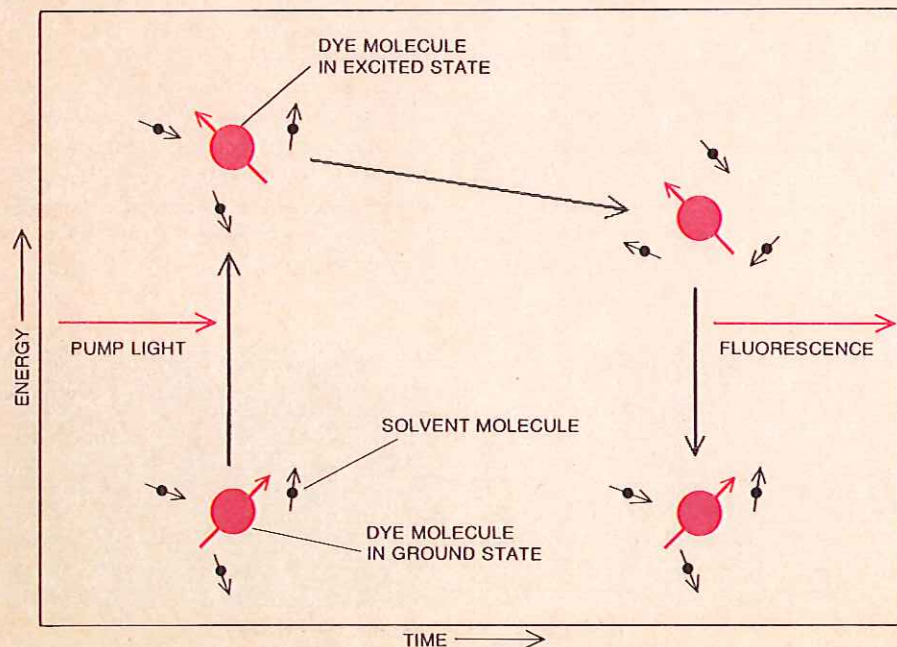


ULTRASHORT LIGHT PULSES are measured by means of the two-photon fluorescence technique developed in 1967 at Bell Laboratories. The technique is based on the special optical properties of an organic solution in which two photons of light must be absorbed to excite a molecule to a higher energy state from which it can decay spontaneously back to the ground, or lowest-energy, state, emitting fluorescent light in the process. Bright spots are produced in such a medium where pulses collide with each other,

because of the intensity at the collision point. The fluorescence from the liquid cell can be photographed, as demonstrated in this picture made by one of the authors (Shapiro). In this case the collisions occur because the beam, which enters from the left, is reflected back on itself by a mirror at the right. The length of the bright spots divided by the velocity of light in the medium yields a measurement of the duration of a single pulse. Laser pulses as short as .3 picosecond have been measured with this technique.



ENERGY LEVELS of a typical organic-dye molecule are shown in this highly schematic diagram. A light pulse can "pump" such a molecule from its ground "singlet" state to a sub-level of the first excited singlet state, from which the molecule decays rapidly by nonradiative processes (vibrational or rotational relaxation) to the lowest sublevel of the first singlet state. The molecule can then fluoresce, returning directly to the ground state, or cross over to a system of "triplet" energy levels, from which it can be deactivated by emitting phosphorescence in the process of returning indirectly to the ground singlet state.



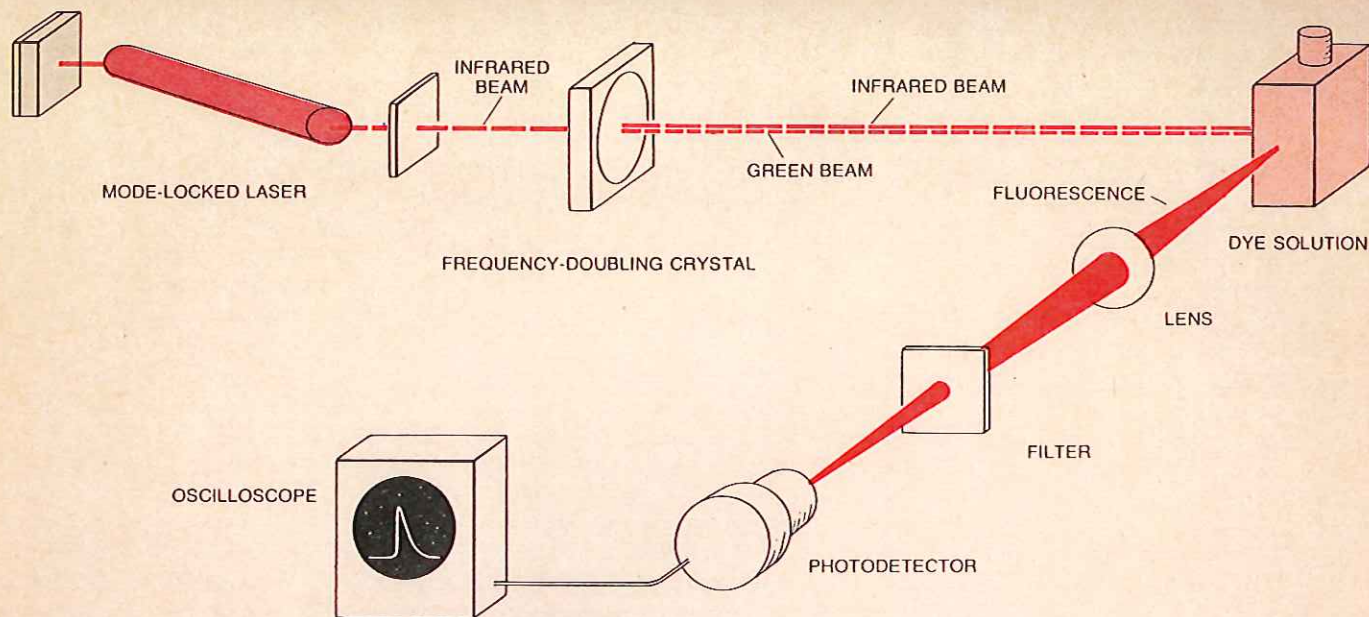
SOLVENT-SOLUTE INTERACTION involving dye molecules dissolved in a suitable solvent can be monitored by measuring changes in the intensity and wavelength of the fluorescence from the excited dye molecules. In this case the solvent molecules (*black*) rearrange themselves spatially in response to a new, excited configuration of a dye molecule (*color*). The fluorescent wavelength becomes time-dependent because the energy levels of the dye molecule shift in time in response to the dynamic molecular interaction.

produce picosecond pulses. The laser medium is contained between two mirrors, which form an optical cavity as in an ordinary laser. This cavity restricts the oscillating wavelengths within the broad bandwidth to just those wavelengths that satisfy nondestructive interference conditions; in other words, an integral number of wavelengths must equal the round-trip optical length of the cavity. The laser oscillates only at discrete frequencies, corresponding to those wavelengths called cavity modes. These closely spaced modes are amplified by stimulated emission, and a typical output spectrum can consist of hundreds or even thousands of them.

To obtain intense short-pulse emission one must establish a definite phase relation between the modes with a modulating element placed in the cavity. This element locks the modes in phase and is the key to the mode-locked laser. A favorite element for mode-locked ruby lasers and neodymium-doped glass lasers is a bleachable dye whose absorption at the laser frequency decreases with light intensity. In a neodymium-glass laser many modes probably start oscillating simultaneously with random phases. When laser action begins over a wide bandwidth, there are fluctuations that have a duration equal to the inverse of the initial bandwidth; the laser has a head start on the production of short pulses because short fluctuations are already present. The dye attenuates the most intense of these fluctuations or pulses less than it does any other pulse, so that after hundreds of passes back and forth through the laser cavity, nonlinear-absorption discrimination results in one prevailing intense pulse.

The dye must be able to return to its ground state much more rapidly than the round-trip time of the cavity so that it can perform its function again and again. Because of the nonlinear characteristics of the dye, the peak of a pulse is attenuated less than its wings, resulting in pulse-sharpening. This pulse-sharpening proceeds until the maximum number of modes that can possibly be coupled together are in phase; then the pulse duration is just equal to the inverse bandwidth of this maximum number of modes, and it can become no shorter.

Pulse-sharpening is equivalent to adding side bands in phase in the frequency domain; the more side bands that are added, the shorter the pulse duration is. Side bands originate because any wave circulating in the laser cavity is amplitude-modulated at the round-trip time by an absorption loss at a frequency that



ULTRASHORT FLUORESCENCE-DECAY TIMES can be measured with this system, developed by Michael E. Mack of the United Aircraft Corporation. Picosecond light pulses from a mode-locked laser excite the sample; the resulting fluorescence is then detected by a fast photodiode and displayed on a traveling-wave oscilloscope. In a typical experiment a neodymium-glass laser is

used to generate short, powerful pulses at the infrared wavelength of 10,600 angstroms (*long dashes*); these pulses are then converted by the nonlinear optical process of second-harmonic generation (frequency-doubling) inside a potassium-dihydrogen-phosphate crystal to the green wavelength of 5,300 angstroms (*short dashes*), a more appropriate wavelength for pumping most materials.

is the inverse of the round-trip time. Therefore any frequency propagating in the cavity develops side bands in phase, which in turn develop side bands in phase, the process continuing until all the modes in the cavity have a well-defined phase relation with one another.

The secret of the high power obtained from the mode-locked laser is that when a certain number of modes oscillate together in phase, the peak power is that number times the average power when they oscillate randomly. Thus if out of a large number of modes oscillating with random phases 1,000 oscillate in phase, the pulse can be 1,000 times as intense. In this way an originally messy waveform can be turned into a well-behaved, intense picosecond pulse circulating in the laser cavity. The transmission through one of the cavity mirrors provides the output for experiments on rapid relaxation times.

One method of measuring the duration of ultrashort pulses utilizes the phenomenon of two-photon fluorescence. In this approach, which was first employed by one of us (Shapiro) at Bell Laboratories in 1967 at the suggestion of J. A. Giordmaine, one first chooses an organic-dye solution that cannot absorb a single photon of light (because there are no energy levels at the single-photon frequency) but can absorb two photons of light (because there are energy levels at twice the photon frequency). Since it takes two photons to excite a molecule

in the solution, the amount of absorption depends on the intensity squared of the incident radiation. After being excited to a higher energy level the molecules can return to the ground state by emitting fluorescent light, the amount of fluorescence being proportional to the amount of absorption.

When two light pulses collide in such a medium, the intensity increases significantly at the crossing point, and the absorption and the fluorescence at that point are much higher. When the fluorescence produced by the colliding pulses is photographed, a bright spot appears at the point of collision, and the length of the bright spot divided by the velocity of light in the medium gives a measure of pulse duration. With this technique pulses as short as .3 picosecond have been photographed, and the resolution of the technique should in principle be as good as .01 picosecond, or a hundred-trillionth of a second [see *bottom illustration on page 49*].

The light pulses emitted from mode-locked lasers are an ideal tool for studying the factors governing the transitions between molecular energy levels. The high energy and power of the laser pulses are suitable for pumping large numbers of molecules to excited states, and the short duration of the pulses is suitable for studying molecular transitions by probing the time behavior of light emitted from excited states. Until recently light emitted from optically ex-

cited molecules for a duration of about a ten-millionth of a second was called fluorescence, whereas light emission continuing thereafter was usually called phosphorescence. Today the definition is more technical, fluorescence corresponding to "spin-allowed" electric dipole transitions and phosphorescence to "spin-disallowed" transitions. Fluorescence and phosphorescence can occur only after molecules are excited by another energy source and can be differentiated from the exciting source by shifts in wavelength, time behavior, polarization properties and angular distribution.

The new techniques enable one to examine the buildup and decay of emitted light. The initial stages of fluorescence are sensitive to the energy redistribution within a molecule and to its environment. Processes where excited molecules change energy level without emitting light, called nonradiative transitions, can also be studied. To understand the mechanisms leading to fluorescence, let us follow the routes of deactivation of a typical organic molecule through its energy levels after it has been excited by a light pulse [see *top illustration on opposite page*].

The electronic level corresponding to the ground, or lowest, "singlet" energy state of the molecule is characterized by an electronic configuration where the paired electrons in the outermost orbits spin in opposite directions. "Triplet"

states arise when the electrons spin together in parallel in the same direction, the nomenclature originating with the fact that on close examination triplet states consist of three closely spaced energy levels. Extra sublevels in the diagram above singlet and triplet levels denote vibrational and rotational degrees of freedom of the molecule associated with that electronic state.

The level corresponding to the first excited electronic singlet state can also have vibrational and rotational energy levels associated with it. A light pulse can excite a molecule in the ground state to a sublevel of the first excited singlet state. Direct transition from a singlet state to the lowest-energy triplet state by light does not occur in the electric-dipole approximation, because light waves cannot supply the rotational momentum necessary to flip an electron spin from the antiparallel to the parallel orientation. From the sublevel of the first excited singlet state the molecule can decay to the lowest vibrational state in

the excited singlet state by transferring its vibrational and rotational energy to the surrounding medium by means of rapid collisions with other molecules. This decay process within an electronic manifold is a nonradiative transition and is characterized by a nonradiative decay time.

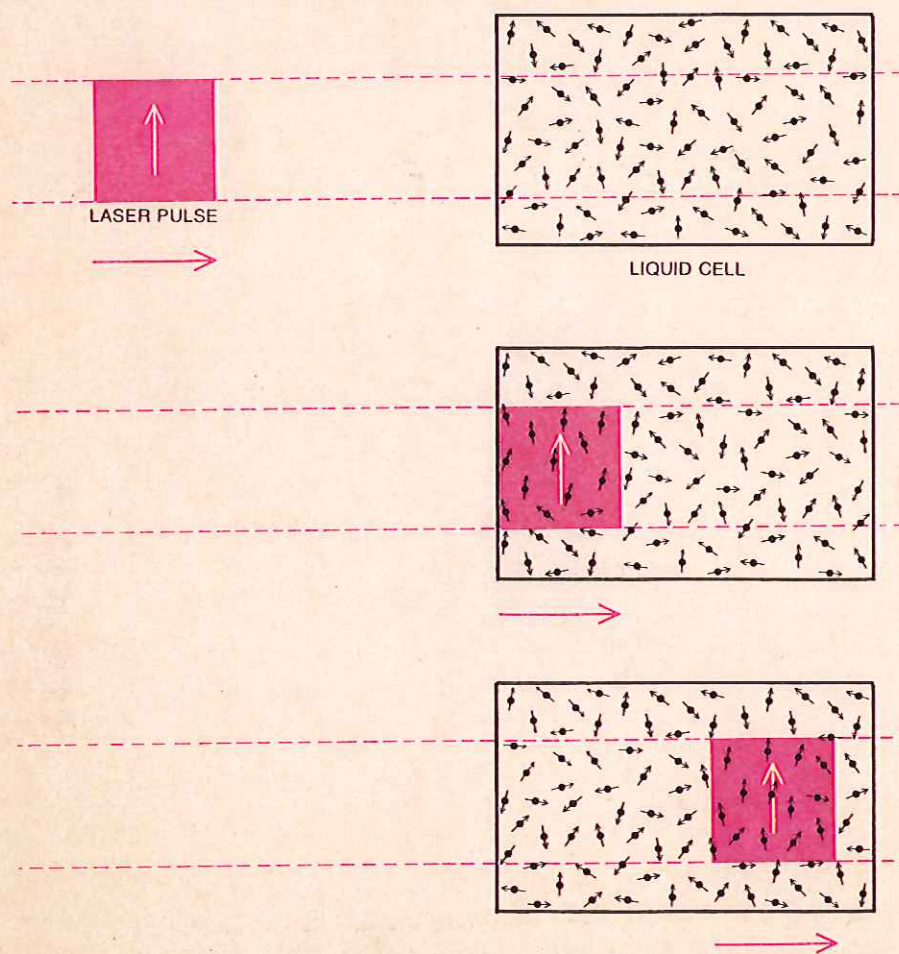
Once the molecule reaches the lowest singlet level it can return to the ground state by emitting fluorescent light, transfer its energy into heat, cross over to the manifold of different spin levels or transfer its energy to another molecule. Weak fluorescence from a dye indicates either a strong coupling between the singlet and triplet levels (leading to a fast intersystem crossing rate), or nonradiative depopulation of molecules to the ground state by vibrational decay, or a very slow decay rate between the singlet states.

A key for understanding molecular interactions is provided by the time behavior of fluorescence, because if a dye molecule is dissolved in a solvent, it can be excited into a new molecular configura-

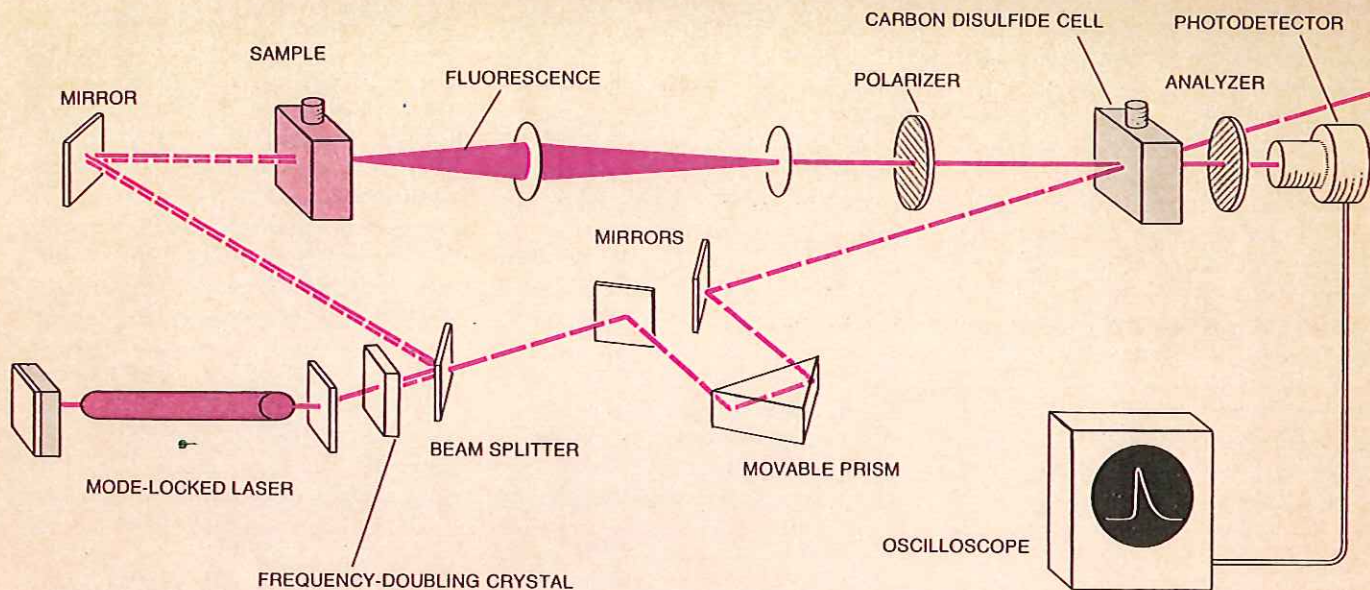
tion, and the solvent molecules will rearrange themselves spatially in response to the new configuration [see bottom illustration on page 50]. This spatial rearrangement is very rapid and can be monitored by changes in fluorescent intensity and wavelength. The fluorescent wavelength becomes time-dependent when the energy levels shift in time in response to dynamic molecular interactions. Such a dynamic interaction occurs when solvent molecules instantaneously "see" a solute-dye molecule change its electronic shape and dipole moment on excitation. A large difference between dipole moments in the ground state and the excited states leads to strong dynamic interactions with the solvent dipole moment; the molecules rapidly readjust by strong electrical dipole-dipole interactions. These dipole interactions cause the fluorescent wavelength to become time-dependent, so that solvent-solute interactions can be studied by choosing solvents with different electrical characteristics.

Many techniques have been developed recently that harness picosecond laser pulses for the study of the fluorescence process in the ultrashort time domains. In the simplest type of fluorescence-decay measurement, developed by Michael E. Mack of the United Aircraft Corporation, the mode-locked laser beam excites the fluorescence, which is then detected by a fast photodiode and displayed on a traveling-wave oscilloscope [see illustration on preceding page]. The resolution of such a system is typically a third of a nanosecond, which is sufficient for measuring the fluorescence-decay time for a number of dyes. For the measurement of relaxation lifetimes the duration of the laser pulse must be shorter than the relaxation lifetime and the laser-pump light must be absorbed in the material. The ruby laser and the neodymium-glass laser fulfill these essential criteria by emitting short, powerful pulses, which can be converted by nonlinear optical processes to any wavelength from the ultraviolet to the infrared.

The fundamental output wavelengths of these lasers are the red wavelength of 6,943 angstroms for the ruby laser and the infrared wavelength of 10,600 angstroms for the neodymium-glass laser. By second-harmonic generation (frequency-doubling) in a potassium-dihydrogen-phosphate (KDP) crystal powerful pulses can easily be generated at the ultraviolet wavelength of 3,472 angstroms and at the green wavelength of 5,300 angstroms. Most substances can be pumped with just the fundamental



SHORT-LIVED BIREFRINGENCE can be caused in a liquid by the passage of an intense pulse of polarized laser light (color). As the light pulse enters the liquid cell it causes the randomly oriented molecules (small black dots with arrows) in the liquid to become re-oriented in the direction of the pulse's electric-field vector (large white arrow). As a result the refractive index of the liquid in the region of the pulse is increased in the direction of the electric-field vector, producing a local, time-dependent birefringent condition.



OPTICAL GATE with a shutter speed of eight picoseconds is used by the authors to measure extremely rapid events such as the rise and decay of the fluorescence of dye molecules. In this system, developed by Michel A. Duguay and John W. Hansen of Bell Laboratories, a mode-locked laser generates an intense, picosecond pulse at the infrared wavelength of 10,600 angstroms (*long dashes*); the infrared beam then passes through a frequency-doubling crystal, which converts part of the beam into a green beam at a wavelength of 5,300 angstroms (*short dashes*). A dielectric mirror transmits the infrared beam and reflects the green beam. The infrared pulse travels along an optical path (whose length can be varied by a

movable prism) before entering a cell containing liquid carbon disulfide, where it induces a short-lived birefringence in the liquid. Meanwhile the green beam is absorbed by the sample, exciting that substance to emit fluorescence. The fluorescence is collected by a lens and is passed through the gate, overlapping the infrared beam in the cell. Birefringence in the liquid induced by the presence of the infrared pulse causes the portion of the fluorescence beam that is coincident in time with the infrared pulse to change its polarization from linear (due to the first polarized filter) to elliptical. In this manner an eight-picosecond section of the fluorescence beam is transmitted through the analyzer for examination.

and second-harmonic pulses emitted by these two lasers.

The oscilloscope-photodiode system is not fast enough to give information on nonradiative relaxation times, fluorescent rise times or ultrashort fluorescent lifetimes. The use of picosecond pulses as the basis of a clock mechanism eliminates these electronic time-resolution difficulties. In two early independent experiments J. Shelton and John A. Armstrong of the International Business Machines Corporation and Richard I. Scarlet, Joseph F. Figueira and Herbert Mahr of Cornell University pumped dye molecules in solution to a higher electronic state with intense picosecond pulses; both groups then used a weak second pulse to measure the rate at which the molecules returned to the ground state. Nonradiative relaxation times as short as six picoseconds were measured in this way.

The next major advance was the development of a technique for actuating an optical gate with picosecond pulses. In this technique, which is applicable for any light-emitting process over a wide range of wavelengths, the mode-locked laser beam both excites the fluorescence and triggers the gate, which operates like a superfast camera shutter. The device is called a gate because

when it is open it allows light to pass, whereas when it is closed it prevents its transmission. One idea behind the optical gate is to try to use the picosecond pulses themselves in a device, because then the time resolution will be in picoseconds and electronic problems will not arise.

The operation of an optical picosecond shutter is based on the principle of the Kerr shutter. The time resolution of a conventional Kerr shutter is not high enough for the measurement of really rapid decay rates, but these difficulties have been overcome with a picosecond Kerr optical gate developed by Michel A. Duguay and John W. Hansen of Bell Laboratories. In this device the temporally ultrashort electric-field pulse applied across the gate is provided not by an electronics system but by the electric field of the light pulse itself.

Since light is an electromagnetic wave made up of electric and magnetic fields it is an ideal source for an electric field. The strength of the electric field associated with the light emitted by an ordinary incandescent lamp, however, is too low to operate the shutter. In a mode-locked laser pulse the electric field can be as high as a million volts per centimeter, which is ideal for operating the ultrashort shutter.

As the laser pulse travels through the liquid, its electric field polarizes the molecules contained within the laser light-pulse duration, the pulse inducing a short-lived birefringence as a function of time [see illustration on opposite page]. Note that the direct-current Kerr gate and the picosecond gate differ; the latter requires no metal-plate electrodes in the liquid, because the intense electric field is provided by the light pulse, not by a voltage source. The time response of the induced birefringence in a given region is the result of both the pulse duration of the laser (typically six picoseconds) and the orientational response time of the molecules, which can be as short as a few picoseconds.

Picosecond optical gates with shutter times of about eight picoseconds have been constructed, and they have been used successfully to measure very rapid events [see illustration above]. In such a system a mode-locked laser generates an infrared pulse of high intensity and short duration at a wavelength of 10,600 angstroms. This beam passes through a frequency doubler (a KDP crystal), where 10 percent of the beam is converted into a new green beam at a wavelength of 5,300 angstroms. A dielectric mirror transmits the infrared beam and reflects the green one. The infrared pulse

travels along an optical path whose length can be varied with a movable prism. The infrared pulse enters a centimeter-long cell containing liquid carbon disulfide (CS_2) and induces a short-lived birefringence in the liquid.

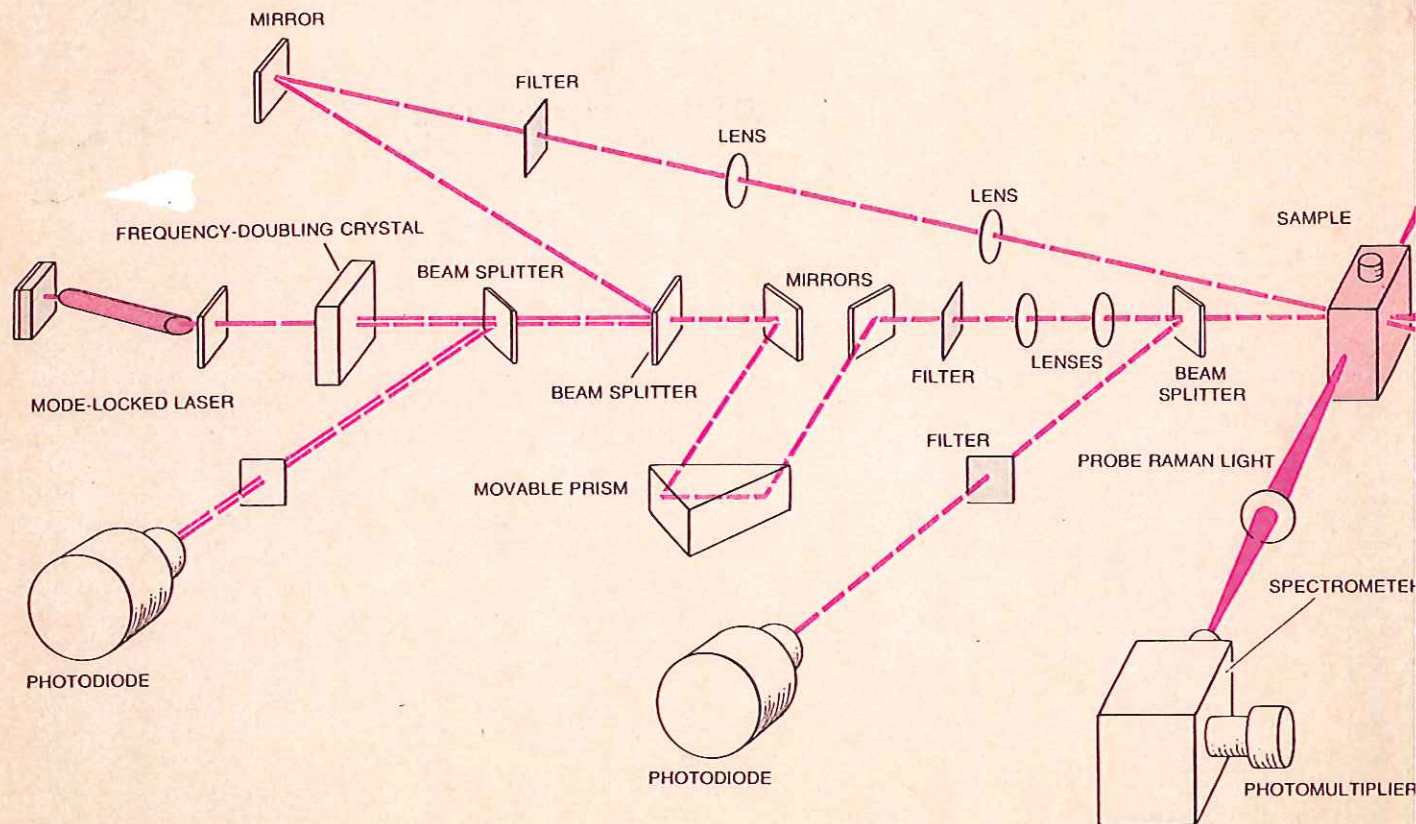
Meanwhile the green pulse is absorbed, thereby exciting the sample to fluoresce. The fluorescence is collected by a lens and is passed through the gate at an angle of about five degrees with respect to the direction of the infrared beam. The fluorescent beam is positioned by a lens at the cell so that it overlaps the infrared beam in the cell. The polarizer is oriented so that the fluorescence becomes linearly polarized at

an angle of 45 degrees with respect to the plane of incidence on passing through the cell. As long as the intense infrared beam does not pass through the carbon-disulfide cell, the fluorescence remains linearly polarized on passing through the cell and the analyzer extinguishes the fluorescence beam.

Birefringence induced by the presence of the infrared pulse causes the portion of the fluorescence beam that is coincident in time with the infrared pulse to change its polarization from linear to elliptical. Then light is transmitted through the analyzer. Essentially an eight-picosecond section is carved out of the fluorescence profile for examina-

tion. Different sections of the profile can be carved out by delaying the shutter pulse with respect to the pulse that excites the fluorescence in order to examine the time behavior of the fluorescence. The exact coincidence time between the infrared pulse and the green pulse can be obtained by measuring the intensity profile of the green pulse with respect to the time it takes for the pulse to pass through the gate. By monitoring the fluorescence signal as a function of delay time between the fluorescence excitation and shutter-opening time, the actual buildup and decay of the fluorescence can be determined.

This novel picosecond shutter was

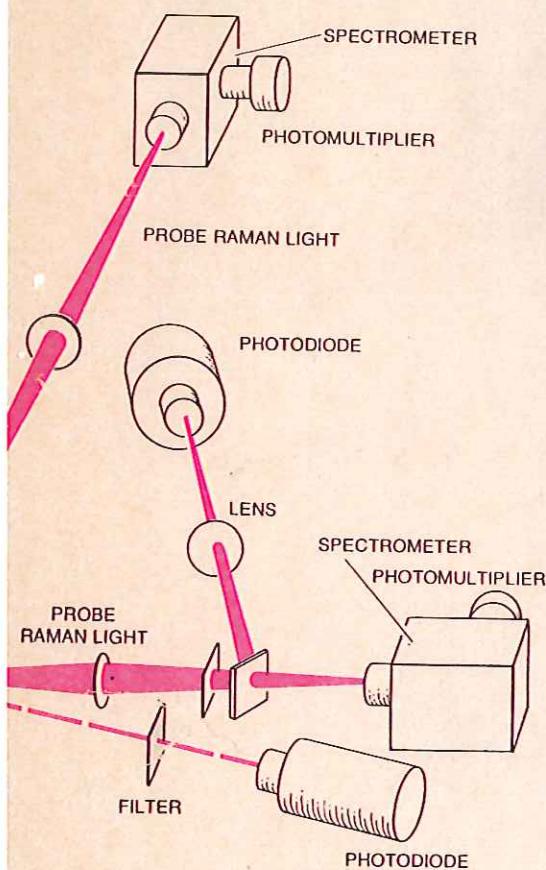


RAMAN CLOCK exploits the phenomenon of spontaneous and stimulated Raman scattering produced by picosecond laser pulses to measure the ultrashort lifetimes of molecular vibrations in liquids. In this system, developed by the authors while they were at the General Telephone and Electronics Laboratories, the molecular vibrations are created in the sample through stimulated Raman scattering by means of a powerful infrared pulse from a mode-locked laser. This treatment increases the population of molecules

in the excited vibrational state in direct proportion to the intensity of the stimulated-Raman-scattering light. A second, weak probe pulse at half the wavelength (green) is then applied some time after the first pulse and undergoes spontaneous Raman scattering off the excited vibrations. The intensity of the probe Raman light is proportional to the number of vibrations still present in the sample. By varying the delay time between the pump pulse and the probe pulse (with a movable prism) and by measuring the inten-

used by Duguay and Hansen to measure the rapid fluorescence decay time of the dye molecules 1,1'-diethyl-2,2'-dicarbocyanine iodide and cryptocyanine to be 22 and 14 picoseconds respectively. We have used the new shutter to measure the entire temporal behavior of the fluorescence intensity for erythrosin dye in water. The fluorescence of erythrosin rises quickly, reaches a sharp peak 60 picoseconds after excitation and rapidly decays to 37 percent of its intensity in a time of 90 picoseconds. These results yield a vibrational-rotational relaxation time in the excited electronic singlet manifold of 40 picoseconds.

An investigation of how different sol-



sity of the probe Raman light created from the scattering off the excited vibrations, one can determine both the growth and the decay of the excess vibrations. By measuring the intensity spectrum of the probe Raman light with respect to delay time, the decay routes and growth and decay times of subsidiary vibrations can also be measured.

vents affect these characteristic times reveals in some measure how vibrational and rotational energy is transferred within the same molecule or to surrounding molecules. The fluorescence-decay time of 90 picoseconds for erythrosin, for example, indicates a strong coupling between the singlet and the triplet levels, resulting in a very fast intersystem-crossing rate, since the lifetime can be this short only if molecules are depopulated from their excited state by mechanisms other than fluorescence.

The use of a picosecond Kerr gate has enabled Figueira and Mahr to measure exciton lifetimes in cadmium selenide of a few hundred picoseconds. (An exciton is a conceptual entity created in a crystal lattice by the exceedingly temporary pairing of an excited electron and an electron "hole.") Other applications of the gate have included measurements by us in collaboration with Michael Seibert of the General Telephone and Electronics Corporation of the fluorescence intensity profile of chlorophyll molecules, indicating a new step in the process of photosynthesis. Furthermore, we have shown that the picosecond broad-band emission discovered in our experiments [see top illustration on page 42] is ideal for detecting short-lived species through their characteristic absorptions. P. M. Rentzepis of Bell Laboratories has also reported measurements of nonradiative relaxation times in dye molecules.

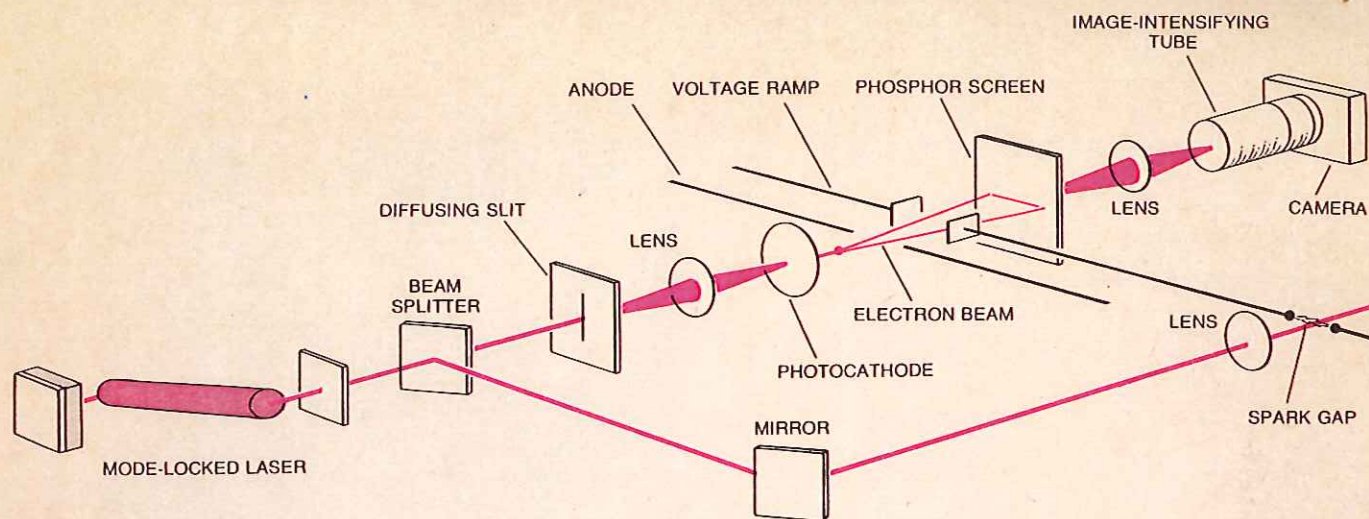
The transfer of the rotational motion of a molecule to its environment has been demonstrated by Kenneth B. Eisenthal, Karl H. Drexhage and T. Chuang of IBM with another picosecond-probe technique. They used a linearly polarized ultrashort light pulse to preferentially excite molecules oriented in a specific direction, thereby creating an anisotropic distribution of excited molecules. Then they monitored the rotation of these molecules back to an isotropic distribution by probing the absorption of the medium with light of a different polarization at later times. Their technique makes use of the phenomenon known as dichroism (the same phenomenon that enables Polaroid sunglasses to absorb one polarization of light while passing another, thereby eliminating the glare of reflections). It provides a unique way of investigating the interactions of a molecule with its environment. Solute molecules can be dissolved in different solvents and excited with picosecond pulses. Direct information on solvent-solute interactions is obtained by measuring the rate of return of the excited distribution to a randomly oriented distribution.

Experimental measurements of orientational relaxation times are surprising because they agree with a simple model that ignores detailed molecular interactions and instead treats a molecule rotating in a liquid much as one might treat a large rotating sphere (except that the gravitational forces in the molecular case are negligible). The surrounding medium is treated as a macroscopic entity. A specific molecular interaction that was expected to be important and to influence the orientational relaxation time is the hydrogen-bonding interaction. In this interaction alcohol molecules are bonded together with the positively charged hydrogen atom of one molecule bonded to the negatively charged oxygen atom of another molecule. This specific interaction, however, was found to play a negligible role in determining the rotational relaxation time of the large dye molecule rhodamine 6G in many liquids.

Further Applications

We shall now describe how picosecond pulses have been adapted to the measurement of vibrational lifetimes in liquids and to the determination of optical-phonon lifetimes in crystals. The adaptation of picosecond pulses for such measurements is perhaps their most important application so far for gaining an understanding of the transfer of energy within and between molecules.

A voluminous scientific literature accumulates each year on the normal vibrational modes of molecules in liquids and on optical phonons in crystals. The principal information for determining the structure of molecules and materials is derived from the frequency, line width, depolarization and intensity of spectral lines in Raman and infrared spectra. All these data tend to present a picture of a rather quiescent molecular world. Actually the molecular world is full of agitation and commotion as it continuously undergoes structural transformations. Because of the lack of an ultrafast clock with picosecond resolution, little attention had been paid to these interesting phenomena. The fact that everything happens so quickly (typically in a tenth of a nanosecond or less) had made it impossible to track the events. Now that these rapid transformations can be followed with picosecond pulses physicists are for the first time obtaining direct answers to such fundamental questions as "How long do molecular vibrations last?" and "What are the routes of decay of a molecular vibration or a phonon to other degrees of freedom in



PICOSECOND STREAK CAMERA, developed recently by workers in several countries, has an electronic circuit fast enough to resolve atomic and molecular events on a time scale of about a trillionth of a second. Light from such an event enters a slit and is focused onto a photocathode, where electrons are released. The electrons are accelerated through an anode and are then deflected

by a voltage ramp, which is actuated by focusing a portion of the original picosecond pulse into a spark gap. The increasing voltage in the ramp streaks the electrons across a phosphorescent screen so that the electrons released at different times strike the screen at different positions. A photograph of the resulting phosphorescent streak then gives a measure of the lifetime of the event.

liquids and crystals?" It is now possible to explore how such vibrations are transformed into one another in the same molecule or are transmitted to neighboring molecules. Moreover, by mixing different liquids one can learn how vibrations are transferred between different types of molecules.

Molecular vibrations and rotations last only picoseconds in liquids because the molecules move very rapidly, colliding frequently with one another. The collision rate is high because liquids are dense (1,000 times denser than air), so that molecules find themselves in close proximity to one another, where the electrical interaction forces are strong. Phonons in crystals collide frequently with one another for much the same reason. At room temperature the thermal energy is so high that much of it is converted into lattice-vibrational energy, with the result that immense numbers of phonons roam through the crystal. Under these conditions the dominant decay mechanism determining the lifetime of an optical phonon is a collision with another phonon that is already present in the crystal. This collisional decay is inferred to be a three-phonon interaction, where one phonon collides with a second phonon to yield a third phonon. At low temperatures, however, the decay mechanism must be quite different, because now few thermally excited phonons are present in a crystal and phonon collisions are relatively rare. Thus the predominant decay mechanism must be a spontaneous breakup of the phonon into two

new phonons. The two new frequencies generated must satisfy the conservation laws of energy and momentum. In addition the frequencies must be limited to lattice-vibrational modes of the crystal, which are finite in number and uniquely determined by the crystal structure. Therefore only certain possible routes of decay exist for phonons. If the crystal contains an impurity, phonons can also decay by interacting with the impurity.

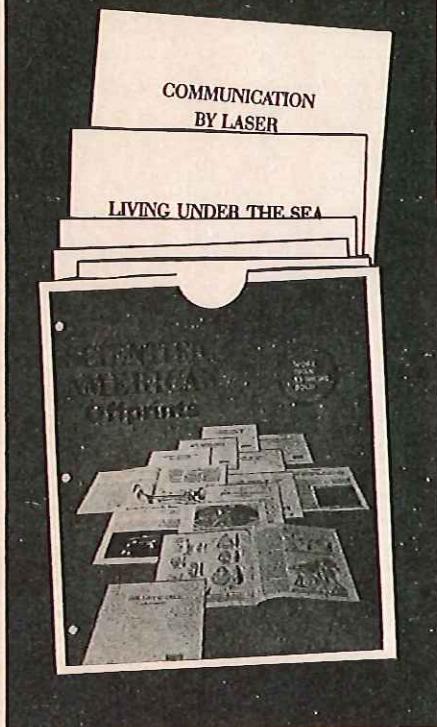
In liquids vibrational energy in a molecule can be transferred either to other vibrational modes of the molecule or to adjacent molecules. Symmetry of the molecular vibration is a determining factor in selecting decay routes. If one mixes two liquids, the vibrational motion of one molecular species can be transferred through collisions to the vibrational modes of the other species.

The mechanism of a clock capable of measuring ultrafast vibrational lifetimes exploits the phenomenon of spontaneous and stimulated Raman scattering produced by picosecond laser pulses. In this type of experiment the vibrations are excited through stimulated Raman scattering by means of a powerful picosecond laser pulse at the infrared wavelength of 10,600 angstroms [see illustration on pages 54 and 55]. This treatment increases the population of the vibrational state in direct proportion to the intensity of the stimulated-Raman-scattering light. A second picosecond probe pulse of weak intensity and different wavelength (5,300 angstroms) is then applied as a function of time after the

first pulse and is spontaneously scattered by the created phonons. The intensity of probe Raman light is proportional to the number of vibrations still present. By varying the delay time between the pump pulse and the probe pulse with a movable prism and by measuring the intensity of the probe Raman light created by the scattering of the excited vibrations, one can determine the rise and fall times of the excess number of vibrations. Moreover, by measuring the intensity of the probe Raman light with respect to delay time, the decay routes and the growth and decay times of subsidiary vibrations created by the excited vibration can be measured.

Two different vibrational-decay times have been measured in liquids: depopulation times and dephasing times. As an example of the dramatic influence that phase can have on the time behavior of a system we have mentioned picosecond-pulse emission from lasers resulting from the fact that the modes of the light-wave field are in phase. Molecules in liquids can also vibrate in phase with one another, producing an enormous vibrational amplitude as they oscillate in step, a far greater amplitude than when they vibrate out of step. Such coherent molecular vibrations are generated in the stimulated Raman process where coherent light waves excite the medium. Vibrations oscillating in phase can go out of step with one another through interaction forces in the medium, and the vibrational amplitude then drops precipitously to a low value. The exponential

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decay of the vibrational amplitude due to molecules' going out of step is called the dephasing time. The depopulation time is a measure of the decay of molecules to an entirely new state and is unlike the dephasing time, where the molecules vibrate out of step but can still remain in the same vibrational state. The depopulation time is a measure of the actual disappearance of created vibrations.

The measurement of depopulation times and dephasing times can be conveniently separated by experimental techniques. To measure the decay of the coherent oscillation by dephasing, the probe beam that is scattered by these vibrations at different delay times must come in at a particular direction such that conservation of momentum is preserved between the momentum vectors of the probe beam, the scattered beam and the coherent molecular vibrations. There are actually two particular directions corresponding to Raman frequencies that are upshifted and downshifted by the molecular vibrations. The depopulation of molecular vibrations is measured by incoherent Raman scattering of the probe beam by vibrations. The probe beam is sent in at an arbitrary angle with respect to the vibrations, and the scattered light is detected at an arbitrary angle. In this procedure the amplitude of the scattered light depends only on the population, since the vibrations at arbitrary angles contain little phase information. Strictly speaking, the two lifetimes are somewhat related. For example, if molecules oscillate in phase and one of them depopulates to a new state, then one less molecule is in phase and so the phase amplitude drops.

Using probe techniques, in 1970 we measured the optical-phonon lifetime in a calcite crystal to be 22 picoseconds at 100 degrees K. and 8.5 picoseconds at room temperature; we later estimated vibrational lifetimes in liquid nitrogen and benzene. In 1971 Alfred Laubereau, D. von der Linde and Wolfgang Kaiser of the Technical University of Munich, working with similar probe techniques, studied the decay of polyatomic molecules in the liquid phase and also investigated the decay of lattice vibrations in diamond. Later they extended their work to measure both the dephasing times and the depopulation times in ethyl alcohol and trichloroethane liquids. For ethyl alcohol they found a population lifetime of 20 picoseconds and a dephasing time 80 times shorter. The probe technique has also been extended by us to measure decay routes

in liquids, where new “daughter” vibrations created from the decay of another vibration were observed.

Three recent developments in picosecond diagnostic techniques lead us to expect further advances in the measurement of rapid relaxation times. These developments are (1) the invention of a picosecond streak camera, (2) the discovery of a new technique for generating still shorter light pulses and (3) the development of a picosecond dye laser that is “tunable” over a range of wavelengths.

In the streak camera, which has an electronic circuit fast enough to measure picosecond events, light from a slit is focused onto a cathode where electrons are released and accelerated toward a phosphorus substance, which emits light [see illustration on page 58]. A voltage increasing with time is provided by focusing a picosecond pulse into a spark gap; the voltage streaks the electrons across the phosphor so that electrons released at earlier times appear at a different position on the phosphor than electrons released later. A photograph of the phosphorescence then gives a measure of the time behavior of the event. Such cameras have been built by A. John Alcock and Martin C. Richardson at the National Research Council in Canada, by D. J. Bradley, B. Liddy and W. E. Sleat at Queens University of Belfast in Northern Ireland, by L. Coleman and S. Thomas of the Lawrence Livermore Laboratory of the University of California, and by several groups in the U.S.S.R.

The second recent development is the discovery of mode-locking procedures capable of generating still shorter light pulses by M. J. Colles at Harvard University and by Kaiser and his co-workers at the Technical University of Munich. Pulses as short as .3 picosecond can now be generated reliably, and it seems probable that still shorter pulses can be obtained by this method.

The third recent advance, the development of a tunable picosecond dye laser, was made by E. Ippen, S. Shank and A. Dienes of Bell Laboratories. This laser combines ultrashort time resolution with convenient wavelength flexibility; moreover, it emits repetitive pulses and thus is adaptable to the averaging techniques required for low signal levels.

We therefore look forward to measurements of still shorter relaxation times, and to further applications of these powerful new techniques that illuminate the mechanisms of energy transfer in the submicroscopic world.