Picosecond spectroscopy and research on fast processes

M. S. Pesin and I. L. Fabelinskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences

The development of techniques for generating picosecond pulses and for isolating and amplifying individual pulses, together with the use of the Kerr effect initiated by the electric field of an intense light wave (the ultrafast optical/shutter), has made it possible to develop various direct optical methods for measuring short times and investigating the kinetics of fast processes in the picosecond range. Methods for the direct measurement of molecular anisotropy relaxation times in various liquids and the lifetimes of optical and acoustic phonons in liquids and solids are described, and results obtained by these methods are given and compared with the values obtained by indirect methods. The results of direct measurements of the luminescence decay times of certain dyes are presented, as well as the results of studies of the kinetics of the absorption of light in dense electron-hole plasmas in semiconductors and of the solvation of electrons in solutions. The use of the ultrafast optical shutter to investigate the structures of picosecond pulses, to obtain separate photographs of objects lying close together, to look through fog, and to obtain successive photographs at picosecond exposures is described. A method of amplifying weak picosecond pulses and recording them on videotape for subsequent display on a kinescope is also described.

CONTENTS

1. INTRODUCTION

Direct optical methods of measuring the lifetimes of phonons and investigating the kinetics of fast processes in the nanosecond ($\sim 10^{-9}$ sec) and picosecond ($\sim 10^{-12}$ sec) ranges became possible after techniques were developed for generating intense short light pulses.

In this review we shall not touch on the applications of image converters or the other electronic methods of investigating fast processes, which have reached a fairly high degree of development. Here we shall discuss only optical methods.

The first direct optical measurements of the lifetimes of acoustic and optical phonons and anisotropy relaxation times, and the first such investigations of certain fast processes, were made about six years ago and have been described in part in a brief review written by one of the present authors.[1] Since then there has been considerable progress in the technique of investigating fast processes, and important new results have been obtained. The present review is devoted to a description of the basic techniques developed and results achieved in the last few years but does not pretend to be exhaustive or complete.

The existing methods of investigating fast processes are based on the splitting of an intense short light pulse into two pulses that differ widely in intensity. The in-

tense part of the split pulse gives rise to nonlinear optical phenomena, whose kinetics are investigated with the aid of the second, low intensity part, whose polarization or wavelength has been altered (in the second case, by using the second or third harmonic pulse) to facilitate identification of the two parts of the split pulse. In many cases the intense part of the beam controls the operation of an ultrafast optical shutter, which we shall discuss in more detail later, and the weak light beam whose wavelength has been altered is used to probe the object under investigation, or is itself the object of study. In experiments of this type one can investigate not only nonlinear optical phenomena, but any fast processes whose light (the light that makes the phenomenon visible—it may be either intrinsic or extrinsic) can be "photographed" at different stages in the development of the phenomenon with the aid of an ultrafast shutter.

The physical basis for the construction of an ultrafast optical shutter was found in the experiments of Mayer and Gires,[2] who showed that an intense laser light pulse traveling in a liquid consisting of anisotropic molecules, but isotropic on the whole, induces birefringence in the liquid and thus makes the isotropic liquid similar in optical properties to an optically uniaxial crystal. In other words, Mayer and Gires showed that an intense light pulse orients the anisotropic mole-
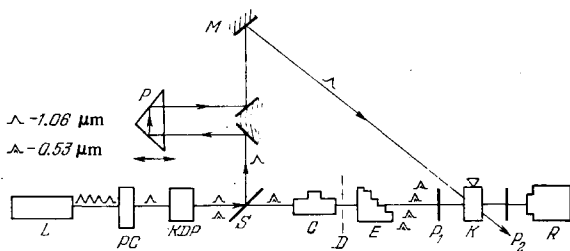
FIG. 1. One possible setup for investigating the kinetics of fast processes: L—laser with mode locking emitting a train of picosecond pulses; PC—Pockels cell for isolating a single picosecond pulse (the KDP crystal generates the second harmonic); S—beam splitter; P—movable prism, part of a variable delay line; M—mirror; C—cell; D—diffuser; E—echelon, acting as a stepwise delay line; P_1 and P_2—crossed polarizers; K—ultrafast-shutter cell, usually filled with carbon disulfide; R—radiation detector, sometimes combined with a spectrometer.

cules of the liquid just as an external electric field does in the Kerr effect.

The resulting birefringence will last as long as the light pulse, provided the light pulse is longer than the relaxation time of the anisotropy of the molecules composing the liquid. A device making use of this phenomenon is usually called a "Kerr light cell" or is designated by some other inappropriate name. Following Duguay and Hansen, we shall call such a device either an ultrafast optical shutter, or simply an ultrafast shutter, and the vessel containing the liquid consisting of anisotropic molecules, we shall call the shutter cell.

Figure 1 is a schematic diagram of apparatus for investigating fast processes. A laser operating in the mode-locking regime emits a train of short (picosecond) pulses, one of which is isolated by a Pockels cell. Part of the light of this isolated pulse is converted to the second harmonic on passing through the KDP crystal. The separating plate S passes the second harmonic light pulse but reflects the fundamental pulse into the adjustable optical delay line P. After passing through the delay line, the fundamental pulse is reflected by the mirror M and falls on the cell K (which is most frequently filled with carbon disulfide), where it induces the Kerr effect.

The second-harmonic light signal passes through the cell C containing the investigated material (the investigated object may be located elsewhere, depending on the purpose of the experiment) and strikes the diffusely scattering plate D, which forms a fairly broad light beam that passes through the echelon E. The light, which illuminates the echelon uniformly, is separated by the echelon into individual light beams. The delay time between two successive light beams is given (for normal incidence) by the formula

$$\Delta t = \frac{d}{c}(n-1),\qquad (1)$$

where n is the refractive index of the echelon glass and d is the thickness of the echelon plates.

Thus, we have a discrete set of "delay lines" for the probe pulses. The presence of two optical delay lines makes it possible to vary the experimental conditions so that the character of the time variation of the intensity of the several light beams from the comparatively weak second-harmonic probe pulse can be determined at various times with respect to the arrival of the peak intensity of the fundamental-frequency pulse at the cell K.

Measurements of this type can be used to investigate both the growth and decay of the birefringence induced in the liquid by the intense light and the kinetics of phenomena induced by the weak (or intense) light that has passed through the echelon. In such a scheme the operation of the ultrafast shutter (the cell K and polarizers P_1 and P_2) is based on the nonlinear phenomenon of optical birefringence, but one can investigate any phenomenon, whether it is associated with nonlinear processes or not. All that is required is that the receiver R, which scans the investigated signal in frequency, be sensitive enough to register the light incident on it. Other delay lines may be used in place of the echelon. An ultrafast optical shutter was first used to investigate fast processes by Duguay and Hansen.[3]

The apparatus diagrammed in Fig. 1 can be altered by removing the polarizers P_1 and P_2 and the cell C, and filling the cell K with the liquid or gas to be investigated or replacing it by a solid specimen in which nonlinear phenomena (or their consequences) induced by the intense light pulse are to be investigated.

Such a method was first proposed by Shelton and Armstrong.[4] Quantitative measurements of the lifetimes of optical and acoustic phonons can be made and the kinetics of various fast processes can be investigated with simultaneous frequency and time resolution, using apparatus of either type.

2. DIRECT AND INDIRECT MEASUREMENTS OF ANISOTROPY RELAXATION TIMES

A. Preliminary remarks

It is well known that the appearance of birefringence in an isotropic liquid consisting of anisotropic molecules on the application of an external electric field, which was discovered by Kerr in 1875, is due to partial alignment of the molecules with their axis of greatest polarizability (easy polarization axis) in the direction of the field. When the external electric field is removed, the thermal motions completely disorient the molecules and the liquid as a whole ceases to exhibit birefringence.

It is also known (see, e.g.,[11]) that if we define the birefringence as the quantity

$$\Delta n(t) = \delta n_\| - \delta n_\perp = \lambda K E^2(t),\qquad (2)$$

where $\delta n_\|$ and $\delta n_\perp$ are the changes in the refractive index in the directions parallel and perpendicular, respectively, to the field E, λ is the wavelength of the light, and K is the Kerr constant, we find that the birefringence decays after sudden removal of the field according to the exponential law
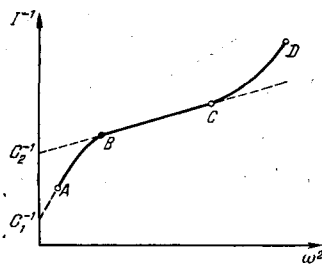
FIG. 2. Typical plot form of the ω^2 vs I^{-1} for the Rayleigh-line wing.

$$\Delta n\,(t) = \text{const}\cdot\exp\,(-t/\tau), \qquad (3)$$

in which τ is the birefringence persistence time, the anisotropy relaxation time, or still another designation, the time in which a molecule almost "forgets" that it has been oriented by the electric field.

On the other hand, the thermal motions of the molecules give rise to density and anisotropy fluctuations in regions of the liquid that are small compared with the wavelength of light. An anisotropy fluctuation occurs when the molecules in a small region have their easy polarization axes accidentally turned to a greater degree in one direction than in any other direction. Since such regions are extremely numerous and their accidentally preferred orientations have the most varied directions, the material as a whole is isotropic. The molecules in each anisotropy fluctuation will become disoriented with time, i.e., the anisotropy fluctuation will be "dissipated." Each such fluctuation is an optical irregularity that scatters light, and the time variation or appearance and "dissipation" of the fluctuations modulates the scattered light. This modulation manifests itself in the spectrum of the scattered light. As is known, [5] the anisotropy fluctuations give the depolarized spectrum of the scattered light or the wing of the Rayleigh line. If there is just one anisotropy relaxation time, then, as has been shown (this problem is discussed in detail in[5]), the half-width of the Rayleigh line will be

$$\Delta\omega = \frac{1}{\tau}\,.$$

Thus, the Kerr birefringence persistence time following sudden removal of the electric field and the anisotropy fluctuation "dissipation" time are the same. The Kerr birefringence persistence time has been repeatedly measured; the first measurements were those of Abraham and Lemoine in 1899, but reliable quantitative results were achieved only 70 years later (Duguay and Hansen, [3] 1969).

B. Indirect methods of determining the anisotropy relaxation time

Indirect measurements of the anisotropy relaxation time from the intensity distribution in the Rayleigh-line wing were begun in 1945 and gave values close to the modern values. [6] They also facilitated the explanation of new aspects of the phenomenon, consisting primarily in the fact that the intensity distribution in the Rayleigh-line wing cannot be described with a single anisotropy relaxation time. [5] In the first quantitative

theory of the phenomenon, developed by Leontovich, [7] the assumption that there is only a single anisotropy relaxation time was made in order to facilitate the calculations.

In this admittedly simplified theory, the intensity distribution in the depolarized-scattering spectrum far from the Mandel'shtam–Brillouin components has the Lorentz shape with the single anisotropy relaxation time τ:

$$I\,(\omega) = C\,[1 + \omega^2\tau^2]^{-1}, \qquad (4)$$

where ω is the frequency reckoned from that of the exciting line. The plot of I^{-1} vs ω^2 should be a straight line whose intercept on the ordinate axis is C^{-1} and whose slope is related to the relaxation time τ by the formula

$$\tau = C^{-1}\sqrt{\frac{d\,[I^{-1}(\omega)]}{d\,(\omega^2)}}\,. \qquad (5)$$

The experimental data have shown that the intensity distribution in the depolarized scattering spectrum is described by a curve similar to that shown in Fig. 2, which, with some differences, corresponds to the pattern observed for almost all the investigated liquids.

Figure 2 shows that there are several sections in which the $I^{-1}(\omega^2)$ curve behaves differently, and the over-all picture of the phenomenon is far from the idealized one.

However, sections AB and BC of the experimental curves can be approximated fairly well by two straight lines, which may be assumed to correspond to two Lorentz curves with two different anisotropy relaxation times.

For some liquids (salol, benzophenone), these relaxation times differ by a factor of 100, or even more. The transition region in the neighborhood of B would naturally be regarded as resulting from the superposition of the tails of two Lorentz curves, but it could also be regarded as a result of the superposition of several different Lorentz curves, each having a low integral intensity and a value of τ that differs slightly from the τ values for the neighboring curves. However, as will be explained below, this latter assumption is the less likely one.

The region CD cannot be described by a Lorentz line shape, but, as Leontovich[7] pointed out, the effect of the inertia of the molecules manifests itself in the distant region of the Rayleigh-line wing. Leontovich's theory does not take the inertia of the molecules into account (the second derivatives in the kinetic equation for the reaction were dropped) and cannot account for this region of the spectrum. Taking the inertial terms into account made it possible[5] to describe this section[1] of the ω^2 dependence of I^{-1} (Zhivlyuk; see[5]).

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[1]This region of the Rayleigh-line wing has been recently interpreted by several investigators as a result of the deformation of the electron shells of the molecules owing to collisions, and in this case the spectral intensity distribution in the far part of the wing should be exponential. This mechanism of the depolarized scattering of light is strictly valid for gases. Here we shall not discuss the validity of transferring this mechanism to the case of liquids.

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The longer relaxation time, corresponding to the section AB of Fig. 2, characterizes the back diffusion of molecules at large angles, while the shorter relaxation time (section BC) characterizes the high-frequency damped vibrations (librations) executed by molecules in equilibrium positions.[5,8] Both these processes lead to modulation of the scattered light and to the formation of the depolarized scattering spectrum. We also note that shearing strain fluctuations also contribute to the depolarized scattering spectrum and that it is just these fluctuations that give rise to the more or less damped transverse modes that manifest themselves as fine structure in the Rayleigh-line wing.[9] Thus, although we bypass details in this meager description, we can still say that two anisotropy relaxation times can be determined from the intensity distribution in the spectrum of the depolarized scattered light.

Rytov[10] developed a theory of the intensity distribution in the depolarized spectrum of the scattered light for any number of relaxation parameters. It follows from this theory that two anisotropy relaxation times, which we can determine from Eq. (5), are sufficient to describe the fine structure of the Rayleigh-line wing. This may serve as an additional indication that the intensity distribution in the wing of the Rayleigh line can be described by two relaxation times—at least for such liquids as salol and benzophenone.

It would seem that the decay of molecular orientation should be governed by the same law, regardless of whether the initial preferential orientation of the molecules was brought about by an external field or by some other causes. It follows from what was said about the nature of the intensity distribution in the depolarized spectrum of the scattered light that the decay of the birefringence in the Kerr effect cannot be described by an exponential law with a single relaxation time: at least two exponentials with different anisotropy relaxation times are required. Even though a single exponential with a single parameter τ was used in the initial stages of the development of methods for the direct determination of the anisotropy relaxation time, this problem must be treated more rigorously in the future.

C. Direct methods of determining the anisotropy relaxation time

In their first paper[3] Duguay and Hansen indicated one method of determining the anisotropy relaxation time using an ultrafast shutter with a setup similar to that diagrammed in Fig. 1 but without the echelon, and this method was later used in a number of studies.

If the pulse controlling the ultrafast shutter is longer than the anisotropy relaxation time and if its rise time and fall time are not negligible, Eq. (3) must be replaced by the more general formula

$$\Delta n(t) = \frac{n_2}{2\tau} \int_{-\infty}^{t} E_{1.06}^2(t') \exp\left(\frac{t'-t}{\tau}\right) dt', \qquad (6)$$

in which $n_2 = \lambda K$ (see Eq. (2)).

The intensity of the second harmonic (0.53 μm) light

passing through cell K will be given by

$$I(t) = \int_{-\infty}^{t} E_{0.53}^2(t') \sin^2\left[\frac{2\pi}{\lambda} \Delta n(t') l\right] dt', \qquad (7)$$

in which l is the length of the cell and $\sin^2[(2\pi/\lambda)\Delta n(t')l]$ determines its transparency.

If the phase shift is not large we can replace the sine by its argument and write the final formula for the intensity of the transmitted light in the form

$$I(t) = \frac{2\pi l}{\lambda} \int_{-\infty}^{t} E_{0.53}^2(t') \Delta n(t') dt', \qquad (8)$$

in which $\Delta n(t')$ is determined by Eq. (6).

Equation (8) gives an $I(t)$ curve which has a maximum and falls off beyond the maximum according to an exponential law (involving one or more exponentials) from which one can determine the anisotropy relaxation time. Mourou and Malley[11] varied τ in numerical calculations based on Eq. (8); the results of these calculations showed that it is advantageous to determine the anisotropy relaxation time from the shift of the peak of the $I(t)$ curve when the relaxation time is shorter than the control pulse, and from the fall of the curve beyond the maximum when the relaxation time is longer than the control pulse.

In[11] a pulse of green light was passed through a vessel containing a turbid medium, an image of the pulse in the scattered light was focused on the photocathode of a light detector (of an "OMA" system), and 500 channels of the digital signal accumulator were "read" (the data in each channel correspond to a definite instant of time). With such a recording system one can accumulate useful information from all the signals produced by a single giant pulse consisting of 50 picosecond pulses. The curves recorded with the "OMA" system for carbon disulfide and nitrobenzene are shown in Fig. 3.

Reintjes and Carman[12] used a rather complicated setup in which the second-harmonic probe pulse (λ = 0.53 μm) was "squeezed" by two diffraction gratings to a length of the order of 0.5–1 psec. The setup is diagrammed in Fig. 4. In this study the self-focusing filaments that arise in the cell were observed directly and their lifetime following penetration of the light producing them into the specimen was measured. In this case the anisotropy relaxation time was measured with a time resolution determined only by the length of the probe pulse (~1 psec). It was established in[12] that orientational phenomena play the principal part in the formation of self-focussing, and anisotropy relaxation times were measured.

Ho, Yu, and Alfano,[13] employing the method that was used in[3], measured birefringence persistence times in nitrobenzene and m-nitrotoluene and in solutions of them in carbon tetrachloride and n-propyl and n-decyl alcohols. They investigated the anisotropy relaxation time as a function of the viscosity of the solution. The relaxation time τ in solutions of m-nitrotol-
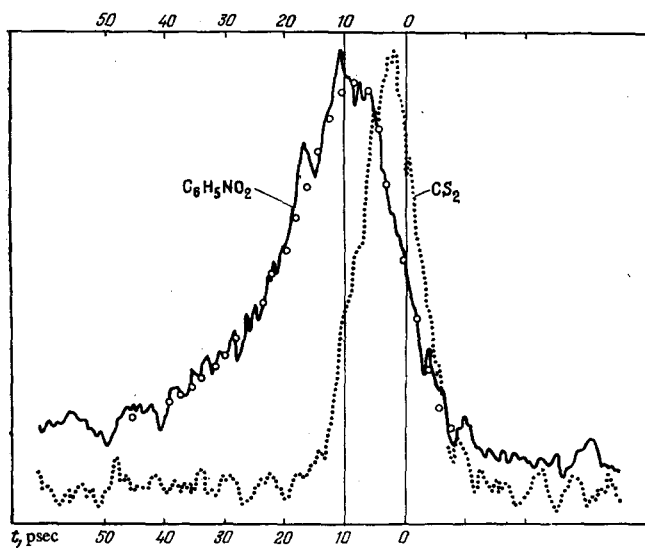
FIG. 3. Second-harmonic probe pulse from a neodymium laser as recorded with a multichannel OMA analyzer[11] for the cases in which the ultrafast-shutter cell was filled with nitrobenzene (full curve) and with carbon disulfide (dotted curve).

uene in n-decyl alcohol decreased with decreasing m-nitrotoluene concentration, although the viscosity of the solution increased appreciably. At low nitrobenzene and nitrotoluene concentrations (~10%) the measured relaxation time fell appreciably, amounting to about 10 psec. The experimental technique, which was based on the use of an ultrafast optical shutter, made it possible to measure anisotropy relaxation times in a number of substances and to investigate diverse fast processes. Table I gives results of direct measurements of the anisotropy relaxation time as well as results of indirect measurements of this quantity using different sections of the Rayleigh-line wing.
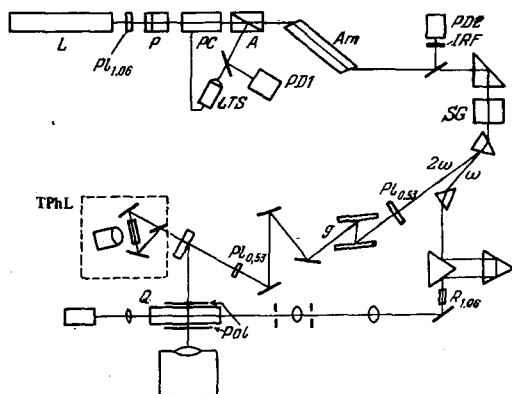

FIG. 4. Setup for measuring the anisotropy relaxation time from the persistence time of the self-focusing filaments[12]: L—laser with mode locking; $Pl_{1.06}$ and $Pl_{0.53}$—half-wave plates for 1.06 and 0.53 μm waves; P—polarizer; PC—Pockels cell; A—analyzer; LTS—laser-triggered spark gap; PD1 and PD2—photodiodes; IRF—1.06 μm filter; SG—second-harmonic generator; g—pulse-squeezing lattice; $R_{1.06}$—plate for rotating the polarization plane of 1.06 μm light through 90°; crossed Polaroids; Q—specimen cell; TPhL—device for observing three-photon luminescence.

TABLE I. Results of direct and indirect measurements of anisotropy relaxation times ($\tau \cdot 10^{12}$ sec).

Substance	Temperature t	Direct measurements, τ	Temperature, °C	From the half-width of the Rayleigh-line wing τ_1	τ_2	Reference
Carbon disulfide	20	2±0.5c				a) M. A. Duguay, J. W. Hansen[3] (1969).
		2.5d	20	2.4f	0.24f	b) J. Reintjes, R. L. Carman[12] (1972).
	−72	~5d	20	2.3g		c) G. Mourou. M. M. Malley[11] (1975).
		2.1±3t		1.96—1.5i		d) M. R. Topp, P. M. Rentzepis[14] (1972).
Nitrobenzene	3	32±6a 22±2b 27.5+2c	20 23±2 22.4	~46h 48k 39l	<1h 3.6k	e) P. P. Ho, W. Yu, R. R. Alfano[13] (1976).
	20	47.4d	24	36m		f) I.L. Fabelinskii[5,6] (1945).
	−72	−68d	22	44.6p		g) V.S. Starunov[8] (1965).
	23±2	32e	22±0,3 20±2	40.4q 40.83s		h) V.S. Starunov et al.[9] (1967).
Toluene		14±2b	20	5.3f		i) S. L. Shapiro, H. P. Broida[15] (1967).
		5±1c	20	4.1s		k) H. C. Craddock et al[16] (1968).
			23±2	4.65±0,2i		j) D. R. Bauer et. al.[17] (1974).
			23.6 25	5.54n 4.4±0.2r	0.12r	l) G. I. A. Stigeman, B. P. Stoicheff[18] (1973).
			20±2	5.76s		m) G. R. Alms at al[19] (1973).
m-Nitrotoluene	23±2	44e	26	50l		n) G. R. Alms et al.[20] (1973).
			22±0.3	53.3q		p) A. Szöke et al.[21] (1967).
Benzene		4±0.5	20	3.3f	0.24f	q) E. Zamir et al.[22] (1971).
			20 23.6	3.8g 2.9i	0.38g	r) B. Simic-Glovaski, D. A. Jackson[23] (1973).
			25	2.91n 3.2±0.15r	0.18r	s) P. Amorim da Costa et al[24] (1975).
			20±2	2.94s		t) E. P. Ippen, C. V. Shank[10] (1975).
Bromobenzene		13±2	23±2 −4 22 22±0,3	11k 16l 15p 11q	1.1k	

Comparison of the results of the direct and indirect measurements shows that, with rare exceptions, the direct measurements are in good agreement with the indirect measurements based on the narrow section of the Rayleigh-line wing (the longer anisotropy relaxation time τ_1). The indirect measurements also give the short relaxation time τ_2, which is about an order of magnitude shorter than τ_1. This means that with a shorter pulse of intense light to control the shutter, one could reduce the resolving time to a fraction of a picosecond even on the basis of the orientation (libration) effects in liquids alone. Of course the contribution from electronic polarizability is even faster, but for liquids its magnitude will be less than that of the orientational contribution. Topp and Rentzepis[14] are of the opinion that even 3-psec intense light pulses will give a smaller value of the Kerr constant than the value obtained in the nanosecond range. Such a result seems natural since the light pulse becomes shorter than the anisotropy relaxation time of some definite liquid. For nitrobenzene, for example, the Kerr constant for an intense light pulse in the nanosecond range is $26.4 \cdot 10^{-8}$. Correspondingly, these quantities are $14.4 \cdot 10^{-8}$ and $2.5 \cdot 10^{-8}$ for bromobenzene, $6.6 \cdot 10^{-8}$ and $3.3 \cdot 10^{-8}$ for toluene, etc. For carbon disulfide, however,

the Kerr constant remains unchanged, being $32.6 \cdot 10^{-8}$ in these units. This might be explained by the fact that the light pulse was longer than the anisotropy relaxation time; according to Topp and Rentzepis, however, the pulse was ~3 psec long while the anisotropy relaxation time is 2 psec, so it would seem that some decrease in the Kerr constant should be expected. Perhaps in this case the ~0.2-psec anisotropy relaxation time comes into play and keeps the Kerr constant at its previous level (see[94]). In this case the integral intensities of the narrow and broad parts of the Rayleigh-line wing should be about the same, and in the case of carbon disulfide, they apparently are.

It should be pointed out that τ_2 has been measured in the broad part of the wing for a large number of liquids (more than are listed in Table I), but that τ_1 has been measured in the narrow part of the Rayleigh-line wing for many more. We want to emphasize again that in order to obtain even faster shutters we must learn how to generate high-intensity pulses with durations of the order of 10^{-13} sec; we may expect that carbon disulfide will then prove to be as good a working substance for optical shutters as it now is for longer pulses.

Here we must call attention to the fact that studies by Varma and Rentzepis[25] of the operation of an ultrafast-shutter cell filled with liquid carbon disulfide showed that the open time of the shutter is not determined by the length of the control pulse and the anisotropy relaxation time alone. Under their experimental conditions, described in[25], when the control pulse was 5 psec long and the delay time between neighboring beams of light that had passed through adjacent steps of the echelon was 2.8 psec, the open time of the shutter reached 90 psec when the carbon disulfide cell was 15 cm long. However, when the cell was shortened to 0.2 cm, other conditions being kept the same, 4–5 beams succeeded in passing through it; and when the cell was made only 0.05 cm thick, only 2–3 of the beams passed through it, which corresponds to an open time virtually equal to the length of the infrared control pulse.

The authors of[25] were inclined to attribute the observed phenomenon to contributions to the induced birefringence from such comparatively slow processes as electrostriction. However, Topp and Orner[26] reasonably pointed out that the frequency dispersion of the group velocity of the picosecond pulses of different wavelengths cannot be neglected in evaluating the open time of an ultrafast optical shutter. Using the Rayleigh formula for the relation between the group and phase velocities, we easily find the formula

$$n_g = n - \lambda \frac{\delta n}{\delta \lambda};$$ (9)

here $n_g = u/c$, where u is the group velocity and n is the refractive index of the medium.

For the specific case of a shutter consisting of a carbon disulfide cell operated with control and test pulses of wavelength 1.06 and 0.53 μm, respectively, we find that the delay of the green pulse with respect to the infrared one will be given in terms of the "group refractive indices" $n_{g,\,0.53}$ and $n_{g,\,1.06}$ as follows:

$$\Delta t = \frac{l}{c} (n_{g,\,0.53} - n_{g,\,1.06}),$$ (10)

where l is the path length in the working substance of the shutter and c is the velocity of light *in vacuo*.

For carbon disulfide we have[26] $n_{g,\,0.53} = 1.769$ and $n_{g,\,1.06} = 1.625$, so for $l = 10$ cm we find $\Delta t = 48 \cdot 10^{-12}$ sec. Of course one should not use shutter cells in which the frequency dispersion of the control and test (investigated) pulses is such that Δt exceeds half the pulse lengths. The above numerical estimates show that for control and test pulses ~5 psec long one should not use a carbon disulfide cell longer than 1 cm.

Secondary phenomena of undoubted interest have been discovered in studies of the behavior of ultrafast-shutter cells. When the cell was filled with carbon disulfide, the authors of[25] observed depolarized scattering of the probe-pulse light in directions parallel and perpendicular to the intense control pulse and to the probe pulse, even though the probe and control pulses were linearly polarized. The scattered-light pulse lasted longer than the control pulse and was the more intense, the shorter the wavelength of the pulse and the higher the intensity of the control pulse.

The authors of[25] did not attribute this light scattering to simple Rayleigh scattering, but assumed that it is due to inhomogeneities of the refractive index induced by the field of the intense light pulse. Nor, unfortunately, did they discuss the onset of the induced Rayleigh-line wing as a possible explanation for the observed phenomenon. Such a discussion would have been the more interesting, since no light scattering was observed when the carbon disulfide was replaced by water. The behavior and unusual properties of ultrafast shutters evidently have still to be studied in detail, but what is already known of them has proved to be enough to make possible many studies of fundamental importance, both for various areas of physics, and for other sciences. [56]

A sufficiently complete theoretical description of induced birefringence for the case in which different relaxation processes take part still remains to be given. However, the first steps have already been taken and we shall discuss them briefly here.

The theoretical discussion of the action of the field of a light wave on the optical dielectric constant goes back to the years 1956–1958 when Buckingham[35,38] and Piekara and Kielich[27,28] indicated the possibility of determining the change in the dielectric constant under the action of intense light. At that time lasers were not yet available as light sources.

Kasprowicz-Kielich *et al.*[29] and Kasprowicz-Kielich and Kielich[30] developed a semiphenomenological theory of the Kerr effect induced by intense light after the phenomenon had been discovered. In these studies it was shown, in particular, that one has to deal with three rotational relaxation times, and ways to study the processes corresponding to these relaxation times were pointed out. A great many problems of nonlinear optics that we cannot touch upon here were also treated
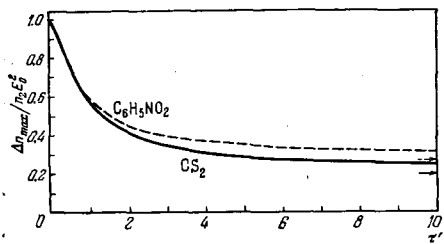
FIG. 5. Maximum value of the induced birefringence vs τ' $= \tau/T_\omega$ for CS_2 and $C_6H_5NO_2$.[40] The arrows at the right indicate the limiting values of Δn_{max} when τ' is large for CS_2 ($\rightarrow$) and $C_6H_5NO_2$ (- - →).

in[29,30]. What is important here is the magnitude of the birefringence arising under the action of an intense light pulse whose duration may not differ much from the anisotropy relaxation time.

A problem closely related to this one—the modulation of a light wave in a Kerr cell when the frequency of the external field is of the same order as the reciprocal of the anisotropy relaxation time—was solved by one of us. [5,31] In that work an equation for Δn of the following form was solved:

$$\tau \frac{d(\Delta n)}{dt} + \Delta n = \lambda k E^2(t). \tag{11}$$

It was assumed that there is just one relaxation time τ associated with molecular orientation. If there are several relaxation times and there is an intense light pulse in the medium instead of an external microwave electromagnetic field, then Eq. (11) must be replaced by the equation

$$\tau_i \frac{d(\Delta n_i)}{dt} + \Delta n_i = n_*^i E^2(t), \tag{12}$$

in which Δn_i is the resultant birefringence and n_2^i is the total nonlinear addition to the refractive index. If there is only one anisotropy relaxation time associated with molecular orientation and one relaxation time of electronic nature, and if these relaxation times differ widely from one another, then Eq. (12) breaks up into two independent equations.

The nonlinear orientational (n_2^0) and electronic (n_2^e) additions to the refractive index were calculated by Kielich[32-37] and can be expressed as follows:
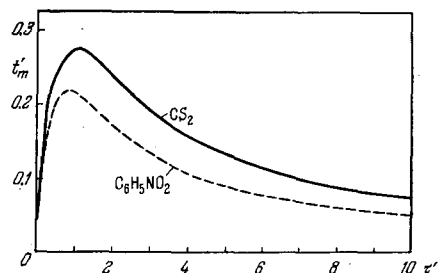

FIG. 6. Maximum delay time t'_m (in units of T_ω) between Δn_{max} and the peak of the optical pulse vs $\tau' = \tau/T_\omega$ for CS_2 and $C_6H_5NO_2$.[40]
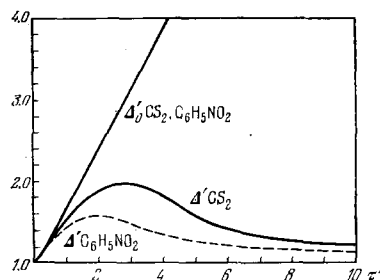

FIG. 7. Full width at half maximum for the duration of the birefringence (Δ') and the orientational birefringence (Δ_0') in units of T_ω vs $\tau' = \tau/T_\omega$ for CS_2 and $C_6H_5NO_2$.[40]

$$n_2^e = \frac{2\pi\rho}{3n_0} \gamma \left(\frac{n_0^2+2}{3}\right)^2 \left(\frac{n_\omega^2+2}{3}\right)^2, \tag{13}$$

where ρ is the density of the liquid in the Kerr cell, γ is a component of the fourth-rank tensor for the electronic hyperpolarizability induced by the probe-pulse light, n_0 and n_ω are the refractive indices for the probe and control pulses, respectively, and

$$n_2^0 \approx \frac{[3\beta_T}{8\pi n_0} \frac{\Delta}{6-7\Delta} \left(\frac{n_0^2+2}{3}\right)^2 (n_\omega^2-1)^2. \tag{14}$$

Here β_T is the isothermal compressibility of the medium and Δ is the depolarization of the scattered light.

In the approximation considered here, $n_2 = n_2^0 + n_2^e$. Sala and Richardson[40] solved Eq. (12) in this approximation, under the further assumption that the function $E^2(t, r)$ has the Gaussian form. Curves showing $\Delta n/n_2 E^2$ as a function of $\tau' = t/T_\omega$, where T_ω is the duration of the control pulse ($r' = \tau/T_\omega$ was taken as a parameter) could be constructed from the solutions. The results of the calculation give an idea of the character of the overall curve and of the orientational and electronic contributions to it. The basic characteristics of an ultrafast shutter can be derived from these curves. Such characteristics for CS_2 and $C_6H_5NO_2$ are shown in Figs. 5-7. The following numerical values were used in the calculation: $n_2^0/n_2 = 0.807$ and $n_2^e/n_2 = 0.193$ for CS_2, and $n_2^0/n_2 = 0.738$ and $n_2^e/n_2 = 0.262$ for $C_6H_5NO_2$. These curves give a fairly complete characterization of an ultrafast shutter controlled by pulses by various lengths under the assumption that $\tau_e \ll \tau$ and that there are only two relaxation times τ and τ_e. As follows from what was said above, however, this is not the case, and a more realistic problem will require a more complete solution.

It is entirely possible that such a more complete solution of the problem will alter our picture of the phenomenon. If the other relaxation times differ greatly from one another and from the relaxation times that have already been taken into account, the general qualitative interpretation will probably not be changed; but if several of the relaxation times turn out to be close to one another we may expect not only quantitative, but also qualitative changes in our picture of the phenomenon.

M. S. Pesin and I. L. Fabelinskiĭ

3. DIRECT MEASUREMENTS OF THE LIFETIMES OF OPTICAL PHONONS

The lifetimes of optical phonons had previously been determined from the half-widths of thermal (spontaneous) Raman scattering (RS) lines. The first measurements of this type were made by Sterin.[41] This method was then used in a number of more recent studies, and information on the lifetimes of optical phonons could be obtained for various lines in the RS spectrum. This indirect method of determining phonon lifetimes is always subject to the possible effects of parasitic factors that might alter the width of the investigated line. The direct determination of the lifetimes of optical phonons, which became possible when techniques for generating picosecond pulses were developed, is therefore of especial interest and value.

Direct measurements of the lifetimes of molecules in excited vibrational states, as well as studies of the energy relaxation of these states, intermolecular interaction mechanisms, and other fast processes, were carried through by Kaiser, Laubereau, and their co-workers[42-49] (a brief review of these and some other papers will be found in[47]), by Rentzepis and his co-workers,[50-52] by Alfano and Shapiro,[53-56] and by a number of other investigators. The apparatus used in these studies were similar to the one diagrammed in Fig. 1, though in many cases there was no echelon, some other delay line being used. In most cases individual picosecond pulses of frequency $\nu_l = 9455$ cm^{-1} and spectral width ~ 3 cm^{-1} were isolated from the train of pulses generated by a neodymium glass laser.

The fundamental pulse was split into two. The more intense part of the pulse was passed through a KDP crystal and was used to excite intense molecular vibrations in the investigated liquids; this led to considerable enhancement (by more than 10^4 times) of the thermal anti-Stokes Raman scattering of the light of the second comparatively weak pulse, which entered the medium after a specified delay time. The fundamental-frequency pulse could also be used to excite the liquid. In this case the comparatively weak probe pulse was passed through the KDP crystal and thus had the second-harmonic frequency $\nu_{2l} = 18\,910$ cm^{-1}.

In most cases the energy of the fundamental pumping pulse was about 10 mJ; then the total number of excited molecules (per unit volume of the medium) was about $5 \cdot 10^{15}$, i.e., the relative population of the excited vibrational state was of the order of 10^{-3}, which is three orders of magnitude higher than the thermodynamic-equilibrium population. By varying the delay time between the fundamental and pumping pulses one could tract the rise and fall of the excess population of the corresponding excited vibrational state of the molecules of the medium.

Simultaneously with the generation of intense intramolecular vibrations incident to stimulated Raman scattering (SRS), coherent vibrations of the molecules themselves are excited; this leads to the appearance of the coherent Stokes component in the SRS of the fundamental pumping pulse, and the intensity of this component

was also measured in most of the studies. It must be pointed out that only the strongest Raman lines appear in SRS, so only they can be investigated by the experimental technique discussed here.

Alfano and Shapiro[53] made one of the first direct measurements of the lifetime τ of optical phonons of frequency 1086 cm^{-1} in a calcite crystal. The lifetime of these phonons was found to be 8.5 ± 2 psec at 297 °K and 19.1 ± 4 psec at 100 °K. On the other hand, Park[57] had found values of τ at those same temperatures of 4.8 and 7.7 psec, respectively, from the width of the thermal RS line. As was pointed out by the authors of[53], this discrepancy lies beyond the limits of experimental error and has not found an unambiguous interpretation.

Laubereau et al.[43] made direct measurements of the lifetime of a transverse optical phonon of frequency 332 cm^{-1} in diamond, obtaining values of 2.9 ± 0.3 psec at 295 °K and 3.4 ± 0.3 psec at 77 °K. On converting these results to the width of the 1332-cm^{-1} line, good agreement is found with previous measurements of the width of this line in the thermal RS of light. Phonons turn out to have longer lifetimes at lower temperatures, apparently because collisions of phonons excited in SRS with the crystal lattice or with thermal phonons become less frequent as the lattice vibrations become weaker.

Direct measurements of the polariton lifetime in gallium phosphide are reported by Laubereau et al. in[44]. In this case a polariton with the wave vector $|k| = 2700$ cm^{-1} corresponding to the frequence ~ 361 cm^{-1} was excited by two light beams in a GaP specimen at the difference of the wave vectors of the two beams. The first beam was that of a neodymium laser. A second beam was separated from the fundamental laser beam and excited the Stokes component in the SRS of light of frequency $\nu = 9087$ cm^{-1} in a vessel containing $SnCl_4$. Light from this line was directed into the GaP specimen at an angle of 5° to the first beam. A third (probe) beam of the same frequency as the first produced anti-Stokes Raman scattering at the polariton frequency. The polariton lifetime was determined from the decrease in the intensity of this scattering as a function of the probe-beam delay time; it turned out to be 5.5 ± 0.5 psec.

In[45], the same authors report studies at 300 °K of the fully symmetric stretching vibrations of the CH_3 group in 1-1-1-tri-chloroethane at a frequency of 2939 cm^{-1}, and those of the CH_3 group in ethyl alcohol at 2928 cm^{-1}. Figure 8 shows the results of the measurements in these liquids. The quantities S_1'' and S_2'' (the intensity of the thermal incoherent anti-Stokes signal from scattering of the probe pulse in ethyl alcohol and tri-chloroethane, respectively) are plotted as functions of the delay time. As the figure shows, the scattered signal rises to a maximum at a definite delay time, which is the time required for accumulating the greatest possible number of excited molecules in the pumping process. When the delay time is increased further, the intensity of the incoherent scattering falls off exponentially, thus making it possible directly to determine the lifetime τ' of the molecule in the excited state. The
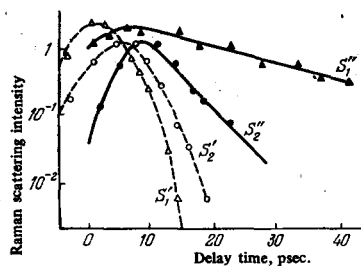
FIG. 8. Raman scattering intensity (coherent and incoherent signals S' and S'', respectively) vs delay time for CH_3CCl_3 and C_2H_5OH.[45]

τ' values were found to be 22 psec for C_2H_5OH and 5 psec for CH_3CCl_3. The intensity S' of the Stokes component in the SRS of the fundamental (pumping) pulse in the direction opposite to that of the incident light is also plotted in Fig. 8. The maximum values of S'_2 and S'_1 occur at delay times of 5 psec for CH_3CCl_3 and ~2 psec for C_2H_5OH. The rapid fall of the coherent signal means that the time constant τ characterizing the lifetime of the coherently excited vibrational field in the medium does not exceed 2 psec for either of the investigated liquids.

The dashed curves for the quantitites S' in Fig. 8 were calculated for the values $\tau = 1.3$ psec for CH_3CCl_3 and $\tau = 0.26$ psec for C_2H_5OH. Thus, the incoherent scattering peak shifts to larger delay times and the intensity of the corresponding signal falls less rapidly than that of the coherent signal. The corresponding difference between the time constants τ' and τ for the individual vibrational state is such that $\tau'_2/\tau_2 = 4$ for trichloroethane and $\tau'_1/\tau_1 = 80$ for ethyl alcohol.

In this case such a large difference between the lifetimes (or the corresponding path lengths) for coherent and incoherent phonons can be fully explained. It means that the coherence resulting from the SRS disappears much more rapidly than does the energy of the corresponding molecular vibration. This is not surprising if we consider the different physical mechanisms responsible for the two relaxation processes. The main factor determining τ is the transfer of vibrational energy between neighboring particles, whereas τ' is determined by the lifetime of the corresponding vibrational level. The experimental technique for measuring τ and τ' by the two-pulse method is distinguished in the following respect: If the angle of incidence of the probe pulse is so chosen that this pulse, the Raman scattering of the probe pulse, and the vibrational field excited as a result of the SRS agree in phase, then the measured lifetime τ is the coherence persistence time, since the Raman-scattering intensity is sensitive both to changes in the population of the corresponding molecular vibrational energy level, and to the phase matching. When the Raman scattering is fixed in such a direction that the phase matching with the excited molecular vibrations does not affect its intensity, however, the measured decay time τ' is the population relaxation time for the corresponding vibrational level, since in this case the intensity of the Raman scattering from the probe pulse is sensitive only to population changes. As

was noted above, τ' is always much larger than τ.

Similar results were obtained in[48] in measurements of τ for the 2326 cm^{-1} fundamental vibrational mode in liquid nitrogen, using the same method. In this case the value $\tau = 75 \pm 8$ psec was obtained; this is in very good agreement with the value $\tau = 79 \pm 9$ psec found by Clements and Stoicheff[58] from the width of the Raman line. The ratio τ'/τ for liquid nitrogen turned out to be of the order of 10^6; this is much higher than the corresponding ratios for the other investigated liquids.

In an earlier study by Alfano and Shapiro[54] of this same 2326 cm^{-1} vibrational mode in liquid nitrogen, much larger values of τ, differing widely from those cited above, were obtained.

Laubereau, Kaiser, *et al.*[46,48,49] report fairly detailed and successful studies of the energy transfer mechanisms in the quasiresonance processes responsible for damping of molecular vibrations. Thus, the stretching and bending vibrations of the CH group in ethyl alcohol at frequencies near 2900 cm^{-1} were investigated in [49]. It was found that the pumping pulse first excites vibrations of frequency 2928 cm^{-1}, and then a very rapid (time constant $\tau_c \sim 0.5$ psec) redistribution of energy takes place between a group of vibrational levels (2972, 2877, and 2897 cm^{-1}) near the 2928 cm^{-1} level. The total vibrational energy accumulates on these levels and then gradually falls off (time constant $\tau_1 = 22 \pm 5$ psec) owing to transfer of energy to a group of vibrational levels in the 1400 cm^{-1} band (levels at 1485, 1456, and 1395 cm^{-1}). The energy in these last vibrational modes falls off with the relaxation time $\tau_2 \simeq 40$ psec. It is just the excess population of the levels grouped near 2928 cm^{-1} that provides the main contribution to the scattering observed near 1400 cm^{-1}. The large difference between the time constants τ_c and τ_1 enables one to discern an analogy between the vibrational decay process described above and the situation obtaining in the phenomenon of the so-called phonon bottleneck in solids.[2]

While investigating SRS in binary liquid mixtures, Laubereau *et al.*[46] made direct observations of the mechanism responsible for the decrease in the vibrational energy of the molecules as a result of intermolecular interaction. The laser pulse of frequency $\nu_L = 9455$ cm^{-1} and peak power 10^9 W used for pumping was directed into a cell containing substance A (liquid CH_3CCl_3) in which a pulse of frequency $\nu_s = \nu_L - \nu_0$ arose as a result of SRS, where $\nu_0 = 2939$ cm^{-1} is the frequency of the normal vibrational mode of the CH_3CCl_3 molecule that was strongly excited by the laser pulse. Then pulses of frequencies ν_L and ν_s passed through a second cell containing the two-component liquid mixture, the second cell being adjacent to the first one. Liquid CCl_4 or CD_3OD was used as the second compo-

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[2] We note that in this case the results differ considerably from those of an earlier study[54] in which the decay of the excitation of the vibrational mode of frequency 2928 cm^{-1} was assumed to be associated with the direct splitting of this mode into two vibrations, each of half the frequency (1464 cm^{-1}).
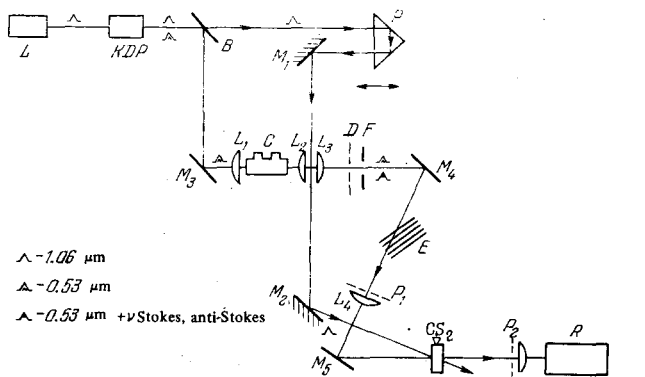
FIG. 9. Setup for a fast optical shutter, including an echelon delay line[50]: L—neodymium laser with mode locking; KDP—frequency doubler; B—beam-splitter; M_{1-5}—mirrors; P—prism (part of a variable delay line); E—echelon; P_1 and P_2—crossed polarizers; C—specimen cell; L_{1-4}—lenses; D—diffuser; F—light filter; R—radiation detector.

nent (substance B). The weak probe signal was scattered in the second cell, and the delay-time dependence of the intensity of the incoherent antistokes scattering at frequency $\nu_{as} = \nu_{2L} - \nu_i$ served as a measure of the excitation of the specific vibrational mode of frequency ν_i.

As a result of the experiments, the dependence of τ' (derived from curves similar to those on Fig. 8) on the concentration of the mixture in the second cell was investigated, and this made it possible to establish that the predominant process when substance B was CD_3OD was three-body interaction of an excited A molecule with unexcited A and B molecules. Then τ' decreased with increasing concentration of substance B in the mixture.

When substance B was CCl_4, the basic process was three-body interaction of an excited A molecule with two unexcited A molecules (i.e., CH_3CCl_3 molecules). In this case component B played a passive role and τ' increased rapidly with increasing concentration of this component since the probability for a collision of three A molecules (including one excited one) decreased with increasing B concentration. Comparison of the level schemes for the normal vibrations of the CH_3CCl_3, CD_3OD, and CCl_4 molecules enables one to explain the observed regularities as results of efficient energy exchange between molecules under conditions close to those for energy resonance.

Actually, when substance B is CD_3OD, a CH_3CCl_3 molecule excited in the 2939 cm^{-1} vibrational mode will lose energy in collisions with a CD_3OD molecule (exciting vibrations of frequency 2227 cm^{-1} in the latter) and with a CH_3CCl_3 molecule) exciting the 713 cm^{-1} vibrational mode). But if substance B is CCl_4, there will be virtually no excitation of the B molecules since the conditions for energy resonance are not satisfied. In this case the most efficient process is three-body interactions of A molecules, one of which is excited. Damping due to intramolecular processes will play virtually no part in the cases under consideration because of the rapidity and efficiency of the intermolecular energy exchange.

Rentzepis et al.[50] were the first experimentally to scan the investigated radiation simultaneously in wavelength and time. The apparatus for such measurements is diagrammed schematically in Fig. 9; it is described in detail in[51]. Part of the isolated neodymium glass laser pulse ($\lambda = 1.06$ μm) opened the ultrafast shutter, while a second, fairly intense, part of the same pulse, which had twice the frequency, was directed into the cell C containing the investigated liquid. After leaving the cell, the frequency-doubled pulse, together with the SRS light that arose in the liquid, struck the diffusely scattering plate D, which produced a rather broad (~ 7 cm) parallel light beam. This broad beam was directed onto the echelon E, where it was separated into a series of beams, each of which was delayed differently in time, although all had the same duration. These delayed beams passed through the ultrafast shutter and were directed onto the entrance slit of the spectrometer R. When the system was carefully adjusted and the shutter was illuminated as uniformly as possible, the light beam issuing from the cell C could be investigated over a wide wavelength range, which was essentially limited only by the material used for the optics and by the transmission of the shutter.

Stokes emission arose in the cell C in the SRS process on account of the highly nonlinear interaction, and this emission was comparable in intensity with the laser pulse and was itself capable of giving rise to a subsequent SRS line. It was found that a strong background in the form of a broad section of continuous spectrum arises simultaneously with the appearance of the SRS Stokes lines.

In Fig. 10 we present photographs of the SRS spectra of normal n-octyl, n-butyl, and n-dodecyl alcohols (a) and of heavy water (b). In these photographs the wavelength and time scanning are in the horizontal and vertical directions, respectively (the direction of increasing time t is indicated by an arrow). The distance between neighboring horizontal lines corresponds to the 2.8 psec difference between the delay times introduced by neighboring segments of the echelon. The duration of a process is indicated by the number of horizontal lines.

The emission in the anti-Stokes region appears with a certain delay, owing to the fact that in SRS the excited vibrational levels of the molecules must already be populated before the anti-Stokes lines appear. The Stokes and anti-Stokes SRS lines emitted by the substances investigated in[51] were due to vibrations of the CH group at $\nu = 3000$ cm^{-1}. Secondary anti-Stokes bands could be observed for each of the investigated substances, indicating that the SRS process was fairly intense. The lifetime of the optical phonons responsible for the appearance of the secondary anti-Stokes bands should be equal to the difference between the observed time delays in the appearance of the first and second SRS lines. Table II gives the delay times for the appearance of the first (τ_1) and second (τ_2) anti-Stokes SRS lines for all the substances investigated in[51]. As is evident from the table, the delay in the appearance of the second anti-Stokes lines is about twice the life-
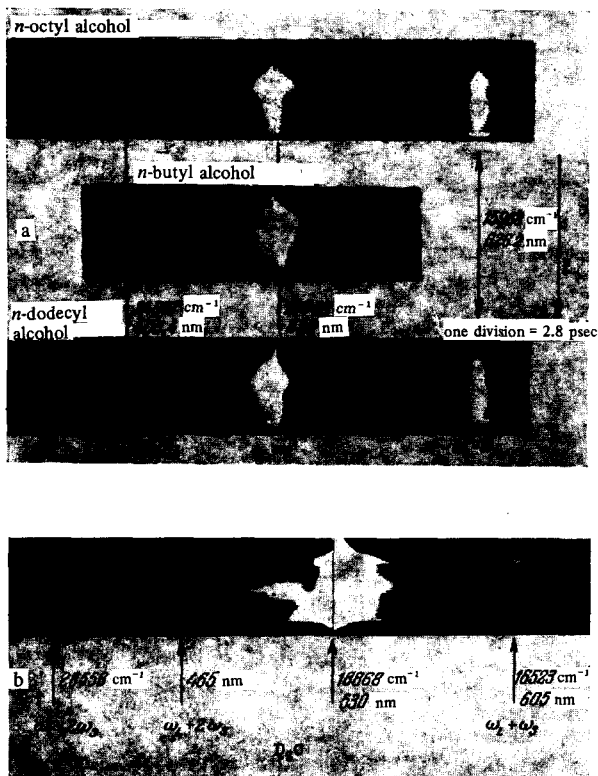
FIG. 10. Simultaneous frequency and time scans of the second-harmonic pulse from a neodymium laser after stimulated Raman scattering in n-octyl, n-butyl, and n-dodecyl alcohols (a) and in heavy water (b).[51]

time of the phonons responsible for the appearance of the first SRS lines in the case of the lighter alcohols, but it is considerably longer for the heavier compounds. This can apparently be attributed to the dispersion that arises on account of the large difference between the refractive indices for the first and second SRS lines.[26]

The appearance of a continuous spectrum simultaneously with the SRS lines is due to the phenomenon of phase modulation in the self-focusing of the laser light and of the SRS Stokes line. This phenomenon has been treated theoretically in a number of papers (see the review by Gaponov et al.[59]). The duration of this continuous spectrum was measured in[51]; it is about 6 psec. Its large spectral width and high brightness makes this radiation very useful for investigating absorption spectra, the dynamics of solvation of excess electrons, inverse Raman scattering of light, and biological systems, and for many other purposes. For example, Alfano and Shapiro[55,56] investigated the spectrum of the inverse Raman scattered light that arises when the exciting pulse and a section of the continuous spectrum pass through the specimen together. As a result of this, an absorption band appears in the continuous spectrum at the frequency of the anti-Stokes Raman line of the specimen. A broad section of the continuous spectrum (from 2900 to 8000 Å) was produced as a result of phase modulation in the self-focusing of the laser pulse in the liquid or solid (fused quartz or borosilicate glass) specimen. The emission persisted for several picoseconds. Inverse Raman

scattering has been investigated in benzene, methyl alcohol, liquid nitrogen, and calcite. It should be noted that the continuous spectrum obtained from glass has a virtually constant intensity over its entire extent, and this makes it very convenient for many practical applications.

Griffiths et al,[52] using a setup similar to the one diagrammed in Fig. 9, made careful measurements of the lifetime of the benzene molecule in the upper energy level of the 991 cm^{-1} fully symmetric fundamental vibrations in the liquid state. In addition to the direct measurements of the lifetime of this level, estimates of this quantity obtained from careful measurements of the width and shape of the corresponding line in the thermal Raman scattering spectrum of benzene were used. By diluting the pure benzene with deuterobenzene (C_6D_6) they were able to investigate the effect of intramolecular interactions on the lifetime of the benzene molecule in the excited vibrational state. In a liquid, when there are nearby vibrational levels, transfer of energy from an excited molecule to an unexcited one takes place in the process of intermolecular interactions, and this reduces the lifetime of the excited state and increases the width of the corresponding Raman line.

Near the ν_2 level (991 cm^{-1}) of the benzene molecule lie the ν_7 and ν_9 levels, which correspond to the 985 and 970 cm^{-1} lines. In the interaction of benzene molecules with one another there is a high probability for nonradiative energy transfer of the type

$$C_6H_6\,(\nu_2') + C_6H_5\,(\nu_7) \rightarrow C_6H_6\,(\nu_2) + C_6H_6\,(\nu_7') \div \Delta E,$$
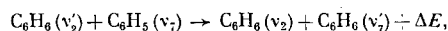
where $\Delta E = 6$ cm^{-1}; here the prime indicated an excited state of the vibrational level. A similar formula can also be written for the interaction of molecules in the ν_2' and ν_9 levels.

For the deuterobenzene molecule (C_6D_6) the difference for the energies of the vibrational states nearest to the ν_2 level of benzene amounts to 28 cm^{-1} and

TABLE II.

Substance	τ_1 psec 2960 ± 50 cm^{-1}	τ_2 psec 5920 ± 60 cm^{-1}
Ethyl alcohol	11.2	25
Butyl alcohol	5.6	*)
Octyl alcohol	5.6	14—16.8
Dodecyl alcohol	5.6	19—22
Ethyl-glycol	11.2	22
Trimethylene glycol	5.6—8.4	16.8—22.4
Tetramethylene glycol	5.6—8.4	22.4
Hexamethylene glycol	5.6	19.6

*)Measurement unsuccessful.

40 cm^{-1}; hence the interaction between C_6H_6 and C_6D_6 molecules has virtually no effect on the lifetime of the ν_2' (991 cm^{-1}) state. From this it follows that diluting the C_6H_6 with C_6D_6 should increase the lifetime of the C_6H_6 molecule in the ν_2' state. On the other hand, there are no nearby energy levels for the 945 cm^{-1} line, so that diluting the C_6H_6 with C_6D_6 should not affect the width of this line.

The experiment showed that the lifetime of the ν_2 level actually increases with increasing C_6D_6 concentration from 5 psec for pure C_6H_6 to 8 psec for pure C_6D_6. The lifetimes obtained from direct measurements and from the widths of the Raman lines agree within the experimental errors, although such agreement cannot always be expected since estimates based on the line width may be too low as a result of the effects of other fairly important line-broadening mechanisms. Direct measurements of the lifetimes of molecules in various energy states are therefore especially valuable.

4. MEASUREMENTS OF THE LIFETIMES OF ACOUSTIC PHONONS

In this section we shall briefly describe methods of determining the lifetimes of acoustic phonons that are based on the use of thermal and stimulated Mandel'-shtam-Brillouin scattering spectra.

It is well known that, as a result of diffraction of a light wave from a Debye thermal elastic wave and modulation of the scattered (diffracted) light by this elastic wave, shifted Mandel'shtam—Brillouin components (MBC) appear in the spectrum of the scattered light. [5]

The shift $\Delta\nu$ of the components is given by the formula

$$2\pi\,\Delta\nu = \Omega_0 = qv, \tag{15}$$

where Ω_0 is the frequency of the hypersound, q is the wave vector of the sound wave ($q = 2nk_0 \sin\theta/2$, where n is the refractive index, k_0 is the wave vector of the exciting light wave, and θ is the scattering angle), and v is the velocity of hypersound. Knowing q determining $\Delta\nu$ from the spectrum, one can easily find v.

The intensity distribution per unit energy range in an MBC is given by[5]

$$I(\omega) = \frac{\Omega_0^2 \delta\omega I_0}{(\omega^2 - \Omega_0^2)^2 + (2\delta\omega)^2 \omega^2}, \tag{16}$$

where $\delta\omega$ is the half width of the MBC and ω is the frequency of the scattered light reckoned from the frequency of the exciting light; moreover,

$$\delta\omega = 2\alpha v. \tag{17}$$

Here α is the spatial damping constant for the sound amplitude.

The lifetime of an acoustic phonon is given by

$$\tau = \delta\omega^{-1} = (2\alpha v)^{-1}. \tag{18}$$

Thus, one can determine the velocity and absorption of hypersound and the lifetime of acoustic phonons from the spectra of thermally scattered light. [5] Such measurements have been successfully made for many substances under various conditions.

There are two ways of using stimulated Mandel'shtam—Brillouin scattering (SMBS) to determine the lifetimes of acoustic phonons. One way is based on determining the SMBS gain, which is directly related to $\delta\omega$, and determining the lifetime of the phonons generated in the SMBS with the aid of a comparatively weak probe pulse.

For the stationary case, when the SMBS is not too intense, one can use the expression[60,61]

$$I_{SMBS}(\omega) = I_s \exp\{g(\omega) I_L L\}, \tag{19}$$

where I_s is the thermal-scattering intensity, I_L is the intensity of the laser-pulse light, L is the range of the nonlinear interaction, and $g(\omega)$ is the gain of the SMBS amplifier. With allowance for the fact that the MBC frequency shifts are small, the relation between the gain $g(\omega)$ and the thermal-scattering intensity $I(\omega)$ can be expressed in the form[62]

$$g(\omega) = \text{const} \cdot \frac{\delta\omega \cdot \Omega^2 (\omega_L - \omega)}{(\omega^2 - \Omega_0^2)^2 + (2\delta\omega)^2 \omega^2}, \tag{20}$$

where ω_L is the frequency of the exciting laser light.

Thus, by measuring the gain as a function of the frequency ω one can find $\delta\omega$ and then can determine the lifetime of the acoustic phonon from Eq. (18). This method for determining the lifetimes of acoustic phonons generated by SMBS was proposed and carried through by Pohl et al.[63] and by Pohl and Kaiser.[64] Two vessels containing the investigated liquid were mounted a short distance apart and served as SMBS generator and amplifier, respectively. SMBS arises in the generator under the action of a monochromatic light pulse of high intensity I_0. The back-scattered SMBS light is attenuated by passing successively through a quarter-wave plate and a polarizer. The intensity I_i of the attenuated SMBS light is measured and the light is then directed into the amplifier and its intensity I_a at the output of the amplifier is also measured. All three quantities develop in time; since $I_i/I_0 \approx 10^{-2}$ and the SMBS takes place under steady state conditions one can use the formula

$$\frac{I_a}{I_i} = 1 + g(\Delta\omega) I_L L. \tag{21}$$

Here L is the range of the nonlinear interaction in the amplifier and $\Delta\omega = \omega - \Omega_0$ is the difference between the generator and amplifier frequencies, which lie within the pass band of the SMBS amplifier.

The lifetimes found in this way for several liquids and solids are listed in Table III. It should be emphasized that the phonon lifetimes listed in Table III for liquids agree well with the corresponding lifetimes determined from the Mandel'shtam—Brillouin spectrum from thermal scattering. This agreement is illustrated for the case of CS_2–CCl_4 solutions by the curves in Fig. 11, which were obtained from thermal and stimulated Mandel'shtam—Brillouin scattering.

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TABLE III. Lifetimes of acoustic phonons in some liquids and solids.[6]

Substance	τ, nsec
Carbon disulfide	2.2
Carbon disulfide + 2.5%	1.9
Acetone	0.9
n-Hexane	0.72
Toluene	0.33
Quartz (Z-cut)	0.25
Schott glasses:	
FK-3	4
F2	3.5 ± 1.5
FS6	3.5 ± 1.5
FK7	2 ± 1
Lucite	1.5 ± 0.5

Another way of determining the lifetimes of acoustic phonons was developed in papers by Winterling and Heinicke,[65] Winterling et al.,[66] and Heinicke et al.[67] Some results of these studies have already been reviewed elsewhere.[11] The method used in these studies was as follows: A light pulse from a Q-switched ruby laser was directed into the solid specimen, which was mounted in a cryostat. Part of the light of this pulse was diverted; the diverted pulse was delayed in time, its polarization plane was rotated through 90° with respect to that of the intense pulse, and it was then made to travel again in the same direction as the intense pulse. If the sound produced by the SMBS has not damped out by the time the probe pulse arrives, the latter will be almost entirely reflected back by the acoustic "lattice"; but if the probe pulse arrives after the sound has damped out, there will be no reflection from the "lattice" at all.

Thus, by varying the probe-pulse delay time or the specimen temperature, one can experimentally determine the character of the acoustic damping and can evaluate the damping constant α. This method has made it possible to determine the lifetimes of phonons in crystalline quartz in a temperature region that is not easily accessible to study by other methods.

A curve was obtained giving the temperature dependence of the lifetime of 29-GHz phonons in a z-cut quartz crystal. This curve shows that the lifetime τ of longitudinal acoustic phonons varies from $\sim 5 \cdot 10^{-7}$ to $\sim 5 \cdot 10^{-8}$ sec over the temperature range from ~ 50 to ~ 105 °K. Also, $\tau \sim T^2$ in the temperature range 150–90 °K.

Heinicke et al.[66] undertook a special study of the lifetime of 24-GHz longitudinal phonons in fused quartz at 2.3 °K. From the measured phonon lifetime it was found that the phonon mean free path is $\approx 2 \cdot 10^{-1}$ cm under these conditions.

Jackobson et al.[68] also measured the lifetime of longitudinal phonons (phonon frequency 33 GHz) from the width of the Mandel'shtam–Brillouin line in fused quartz for thermal scattering at 2.4 °K. The phonon mean free path obtained in this experiment turned out to be $1.2 \cdot 10^{-2}$ cm. In view of the frequency difference,

we can hardly speak here of an important disagreement between the results of the two experiments. The authors of both papers compare their results with the mean free path derived from measurements of the heat conductivity $\varkappa$ (at a temperature at which the phonon frequency plays a dominant part: ~ 0.4 °K, i.e., $\hbar\omega \approx 3kT$), assuming that here one can use the well-known Debye formula

$$\varkappa = \tfrac{1}{3} C_v v l_\varkappa; \tag{22}$$

here C_v is the heat capacity at constant volume, which under these conditions is practically equal to C_p, v is the Debye velocity of sound, and l is the mean free path. It turns out that $l_\varkappa \approx 3 \cdot 10^{-3}$ cm at these frequencies. Here there is an evident difference between the results obtained from SMBS and thermal scattering, and the results obtained with Eq. (22) from measurements of $\varkappa$. The physical reason for this discrepancy is still unknown. However, we may well doubt that the Debye formula for $\varkappa$ is as suitable for fused quartz as it is for crystals. There are definite reasons for such doubt.[70]

Liderer et al.[71] altered the probe-pulse method used in[65–67]: Instead of taking the weak probe pulse from the same laser as emitted the intense pulse, they took the probe pulse from a second laser synchronized to the laser that emitted the pulse giving rise to the SMBS. While the intense pulses were taken from a Q-switched laser emitting 10-MW pulses 20 nsec long, the laser emitting the probe pulses operated in the free-generation mode and emitted 1–10 kW pulses 0.5 μsec long.

This method was tested by measuring the lifetime of phonons in liquid helium at 1.67 °K under its own vapor pressure; the lifetime of a 0.7-GHz acoustic phonon was found to be 49 ± 3 nsec. This method has an obvious advantage, but it is much more laborious in practice.

5. KINETICS OF FLUORESCENCE AND OF THE EXCITON ABSORPTION OF LIGHT IN DENSE ELECTRON-HOLE PLASMAS IN SEMICONDUCTORS

A. Kinetics of fluorescence

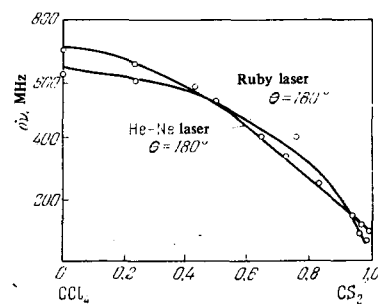The mechanism of fluorescence quenching in one of the representatives of the group of substituted triphenyl

FIG. 11. Line widths in thermal and stimulated Mandel'shtam–Brillouin scattering in CS_2–CCl_4 solutions vs concentration.[64]
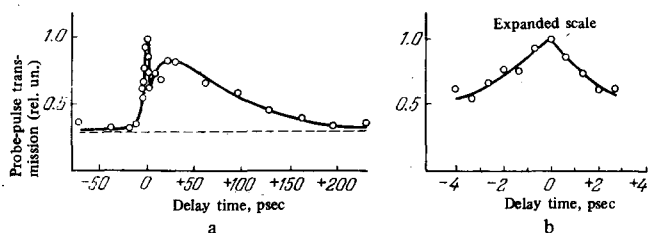
FIG. 12. Probe-pulse transmission of a thin germanium layer vs delay time following excitation in the germanium of a dense electron-hole plasma.[78]

methane dyes (crystalline violet) was investigated by Madge and Windsor,[72] using a setup similar to the one diagrammed in Fig. 1. Such dyes are known to have a fairly high fluorescence quantum yield in the solid state, whereas in solution they hardly fluoresce at all.

Direct measurements of the lifetimes of crystalline-violet molecules in the excited state in solutions differing in viscosity showed that there is a radiationless process that competes with fluorescence in depopulating the excited singlet state and has a characteristic time of 10^{-10} to 10^{-12} sec, depending on the viscosity of the solution. The results obtained in[72] are especially important in connection with the use of such dyes in devices for ensuring mode locking of lasers.

It is known[73] that effects of the time structure of the picosecond pulses can be avoided only if the following condition is satisfied:

$$\Delta\omega \cdot t_s = 1, \tag{23}$$

where $\Delta\omega$ is the frequency width of the stimulated-emission band and t_s is the relaxation time for saturating the shutter. In view of the dependence of t_s on the viscosity of the dye solution, investigated in[72], condition (23) can be satisfied by proper choice of the viscosity.

Solutions of the same dye in methyl alcohol and ethylene glycol were investigated by Lin and Dines.[74] Whereas in[72] it was the transition of the dye molecule from the first excited state to the ground state $(S_1 \to S_0)$ that was investigated, in[74] the time for the radiationless transition from the second to the first excited singlet state $(S_2 \to S_1)$ was measured. Since the decay time of the fluorescence in crystalline violet is shorter than the interval between successive picosecond pulses from the ruby laser used in[74], there was no danger that the population of the excited state would be built up by the series of successively arriving pulses. The experiment showed that the time for the $S_2 \to S_1$ radiationless transition was 30 psec for the dye solution in methyl alcohol and 56 psec for the solution in ethylene glycol. In view of the fact that the viscosities of the two solutions differed by more than 30 times, one would have expected a much greater difference if the transition time were substantially dependent on collisions. Nevertheless, the results indicate that the solvent molecules play a quite appreciable part in the absorption of the energy released in the $S_2 \to S_1$ radiationless transition, and these transitions themselves may be an important

factor in limiting the duration of the pulses obtained from lasers using dye solutions for mode locking.

The kinetics of the spontaneous fluorescence of another dye, erythrosine B, was investigated by Mourou and Malley,[75] who measured the rise and fall of the fluorescence of erythrosine solutions in water and methyl alcohol. The ultrafast shutter was controlled by an infrared pulse from a neodymium laser, while a pulse at twice the frequency was used to excite the fluorescence. The experiments showed that the erythrosine molecule begins to emit immediately after reaching the excited state, so there is virtually no time delay between the arrival of the exciting pulse and the onset of fluorescence.

In an earlier study, Alfano and Shapiro,[76] investigating an aqueous solution of erythrosine, found a considerable delay of the order of 60 psec between the exciting pulse and the peak of the fluorescence, which was attributed to the vibrational relaxation of erythrosine B molecules. However, these results have not been confirmed.

B. Kinetics of the absorption of light by plasmas and by excitons in semiconductors

The technique of exciting dense plasmas in semiconductors by picosecond pulses has made it possible to establish the essential properties of such plasmas with electron concentrations of $\sim 3 \cdot 10^{20}$ cm^{-3}.

Kennedy et al.[77] used an isolated pulse several picoseconds long (intensity $3 \cdot 10^{12}$ photons, wavelength 1.06 μm) to excite a dense plasma in pure germanium and then probed the plasma with a weak pulse of the same wavelength. They measured the transmission factor of a thin germanium layer as a function of the power of the intense pumping pulse and also measured the transmission factor for the probe pulse as a function of the delay time between the probe and pumping pulses. These measurements were made at 80 °K. Later, Shank and Aston[78] made similar studies at room temperature, also using a thin germanium layer. The results of the two studies were concordant, but different physical interpretations were suggested for them. Figure 12 shows the transmission factor for the probe pulse as a function of the delay time between the probe and pumping pulses. The effect of absorption saturation can also be seen in the figure, and there is an extremely narrow (~ 2 psec) peak in the delay-time region $\Delta t \approx 0$. The presence of the narrow peak was interpreted by Kennedy et al.[77] as indicating that electrons are transferred from the conduction band to the valence band in a very short time ($\tau < 5$ psec). According to Shank and Aston,[78] the narrow peak may be attributed to scattering of the intense pulse into the direction of the probe pulse. As a result of the parametric interaction of the intense and "weak" pulses in the electron-hole plasma, a phase lattice arises in the plasma on account of spatial modulation, and this leads to modulation of the refractive index. The period and phase of this lattice are just such that the light scattered from the strong pulse by the lattice will have the same direction as the probe pulse. The angle between

the propagation directions of the intense and probe pulses was about 20° in both experiments. If this is the mechaniam for the production of the narrow peak, one would expect the peak to occur in the delay-time region $\Delta t \approx 0$. The transmission factor for the probe pulse should decrease when the delay time becomes longer than the coherence time of the pulse. An attempt to make this latter interpretation quantitative did not lead to good agreement between the calculations and the experimental results. [78]

The interesting and important experimental result found in both studies opens the path for new experimental and theoretical investigations.

Even earlier, Aston and Shank[79] had developed a method for the ellipsometric measurement of the refractive index of a dense plasma ($1.7 \cdot 10^{20}$ cm^{-3}) in a picosecond time interval. They used an isolated picosecond pulse at the surface of a germanium crystal and probed the plasma with a beam that was 20 times weaker than the first one. The experimental setup was such that refractive-index changes $\delta n/n < 10^{-3}$ could be determined. The sign and magnitude of $\delta n/n$, and also the ambipolar diffusion constant, could be determined from the delay-time dependence of the ellipsometer transmission. Using a $\sim 10^{-2}$ J/cm^2 pulse, it was found that $\delta n/n = -0.05$ at the peak of the curve giving the ellipsometer transmission as a function of the delay time. In this case the peak ellipsometer transmission occurred at a delay time of about 11 psec. The conditions here are favorable for determining the diffusion constant, since any recombinations taking place in this time interval can be neglected. The ambipolar diffusion constant turned out to be 230 ± 5 cm^2/sec, i.e., about twice its value for a low-density plasma.

Irradiation of semiconductor crystals with short intense light pulses resulted in very substantial exciton concentrations ($\sim 10^{20}$ cm^{-3}) in some semiconductors. New and interesting features have been found in the luminescence and absorption spectra at such exciton concentrations. Mahr et al. [80, 81] and Kuroda et al. [82-85] found new bands in the luminescence of CdS and CdSe under excitation by intense light pulses at 1.8–4.2 °K. The authors of [82-84] claim to be the first to have experimentally observed Bose condensation of exciton structures. They found that on exciting CdSe at 1.8–4.2 °K with picosecond infrared pulses on the long-wavelength side of the spectrum there appears an extremely narrow luminescence line, which is present in a limited region of exciting-light intensities. The authors interpreted the appearance of such a narrow luminescence line under intense excitation as a result of Bose condensation of exciton molecules. This observation is important and its interpretation is very intriguing, but one would want to have substantial proof that the line is not due to some other mechanism, e.g., to impurity luminescence, stimulated emission, or something else.

Using the techniques for direct study of fast processes, Kuroda and Shionoya[85] investigated the kinetics of the exciton absorption band of cadmium arsenide at 4.2 °K. In this experiment they observed the time-

scanned absorption spectrum of high-density excitons excited in CdSe by an intense infrared pulse. The apparatus was similar to that diagrammed in Fig. 9, but there were some special features that we want to call attention to. The neodymium glass laser operated in the mode locking regime. In each giant pulse there were about two or three dozen picosecond pulses, each 7 psec long and having a power of 700 MW. The pulse was divided into two parts; one part with its wavelength unchanged ($\lambda = 1.06$ μm) was directed onto the CdSe specimen, while the second-harmonic light, after passing through a delay line, struck a piece of glass where, as a result of phase modulation, it was converted into a continuous spectrum, which covered almost the entire visible region at a power level of about 2.5 W/Å and also lasted for 7 psec. This probe pulse also entered the CdSe specimen after a suitable time delay with respect to the exciting pulse.

As a result of this experiment it was found that when high-intensity light is used for excitation instead of the comparatively weak light from a mercury lamp, the peak of the A-exciton absorption band of CdSe at 4.2 °K shifts toward the shorter wavelengths. This shift toward the higher energies is maximal and reaches a value of 3.2 MeV for a probe-pulse delay time of 20 psec, but it falls rapidly on both sides of the maximum. The authors of[85] attribute this observed shift to the presence of excitons at high density and discuss their results in terms of the theory proposed by Hanamura.[86]

Gale and Mysyrowicz[87] excited biexcitons in a CuCl single crystal at 4.2 °K with 25-psec pulses from a ruby laser. Study of the kinetics of the luminescence band showed that the lifetime of the biexciton was 3 ± 1 psec.

It is not part of our purpose to discuss the physical results obtained for semiconductors in detail. We wish only to call attention to the diversity of the subtle experimental problems that can be solved by direct methods of investigating the kinetics of fast processes.

6. OTHER APPLICATIONS OF PICOSECOND PULSES AND ULTRAFAST OPTICAL SHUTTERS

In this section of the review, we briefly discuss a few other studies in the picosecond time range and a few practical applications of ultrafast optical shutters that have already been made, as well as the prospects for such applications in the future.

The brevity with which these matters are treated and the fact that they are relegated to the end of the review does not at all mean that the authors of the review regard them as less important than those that were discussed in more detail above. The unequal adequacy of the discussions of different subjects is due to a considerable extent to the scientific interests and tastes of the authors of the review and to space limitations.

A. Dynamics of electron solvation processes

Rentzepis and his colleagues[88-90] investigated the dynamics of the solvation of excess electrons and of the

localization of electrons in liquid solutions. Employing a more complicated setup than that diagrammed in Fig. 1, but one of the same type, they simultaneously generated and used single pulses of picosecond duration at the fundamental and second- and third-harmonic frequencies of a neodymium laser.[88] The dynamics of the solvation of excess electrons in an aqueous ferrocyanide ($K_4Fe(CN)_6$) solution was investigated. The first ferrocyanide anion was photoionized by the third-harmonic light ($\lambda = 0.265$ μm). It was found that the infrared absorption at 1.06 μm due to the excess electrons in water appeared 2 psec after the generation of quasifree electrons. It was also found that the absorption of second-harmonic light ($\lambda = 0.53$ μm) by hydrated electrons appeared ~4 psec after the generation of quasifree electrons. The time evolution of the absorption band at $\lambda = 0.53$ μm was also investigated in this study. The band shifted toward the higher energies, and after about 4 psec it occupied the same place as it characteristically does when the specimen is illuminated by a constant light source.

Huppert et al.[89] observed bleaching in the vicinity of the absorption band due to solvated electrons in Na–NH_3 and Na–ND_3 solutions ($2 \cdot 10^{-4}$ M) at temperatures from -85 to -75 °C under the action of an 8 psec light pulse of energy 30 ± 10 mJ. The probe beam passed through a cell 20 cm long containing CCl_4. A pulse having a continuous spectrum arose as a result of phase modulation, and this pulse was passed through a delay line consisting of an echelon, which gave a time resolution (pulse separation) of 20, 6.7, or 3.3 psec. The probe pulse was symmetric in shape before the bleaching and remained so afterward.

The fact that the light beams formed by the echelon were not distorted indicates that the times required for bleaching and for recovery of the absorption were much shorter than the time resolution of the apparatus. The authors[89] estimate this time as $6 \cdot 10^{-13}$ sec. A quantitative determination of the degree of brightening in the 850–1100 nm region of the spectrum was also made in this study.

Huppert and Rentzepis,[90] using a setup of the same type as in[89], investigated the dynamics of electron localization in an Na-methylamine solution in which electrons were produced by a picosecond pulse at $\lambda = 0.53$ μm. The result of this study showed that the time required for localization of an electron is shorter than 5 psec. Bleaching of the absorption band due to solvated electrons by a 1.06 μm pulse in the 1000 nm region took place in a narrow section of ~100 cm^{-1}. The solvated-electron relaxation time was found to be ~ $2 \cdot 10^{-13}$ sec.

B. Study of the structure of picosecond pulses

The use of an ultrafast shutter in a study of the structure of the giant pulse from a neodymium glass laser[91] resulted in very sharp photographs of a series of picosecond pulses separated by a time interval of $2L/c$, where L is the optical length of the laser cavity. The photographs also confirmed the presence supplemen-

tary pulses[92] at a distance $2d/c$ from the main pulse, where d is the distance from the mode-locking cell to one of the laser mirrors. The high contrast ($> 2 \cdot 10^3$) of the photographs permitted the structure of the background between the main and supplementary pulses to be studied. The background turned out to consist of very weak pulses (of intensity 0.1–0.5% of that of the main pulses) whose position varied randomly from exposure to exposure. On increasing the laser pumping level, the number of these small pulses also rose, so that in sum, their contribution amounted to as much as 30% of the total emitted energy.

Rubinov et al.[93] used an ultrafast shutter in a detailed study of the spatial and temporal structure of the second-harmonic pulse from a neodymium glass laser. The investigated pulses had a wavelength width of about 30 Å and a duration of ~10 psec. It was found that the frequency at which the maximum intensity occurs shifts within the pulse toward the lower frequencies by an amount roughly equal to the frequency width of the pulse. The magnitude of the maximum intensity reached its greatest value in a time of the order of 5 psec, and then it decreased.

The subpicosecond structure of the second harmonic pulse was investigated by Groshkov et al.,[94] who, using a setup including a fast CS_2 shutter, achieved a high time resolution that enabled them to record pulses only 0.4 psec long. They discovered a subpicosecond structure in the second harmonic pulse, individual elements of which had a duration of 0.4–0.7 psec and a positive frequency drift of 5 to 30 Å/psec. As the authors point out,[94] the possibility of detecting the fine structure is connected with the presence in carbon disulfide of libration-type processes that are faster than the orientational Kerr effect, and also with the presence of phase modulation of the substructure pulses and the subsequent spectral breakup. This was already mentioned in Chap. 1.

Richardson and Sala[95] made use of ultrafast photography to obtain successive picosecond photographs of the plasma produced in air by pulses from a neodymium glass laser. The plasma was photographed at intervals equal to the gaps between successive picosecond pulses. From their photographs they were able to trace the kinetics of the expansion of the plasma flare.

Fischer and Rossmanith[96] investigated the shape and measured the duration of the light pulses emitted by relativistic electrons in high-energy accelerators. Since the velocity of the beam of electrons was close to the velocity of light, the time structures of the electron beam and the light pulse that it emitted could be regarded as quite identical.

C. Photographing objects moving with the velocity of light, separating objects lying close together, seeing through fog, and other applications of ultrafast optical shutters

Duguay and Hansen, the first to make an ultrafast shutter, used it to investigate fast processes and were
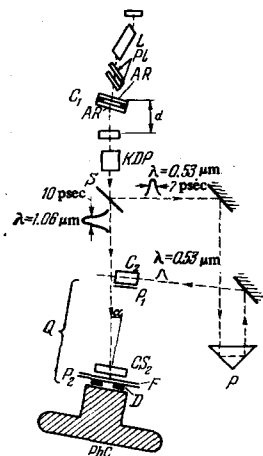
FIG. 13. Experimental setup for photographing a light pulse "in flight"[91]: L—laser; Pl—plates set at Brewster's angle; C_1—cell containing dye; KDP—second-harmonic generator; S—beam splitter; C_2—turbid-water cell; Q—ultrafast shutter; F—filter; P—translatable prism; D—iris diaphragm; P_1 and P_2—crossed polarizers; PhC—camera.

the first to photograph light "in flight." The apparatus used for such experiments by Duguay and Hansen[97] and Duguay and Mattick[91] is diagrammed in Fig. 13. In addition to photographing light "in flight," these authors investigated the question of what a stationary observer would see on his "instantaneous" photographs of a microscopic object moving past him at a velocity close to the velocity of light *in vacua*.

To perform such an experiment, Duguay and Mattick[91] split the green light pulse into two parts with a separating plate and, using a mirror, caused these two pulses to move in the same direction with one pulse directly above the other in a vertical plane. Thus, they produced a "light dumbbell." To make the dumbbell visible, the two pulses were sent together into a slightly turbid medium where they would be visible in the scattered light. Now if the dumbbell be photographed with a camera having an ultrafast shutter (Fig. 13) arranged so that its axis is a perpendicular bisector of the axis of the dumbbell, the photograph will show two spots lying precisely one above the other. Now if the upper pulse be tipped backwards (away from the camera) by rotating the mirror, its light will arrive later and its image will be shifted backwards (in the direction opposite to the propagation direction of the pulses). Finally, if the rotation reaches 90° with respect to the vertical plane, the photograph will show images of two pulses lying one directly behind the other. What is being observed here is the rotation of the investigated object that was pointed out by Terrell in a theoretical study.[99] This experiment is described in detail in[91,98]. Such rotation of the object (e.g., a cube) so that the face farthest from the observer becomes a side face is a consequence of retardation, or of the finite propagation velocity of light. Questions connected with the Lorentz contraction have been discussed in detail by Feinberg.[100]

By using an ultrafast optical shutter and picosecond pulses, one can separately observe (photograph) two or more objects lying close together and fairly far from the observer. If the light-travel time between the objects is larger (preferably much larger) than the exposure time, the light waves reflected from the objects can be recorded separately. As an example we present

the result of an experiment by Duguay and Mattick.[91]

Two glass plates were mounted 1 cm apart. The word "FRONT" was written on the plate nearer the observer, and the word "BACK" on the farther one. A pulse of green light was directed at the plates, and, with the aid of a suitable delay line, a camera (Fig. 13) was made to record first the front plate, and then the back one. Since the light time back and forth between the plates was $2 \text{ cm}/c \approx 66$ psec and the exposure time was 10 psec, two quite sharp photographs could be separately obtained; these photographs are shown in Fig. 14, together with a diagram of the experiment. The good quality of these photographs shows that the shutter does not cause deterioration of the image. With minimal exposures of ~10 psec one can reliably resolve distances between the objects of the order of a centimeter. With the pulses of duration $\sim 5 \cdot 10^{-13}$ sec even now being obtained (with the possibility of using them for an ultrafast shutter), resolutions in the submillimeter range can be achieved. It is quite obvious that such systems are not only of purely scientific significance, but that they will doubtless also prove to be important for the solution of various practical problems.

The ability to control such ultrafast optical shutters makes it possible to receive images through thick fog or other turbid media. Visibility is lost in a fog because of loss of contrast. A thick layer of dense fog between the observer and the object to be observed gives rise to such intense back scattering that nothing but the scattered light can be seen.

Suppose that an object in a turbid medium is illuminated with light pulses. If one has a camera with an ultrafast optical shutter and an adjustable delay line between the pulse that controls the shutter and the pulse that illuminates the object, one can arrange for the shutter to open just when the light wave reflected from the object reaches the camera. In this case all the light scattered by the fog, which reaches the camera before or after the light reflected from the object, will be cut off and one will obtain a fairly clear image of the object. Thus, an object, invisible because it is in a turbid medium, is made visible.

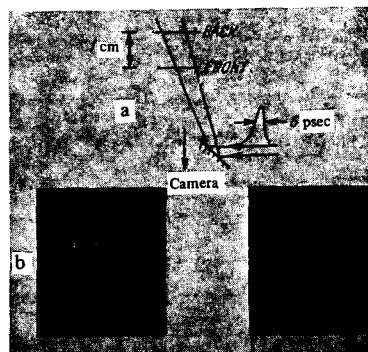Duguay and Mattick[91] conducted the following experiment to illustrate the action of such strobing. The

FIG. 14. Scheme used for separately photographing objects lying close together (a) and the resulting photographs (b).[91]
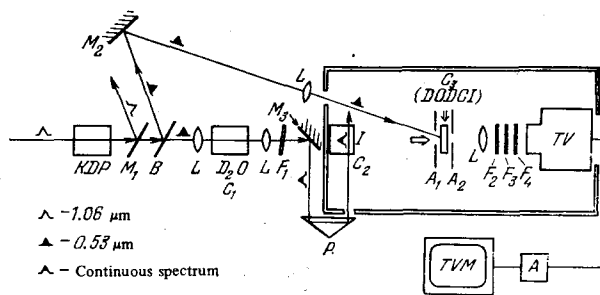
FIG. 15. Setup for amplifying weak picosecond pulses[101]: M_1—plate for separating the infrared and green pulses; B—beam splitter; M_2 and M_3—mirrors; P—translatable prism; C_1—heavy-water cell; C_2—cell containing a slightly scattering solution; C_3—dye cell for amplifying the weak pulse; F_{1-4}—neutral filters; A_1 and A_2—iris diaphragms; L—lenses; TV—television camera; A—videotape unit; TVM—television monitor. The letter I denotes the image shaper.

outline of a bell was drawn on a sheet of paper and the drawing was covered with a sheet of tissue paper. Under ordinary illumination the drawing could not be seen at all through the tissue paper. But illuminating and photographing through the tissue paper by the picosecond strobe method gave a fairly sharp image of the bell, although the contrast was lower than that of the original drawing. These photographs can be seen in papers already cited.[91,98] The use of subpicosecond pulses offers the interesting possibility of looking through the skin of a human being.[91]

The strobe method in the picosecond range for radically improving visibility will doubtless find wide scientific and technical application, and this is the more likely because a weak (e.g., reflected) pulse can be amplified. Such amplification of a weak light pulse has been achieved by Busch et al.[101] In their experiment, which is diagrammed schematically in Fig. 15, a single light pulse of picosecond duration and wavelength $\lambda = 1.06$ μm was directed through a frequency doubling KDP crystal, after which the fundamental-frequency pulse was directed out of the apparatus, while the second-harmonic light was split into two parts, which followed different paths. One beam of $\lambda = 0.53$ μm light entered a cell containing a solution of a saturable absorber based on the dye 3,3-diethyloxadicarbocyanine iodide (DODCI). The second pulse entered a vessel containing D_2O, where there arose a broad band of light which was directed through a delay line into a vessel containing a slightly scattering medium. The scattered light was amplified by a factor of 10^2 in the cell containing DODCI, and the resulting signal from the television camera was recorded on videotape and was later displayed on a kinescope. The weak scattered light could not be recorded without amplification. Kuroda et al.[102] used this system, including the television camera and the videotape, in their studies. They regard it as the most sensitive and suitable for work with an ultrafast shutter.

On the other hand, the studies of Ippen and Shank[103] showed that by using a dye laser operating in the mode locking regime one can control an ultrafast shutter in

such a manner that it can be operated at a repetition rate of 10^5 sec^{-1}. The union of all these separate achievements of picosecond technology may provide a unique possibility of seeing through fog or other turbid media. Of course serious work is still required to achieve this, but perhaps some of that work has already been done. Here we should also point out that an ultrafast shutter can be based on the saturable absorption of a dye. Such a gate with a variable exposure from 10 to 40 psec has been realized in the work of Mourou et al.[104] and has been used to investigate laser-pulse lengths and fluorescence decay times, and of course it may find wider application.

In this review we have not touched at all upon the applications of picosecond spectroscopy to the study of the mechanisms of photosynthesis[105] and human vision, nor to many other doubtless interesting matters.

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