

# Bleaching of water by intense light at the maximum of the $\lambda \sim 3 \mu\text{m}$ absorption band

K. L. Vodop'yanov

*Institute of General Physics, Academy of Sciences of the USSR, Moscow*

(Submitted 5 May 1989; resubmitted 4 August 1989)

Zh. Eksp. Teor. Fiz. 97, 205–218 (January 1990)

A strong bleaching effect (reduction in the absorption of light) was observed at the wavelength of  $2.94 \mu\text{m}$  for water and other hydroxyl-containing liquids under the influence of high-intensity laser radiation pulses of this wavelength and of  $10^{-7}$ – $10^{-10}$  s duration. At  $2.79 \mu\text{m}$  an increase in the intensity of the incident light increased the absorption and this was followed by bleaching. These effects were attributed primarily to an increase in the temperature of a liquid, which "followed-up" the changes in the laser radiation intensity, as a result of very fast ( $\sim 10^{-11}$  s) relaxation of the vibrational excitation of water; this causes hydrogen-bond weakening which has a considerable influence on the absorption spectrum of water in the region of the valence (stretching) vibrations of the OH group.

## 1. SOME PROPERTIES OF HYDROXYL-CONTAINING ASSOCIATED LIQUIDS (WITH WATER USED AS THE EXAMPLE)

Near the frequency of  $3400 \text{ cm}^{-1}$  ( $2.94 \mu\text{m}$ ) the optical extinction coefficient  $\kappa$  (imaginary part of the refractive index) of water has a record value reaching  $\kappa = 0.3$  at room temperature.<sup>1</sup> This is due to an absorption band representing the valence (stretching) mode of the vibrations of  $\text{H}_2\text{O}$ . The intensity of  $\lambda = 2.94 \mu\text{m}$  light transmitted by a layer of water decreases in accordance with the Bouguer law with an absorption coefficient  $\alpha = 4\pi\kappa/\lambda = 1.28 \times 10^4 \text{ cm}^{-1}$ , so that the depth of penetration of light in water is only  $0.78 \mu\text{m}$ . Knowing the density of water and the extinction coefficient  $\kappa$ , we can readily find the cross section  $\sigma_{\text{H}_2\text{O}}$  of a transition in water at the wavelength of  $2.94 \mu\text{m}$ :

$$\sigma_{\text{H}_2\text{O}} = 4\pi\kappa/\lambda n = 3.9 \cdot 10^{-19} \text{ cm}^2,$$

where  $n$  is the number of molecules of water in  $1 \text{ cm}^3$ .

An isolated water molecule has the point symmetry group  $C_{2v}$  and has three main frequencies of the normal vibrations: symmetric ( $\nu_1 = 3657 \text{ cm}^{-1}$ ), bending ( $\nu_2 = 1595 \text{ cm}^{-1}$ ), and antisymmetric ( $\nu_3 = 3756 \text{ cm}^{-1}$ ).<sup>2</sup> The vibrations of frequencies  $\nu_1$  and  $\nu_3$  are known as the valence or stretching vibrations. The spectrum of water vapor at a pressure of 15 Torr and a temperature of  $25^\circ\text{C}$  (curve 3 in Fig. 1)<sup>2</sup> consists of a very large series of lines of half-width  $0.05$ – $0.5 \text{ cm}^{-1}$ , representing vibrational-rotational transitions in the valence vibration range. The spectrum of spontaneous Raman scattering has a narrow line of frequency  $3654 \text{ cm}^{-1}$  (Ref. 3).

A characteristic feature of many substances containing the OH group is the formation of the hydrogen (H) bonds in the condensed state of (at moderately low pressures) in the vapor state, resulting in the association of molecules into complexes. The strongest spectroscopic manifestation of the hydrogen bond is a considerable (up to 10%) reduction in the frequency of the valence vibration of the OH group. Such frequency changes have been observed in the Raman scattering band in the infrared absorption spectra in the region of the fundamental tone and its overtones. For example, the valence vibrations in the Raman scattering and infrared absorption spectra of liquid water at  $30^\circ\text{C}$  (curve 1 in Fig. 1) are characterized by a smeared-out band of  $\sim 400 \text{ cm}^{-1}$

width with a maximum near  $3400 \text{ cm}^{-1}$ . In this case the spectrum of liquid water is a superposition of shifted (because of H bonds) bands  $\nu_1$  and  $\nu_3$  and an overtone of the band  $\nu_2$  (Ref. 2).

Figure 1 (curve 4) shows also a vibrational infrared absorption band of water dissolved in a nonpolar liquid ( $\text{CCl}_4$ ) in which the hydrogen bonds do not form.<sup>4</sup> Clearly, in this case the frequency of the absorption maximum ( $\sim 3700 \text{ cm}^{-1}$ ) lies within the absorption range of water vapor. Thus, the formation of the H bonds in water has two results: 1) the valence absorption band shifts by  $300 \text{ cm}^{-1}$  toward lower frequencies; 2) there is a strong (by a factor of  $\sim 10$ ) increase in the integral intensity of the absorption band per molecule, which is due to the collective interaction in the presence of the H bonds.<sup>5</sup>

Similar effects are exhibited also by other substances containing the OH group, such as alcohols, phenols, glycols, carboxylic acids, etc. In the case of these substances the transition from the vapor to the liquid phase results in such major changes in the frequencies of the internal molecular vibrations only for the OH groups and the shift is proportional

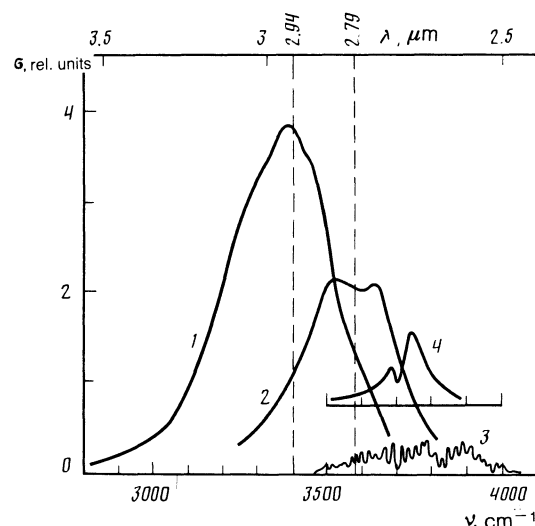


FIG. 1. Infrared absorption spectra of water at  $30^\circ\text{C}$  (1) and  $374^\circ\text{C}$  (2), of water vapor at 15 Torr and  $25^\circ\text{C}$  (3), and of water dissolved in  $\text{CCl}_4$  (4); curves 1–4 are reduced to the same scale.

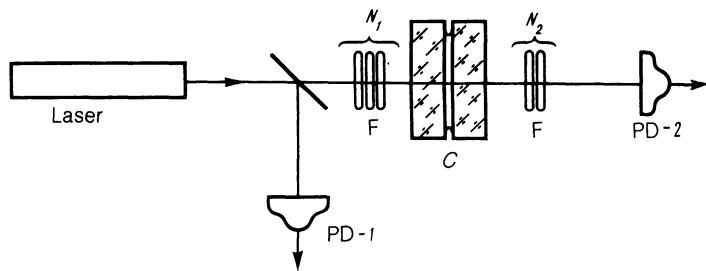


FIG. 2. Experimental setup used in investigations of the transmission of a cell as a function of the energy and intensity of laser radiation. Here, PD represents an infrared photodetector, C is the cell with the liquid, and F are the attenuating filters.

to the H-bond energy (Badger-Bauer law<sup>4</sup>), whereas other frequencies, such as those of the CH<sub>2</sub> and CH<sub>3</sub> groups in alcohols, are practically unaffected. Hence it follows that the vibrations of the OH group are most sensitive to the intermolecular interactions.<sup>3</sup>

Broadening of the band in the infrared absorption and Raman scattering spectra of liquids is naturally inhomogeneous and is a consequence of the random nature of the hydrogen bonds<sup>6</sup>: each group of hydroxyl-containing molecules is characterized by its own H-bond strength and a proportional shift of the maximum of the absorption spectrum toward higher frequencies.

An estimate of the energy per H bond in liquids, carried out using different physical chemical and spectroscopic methods, gives a value of 2–8 kcal/mol in Ref. 4. The modern value of the hydrogen-bond energy in water, given by Luck,<sup>7</sup> is ~3.8 kcal/mol (0.17 eV) per H bond. Since each water molecule participates in four bonds (in two it acts as a donor and in the other two as an acceptor), it follows that there are two H bonds per molecule, which corresponds to an energy of 0.34 eV or a specific energy 1.8 kJ/cm<sup>3</sup>. This energy is naturally small compared with the energy of the internal molecular bonds, which is on the average 100 kcal/mol, but it is several times greater than the energy of the usual van der Waals interaction, which amounts to 1–2 kcal/mol.

It therefore follows that the major change in the nature of the vibrations of the OH group, manifested by a considerable shift and broadening of the relevant absorption band and by a strong increase in the absorption intensity, is the most striking spectroscopic manifestation of the H bond. For comparison, we must point out that in the case of ice for which the H-bond energy given by Whalley<sup>7</sup> amounts to 6 kcal/mol per bond, the valence infrared absorption band is shifted even further toward lower frequencies and its maximum is located near 3200 cm<sup>-1</sup>; the absorption intensity at the maximum is even higher than in water.

## 2. EXPERIMENTAL METHOD

The interaction of laser radiation with water and other hydroxyl-containing liquids was investigated by us using two types of erbium-activated garnet lasers emitting at wavelengths of 2.94 and 2.79 μm. The former was an erbium-activated yttrium erbium garnet Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Er<sup>3+</sup> (λ = 2.94 μm) laser with an enhanced (5 × 10<sup>21</sup> cm<sup>-3</sup>) concentration of the Er<sup>3+</sup> ions,<sup>8</sup> used successfully already as a promising tool in laser surgery because of the high absorption coefficient of living tissues consisting mainly of water.<sup>9</sup> The emission wavelength of this laser is located at the maximum of the valence absorption band of liquid water.

The emission wavelength of the latter laser (2.79 μm),

with an active element consisting of erbium-activated yttrium scandium gallium garnet,<sup>10</sup> was located in the high-frequency wing of the same absorption band of water (Fig. 1) and the absorption coefficient α = 5.16 × 10<sup>3</sup> cm<sup>-1</sup> was 2.5 times less than at the band center.

These lasers were operated at a repetition frequency of 1 Hz in one of three possible time regimes:

1) Emission of "giant pulses" as a result of electrooptic Q switching with a lithium niobate crystal, resulting in an output pulse with a Gaussian time profile, a total duration at half-amplitude τ<sub>1</sub> = 120–130 ns, and an output energy of 10–20 mJ.

2) A "train of ultrashort pulses" generated by active mode locking, when the laser emitted a series of ultrashort pulses of 100 ps duration separated by an interval of 7 ns, with an envelope of 150–160 ns duration<sup>11,12</sup> and delivering an energy of 10–20 mJ for the whole train.

3) A single spike separated from a train of ultrashort pulses by electrooptic methods and then amplified to produce a single pulse of ~100 ps duration and up to 2 mJ energy.

The laser beam with the Gaussian spatial distribution of the intensity (TEM<sub>00</sub> mode) was directed to a quartz cell (Fig. 2) containing the investigated liquid and characterized by an inner gap of thickness 1–10 μm. The energy of the radiation incident on the cell was varied by attenuating filters F. Selection of the focusing lens made it possible to vary the laser spot on the cell within the range S = 5.7 × 10<sup>-5</sup>–1.3 × 10<sup>-2</sup> cm<sup>2</sup>. Photodetectors PD-1 and PD-2 were used to record the intensity or energy of the incident and transmitted radiation.

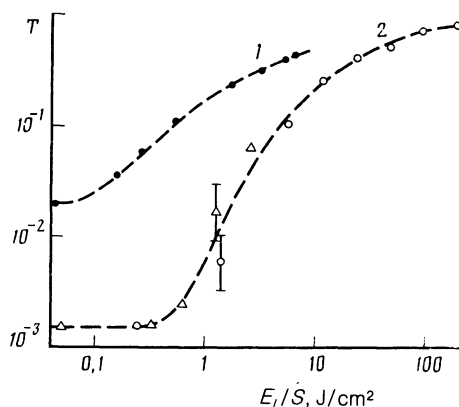


FIG. 3. Dependences of the integral transmission cell with water on the incident energy density (λ = 2.94 μm): ●) giant pulse, S = 2 × 10<sup>-3</sup> cm<sup>2</sup>, T<sub>0</sub> = 2%; △) single spike and ○) train of pulses, S = 2.5 × 10<sup>-5</sup> cm<sup>2</sup>, T<sub>0</sub> = 0.15%.

TABLE I. Bleaching of different liquids by giant ( $\tau_l = 120$  ns) erbium laser pulses of  $\lambda = 2.94$   $\mu\text{m}$  wavelength.

Liquid	$S \times 10^2, \text{cm}^2$	$T_0, \%$	$T_{\text{max}}, \%$	$E_l, \text{mJ}$
Water	1.3	1	16	20
	1.3	16	49	20
	1.3	19	52	20
	0.2	2	47	12
Ethanol	1.3	18	46	20
Methanol	1.3	30	69	20
Glycerine	1.3	1	14	20
		18	44	
		38	65	

Notation:  $S$  is the laser spot area,  $T_0$  is the initial transmission of the cell,  $T_{\text{max}}$  is the transmission at the maximum of the laser radiation intensity, and  $E_l$  is the laser radiation energy.

### 3. EXPERIMENTAL RESULTS OBTAINED USING $\lambda = 2.94$ $\mu\text{m}$ LASER RADIATION

Measurements employing a giant pulse ( $\tau_l = 120$  ns) were carried out first. Curve 1 in Fig. 3 represents the dependence of the integral transmission  $T$  of the cell, defined as the ratio of the energy of the transmitted laser pulse to the energy of the incident pulse, on the energy density in the incident beam. It is clear from Fig. 3 that an increase in the energy density of the incident radiation resulted in a monotonic increase in the integral transmission. Similar experiments were carried out also on other hydroxyl-containing liquids with hydrogen bonds, namely on ethanol, methanol, glycerin, etc. The results of these experiments are collected in Table I, showing that the increase in the cell transmission compared with the initial value could be appreciable (one or two orders of magnitude).

The dynamics of bleaching of water and other liquids by giant erbium laser pulses was also investigated by the Lissajous-figure method. A signal from the fast-response detector PD-1 (Fig. 2) and proportional to the intensity of the radi-

ation reaching the cell was applied to the  $x$  plates of an oscilloscope and the signal from PD-2, proportional to the intensity of the transmitted beam, was applied to the  $y$  plates. In this experiment the photodetectors PD-1 and PD-2 were thin films exhibiting the pyroelectric effect. Had the transmission of the cell been independent of the intensity of the incident light, the oscilloscope screen would have shown a straight line with a slope representing the transmission coefficient of the cell. In the case of transmission dependent on the laser intensity the oscillogram should deviate from a straight line.

Figure 4 shows oscillograms obtained for the cells containing water and glycerine. The experiments were carried out in such a way that the total number of filters  $N_1 + N_2$  attenuating the radiation (each by a factor of two) before and after the cell remained constant. The area of the laser spot was  $S = 1.3 \times 10^{-2} \text{cm}^2$ . The maximum laser energy reaching the cell was 20 mJ. Reliable reconstruction of the time pattern was ensured by modulating periodically (20 ns) the brightness of the cathode-ray beam inside the oscilloscope. When the density of the laser beam reaching the cell

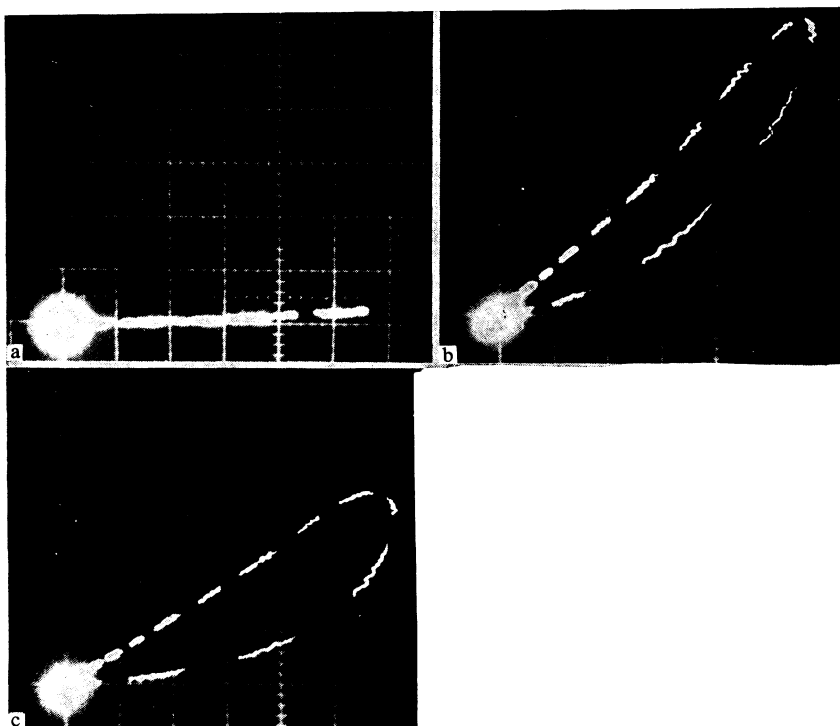


FIG. 4. Oscillograms illustrating the dependence of the intensity of the transmitted light on the intensity of the incident light in the case of water (a,b) and glycerine (c): a) low light intensity; b), c) maximum light intensity. The initial transmission was  $T_0 = 1\%$ , the timing marks are separated by 20 ns, the arrows identify the direction of increase in time.

was low (i.e., when  $N_1$  was maximal) the cell transmission coefficient was constant (Fig. 4a) representing the absorption deduced from the tabulated values in Ref. 1; at the highest laser intensities ( $N_1 = 0$ , Figs. 4b and 4c) the slopes of the curves varied with time, indicating bleaching of the substance inside the cell. We also found that the hysteretic path of the electron beam striking the oscilloscope screen formed close loops. This hysteresis demonstrated that the recovery (relaxation) time of the absorptivity of the cell was quite long ( $\chi\tau_{\text{rel}} > 120$  ns).

We shall now consider four possible mechanisms of bleaching of water under the influence of intense erbium laser radiation of  $\lambda = 2.94 \mu\text{m}$  wavelength.

1. *Spectroscopic saturation of a transition between two vibrational-rotational levels of water.* Since the characteristic laser radiation energy needed to halve the optical density of water at  $\lambda = 2.94 \mu\text{m}$  (curve 1 in Fig. 3) is  $I_1 \sim 10^7$  W/cm<sup>2</sup>, the relationship describing the saturation intensity of a two-level system

$$I_s = \hbar\omega / 2\sigma_{\text{H}_2\text{O}}\tau_{\text{rel}} \quad (1)$$

yields the relaxation time  $\tau_{\text{rel}} \sim 10^{-8}$  s, which is far too long for vibrational relaxation in condensed media; it follows from the Lissajous loop experiments that this time is even longer:  $\tau_{\text{rel}} > 10^{-7}$  s. It is known that, for example, in the case of the valence vibrations of the C—H bond the energy relaxation time is 20 ps in ethanol and 5 ps in trichloroethane.<sup>13</sup> We have to consider also the possibility of multistage absorption accompanied by transitions to higher vibrational-rotational levels.

2. *Formation of a bubble due to the high specific input energy on absorption of laser radiation.* In this case the absorption spectrum in the region of a laser spot becomes typical of a vapor filling this bubble (Fig. 1), so that the absorption at the laser wavelength falls strongly.

3. *Breaking of hydrogen bonds due to the excitation of the valence vibrations of water, resulting in a shift of the absorption spectrum towards shorter wavelengths.* This mechanism many operate if the recovery time of the hydrogen bonds is not too short ( $\tau > \tau_1 \approx 10^{-7}$  s).

4. *Heating of water by the laser radiation even by a few tens of degrees, which can result in significant changes in the absorption spectrum.* It follows from the fluctuation theory of the hydrogen bonds that heating of water shifts the equilibrium toward formation of weaker hydrogen bonds.<sup>6</sup> Consequently, the maximum of the valence infrared band shifts toward shorter wavelengths and the integral intensity of the band decreases.<sup>2</sup> This is illustrated in Fig. 1 (curve 2) by the absorption spectrum of water at the critical point ( $t_c = 374^\circ\text{C}$  and  $p_c = 225$  bar).<sup>2</sup>

If nevertheless the generalized model of a two-level system with  $\tau_{\text{rel}} \gg \tau_1$  is valid, then in the first approximation the reduction in the number of the absorbing centers should be proportional to the integral of the incident light intensity. This means that if the input energy is distributed homogeneously throughout the thickness of the cell, then

$$\ln(T_{\text{max}}/T_0) \sim \int_0^t (1-T) I_l d\tau \sim E_{\text{abs}}/S.$$

The oscillograms in Fig. 4 allow us to plot the dependences of  $\ln(T_{\text{max}}/T_0)$  on  $E_{\text{abs}}/S$ . Such graphs are plotted

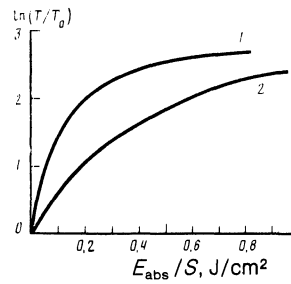


FIG. 5. Experimental dependences of the logarithm of the transmission of water (1) and of glycerine (2) on  $E_{\text{abs}}/S$ ;  $T_0 = 1\%$ .

for water and glycerine in Fig. 5 and they show that the two quantities are not proportional. Therefore, the effect in question cannot be described by the simplest model of a two-level system; this also follows from the discussion given below.

Next, we carried out experiments in which we used single  $\lambda = 2.94 \mu\text{m}$  ultrashort pulses and whole trains. We included in Fig. 3 (curve 2) the dependence of the integral transmission on the energy density of the incident radiation in those cases when a single spike or the whole laser train was incident on the cell. The area of the laser spot was  $S = 2.5 \times 10^{-5}$  cm<sup>2</sup>. Clearly, the dependences obtained for a train were approximately the same as those for a single spike. Since the effective durations of a single spike and a train of pulses differed by three orders of magnitude, the results indicated that the transmission was a function not of the intensity but of the input energy. Moreover, as in the case of the experiments described earlier, the recovery time of the absorptivity was at least 160 ns.

On the other hand, the observation that in the case of a single spike right up to the maximum value  $I_1 = 2.6 \times 10^{10}$  W/cm<sup>2</sup> the peak intensity had no effect (and only the energy density was important) led us to the conclusion that the laser radiation intensities were insufficient to reach spectroscopic saturation of the transition between the zeroth and first vibrational levels of the water molecule:  $I_1 < I_s$ ; it is clear from Eq. (1) that the vibrational relaxation time of water is  $\tau_{\text{rel}} < \hbar\omega / 2\sigma_{\text{H}_2\text{O}} I_1 = 3$  ps. Clearly, the lower limit of the relaxation time should be the reciprocal of the width of the absorption band ( $400 \text{ cm}^{-1}$ ) amounting to 0.1 ps. Therefore, we obtained the estimate  $0.1 \text{ ps} < \tau_{\text{rel}} < 3 \text{ ps}$ .

It should also be noted that the degree of bleaching of water became quite considerable: the integral transmission of the cell increased from the initial value  $T_0 = 1.5 \times 10^{-3}$  (Fig. 3) to  $T_{\text{max}} = 0.9$ , i.e., by almost three orders of magnitude. The optical density  $D$  decreased by a factor of  $\sim 10$ .

Since it was difficult to compare the results of experiments carried out under different initial conditions, namely for different cell thicknesses (and, consequently, different initial transmissions) as well as for different laser spot dimensions and pulse durations, we attempted to combine all the experimental results by finding suitable functions of the initial quantities.

Figure 6 shows the dependence of the relative reduction in the optical density of water at the  $\lambda = 2.94 \mu\text{m}$  wavelength

$$-\frac{\Delta D}{D} = \frac{\ln(T_{\text{max}}/T_0)}{\ln(1/T_0)}$$

on  $E_{\text{abs}}/V$ , representing the energy absorbed by 1 cm<sup>3</sup> and averaged over the cell thickness and the transverse dimen-

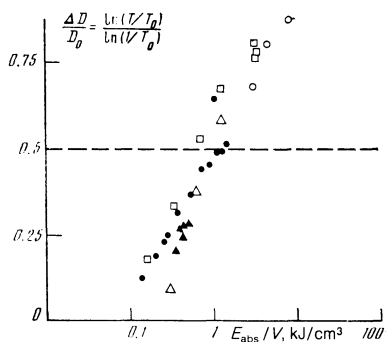


FIG. 6. Dependences of the relative reduction in the optical density of water at  $\lambda = 2.94 \mu\text{m}$  on the specific input energy obtained under different experimental conditions:  $\blacktriangle$ ,  $\square$ ,  $\bullet$  giant pulse,  $S = 1.3 \times 10^{-2} \text{ cm}^2$ ,  $d = 1.6 \mu\text{m}$ ,  $T_0 = 12\%$  ( $\blacktriangle$ ),  $S = 1.5 \times 10^{-2} \text{ cm}^2$ ,  $d = 3 \mu\text{m}$ ,  $T_0 = 1.8\%$  ( $\square$ ),  $S = 1.3 \times 10^{-2} \text{ cm}^2$ ,  $d = 3.5 \mu\text{m}$ ,  $T_0 = 1.2\%$  ( $\bullet$ );  $\circ$ ,  $\triangle$  train of ultrashort pulses and a single spike,  $S = 2.5 \times 10^{-5} \text{ cm}^2$ ,  $d = 5 \mu\text{m}$ ,  $T_0 = 0.15\%$ .

sions of the laser spot; here,  $T_0$  is the initial transmission and  $T_{\text{max}}$  is the transmission at a given absorbed energy density. We used the experimental results obtained employing laser pulses of different durations ( $\tau_l = 10^{-7} - 10^{-10} \text{ s}$ ) and cells of different thicknesses with different areas of the laser spot.

It is clear from Fig. 6 that the change in the optical density of water was a function of the specific input energy, in spite of the difference between the experimental conditions. The scatter of the experimental points was clearly due to errors in the determination of the laser spot area. The characteristic input energy density which halved the optical density was  $\sim 1 \text{ kJ/cm}^3$ . This input energy density increased the temperature of the irradiated water layer by  $240^\circ\text{C}$ .

Our experiments on picosecond pulses led also to another important conclusion, namely that the formation of a bubble (second mechanism) was not the reason for an increase in the transmission. In fact, in the case of a single laser spike of  $\tau_l \sim 10^{-10} \text{ s}$  duration the formation of a bubble would require an unrealistic mass removal from the irradiation zone at a velocity  $v \sim \omega_0 / \tau_l \sim 10^7 \text{ cm/s} \gg c_s$ , where  $\omega_0$  is the radius of the laser spot and  $c_s$  is the velocity of sound in water. Expansion of a liquid in the direction of the normal to the cell will be shown later to reduce the optical density by less than 10% in the available time.

#### 4. THERMODYNAMIC PARAMETERS OF A LIQUID IN THE IRRADIATION ZONE

Determination of the temperature of a layer of water irradiated with a short erbium laser pulse was of considerable interest and it could provide information on how fast were the excited vibrations of the valence mode thermalized. In principle, the temperature could be measured using thermal radiation, but because of the smallness of the irradiated volume the integral thermal radiation signal was below the sensitivity limit of fast infrared detectors. Since the increase in the temperature of a liquid was related uniquely to the increase in the pressure, we tried to measure the pressure in the irradiated zone with the aid of fast-response piezoelectric sensors.<sup>14</sup>

The quartz cell irradiated with ultrashort ( $\sim 100 \text{ ps}$ ) erbium laser pulses characterized by  $\lambda = 2.94 \mu\text{m}$ . The cell gap containing the investigated liquid was  $10 \mu\text{m}$  thick. Acoustic (pressure) pulses were recorded using fast-re-

sponse thin-film piezoelectric sensors with a time resolution of 0.5 ns and an oscilloscope with a pass band of 1 GHz.

When the intensity of the incident laser radiation was  $I_l = 24 \text{ GW/cm}^2$  (corresponding to a volume input energy of  $8 \text{ kJ/cm}^3$ ), pressure pulses of 20-kbar amplitude and 0.75-ns duration were recorded in water. The minimum duration of the pressure pulses found by calculation was limited by the time taken by sound to travel a distance equal to the depth of penetration of light  $\tau_s = 1/\alpha c_s$ , and it amounted to 0.5 ns for water; this was in agreement with the measured pressure pulse duration, when allowance was made for the instrumental function of the apparatus and for an increase in the depth of penetration of light due to the bleaching effect. The measured pressure was also in good agreement with the calculations.<sup>14</sup>

In the case of glycerine the amplitude and duration of the pressure pulses were 14 kbar and 3 ns, respectively; this was mainly due to the fact that the absorption coefficient of light was less than for water.

Since the equation of state of water is well known,<sup>15,16</sup> it follows that if we know the pressure in the irradiation zone and the change in the volume of the zone, we can find the temperature of the liquid during irradiation. In the course of a laser pulse ( $10^{-10} \text{ s}$ ) the volume of the liquid in this zone changed only slightly (by 5–10%).<sup>12</sup> Hence, using the data from Ref. 15 we found that the water temperature reached 1500–2000  $^\circ\text{C}$ . Approximately the same values of this temperature were obtained by simple division of the density of the input energy by the specific heat of water under normal conditions.

We thus found that the interaction of laser radiation with water and other liquids created high temperatures and pressures in the irradiated zone. In the case of water when the input energy was  $8 \text{ kJ/cm}^3$  the temperature was  $\sim 2000 \text{ K}$  and the pressures was  $p \sim 20 \text{ kbar}$ . Since in our case the energy transferred to the liquid involved excitation of the valence vibrations of the molecules, the very fact of generation of acoustic pulses of such short duration indicated that the thermalization of the excited molecules in the investigated liquids occurred in  $< 1 \text{ ns}$ .

The relaxation time of the pressure in the cell with a characteristic thickness  $d = 5 \mu\text{m}$  was  $\tau_p \sim d/c_s \times (1 - R) \sim 20 \text{ ns}$ , where  $R = 0.8$  is the reflection coefficient of the pressure pulse at the quartz–water interface because of the difference between the acoustic impedances of the two materials.

The density relaxation time, i.e., the time in which the density  $\rho$  of water was halved, corresponded to bending of walls in the direction of the normal to the cell by  $\sim d/2$  (expansion in the rate of direction had little effect on the reduction in the density). For  $p \sim 10 \text{ kbar}$  and  $d = 5 \mu\text{m}$  the density relaxation time was

$$\tau_\rho \sim d \rho c_s^2 / 2 p_{\text{eff}} \sim 100 \text{ ns},$$

where  $p_{\text{eff}}$  is the effective pressure representing the average between the initial and final pressures.

Shadow and interference-holographic methods were used in Ref. 17 to study the dynamics of the interaction of giant ( $\tau_l = 100 \text{ ns}$ ) erbium laser pulses with a layer of water  $5\text{-}\mu\text{m}$  thick enclosed in a cell. The diagnostic light pulse was the second-harmonic of a neodymium laser ( $\lambda = 0.53 \mu\text{m}$ ), of 10 ns duration and synchronized with the erbium laser

pulse. The delay between the exciting and diagnostic pulses was varied within a wide range. These experiments showed that during an exciting pulse of 5–7 mJ energy (forming a spot of  $1.4 \times 10^{-3} \text{ cm}^2$  area) there was no transverse expansion of water. However, a bubble formed (when the input energy density was  $\sim 10 \text{ kJ/cm}^3$ ) only  $0.5 \mu\text{s}$  after the erbium laser pulse and it collapsed in a reversible manner in 1 ms.

Clearly, the density of water could not change significantly during a pulse of 100-ns duration as a result of the transverse expansion of the liquid or due to bending of the cell walls, so that the bleaching effect occurred under  $\rho \sim \rho_0$  conditions.

The relaxation time of the temperature of water in the cell (assuming arbitrarily that the temperature was constant across its thickness) was governed by the thermal conductivity of quartz and amounted to  $\tau_T = 1\text{--}20 \mu\text{s}$  for  $d = 1\text{--}5 \mu\text{m}$ .

### 5. POSSIBLE MODEL OF THE BLEACHING EFFECT

We reported in Ref. 18 the use of water and ethanol as bleachable absorbers of radiation emitted by an yttrium erbium aluminum garnet ( $\lambda = 2.94 \mu\text{m}$ ) laser. These liquids behaved like passive saturable filters utilizing dye solutions and employed in lasers emitting visible and near-infrared radiation; single giant radiation pulses with an energy 20 mJ and of 120 ns duration were generated. When the laser pumping rate exceeded a certain value, a second giant pulse was observed 20–25  $\mu\text{s}$  after the first pulse. This was typical of lasers with saturable filters. In our case the appearance of the second giant pulse indicated that the absorptivity of the liquid was restored in a time which was certainly shorter than 20  $\mu\text{s}$ .

The experiments described above and the preceding studies indicated that the recovery time of the absorptivity of a water layer was within the range  $100 \text{ ns} < \tau < 20 \mu\text{s}$ . This was further evidence that in the case of laser pulse durations used in our study the bleaching was primarily due to a change in the water temperature, because the cooling time of the cell was also of the order of microseconds.

This hypothesis was checked by plotting (Fig. 7) the temperature dependence of the intensity of the OD infrared absorption band of liquid HDO at a constant density of  $\rho = 1 \text{ g/cm}^3$  (Ref. 2). The spectroscopic behavior of HDO was qualitatively similar to  $\text{H}_2\text{O}$ , except that under normal conditions the maximum of the valence band of OD was close to  $2500 \text{ cm}^{-1}$  (instead of  $3400 \text{ cm}^{-1}$ ) and, in contrast

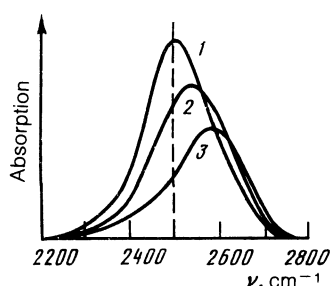


FIG. 7. Influence of temperature on the OD absorption band of liquid HDO for water density of  $1 \text{ g/cm}^3$ . Temperature ( $^{\circ}\text{C}$ ): 1) 30; 2) 100; 3) 300.

to  $\text{H}_2\text{O}$ , the band profile was symmetric. At  $300^{\circ}\text{C}$  the absorption coefficient at  $2500 \text{ cm}^{-1}$  decreased almost threefold compared with the absorption at  $30^{\circ}\text{C}$ . The order of magnitude of the reduction in the absorption at the frequency corresponding to the maximum under normal conditions on increase in temperature was in reasonable agreement with our results. In fact, the dependences plotted in Fig. 6 demonstrated that the threefold reduction in the optical density of  $\text{H}_2\text{O}$  at the wavelength of  $2.94 \mu\text{m}$  corresponded to an input energy density of  $1.6 \text{ kJ/cm}^3$ , which was equivalent to an increase in temperature by  $380^{\circ}\text{C}$ .

The considerable change in the absorption spectrum of liquid water was therefore due to a change in the function representing distribution of the H-bond energy caused by an increase in temperature.<sup>19</sup> However, it was difficult to say anything about the presence of the H bonds in water at the maximum input energies corresponding to  $T \sim 2000 \text{ K}$ ,  $p \sim 20 \text{ kbar}$ , and  $\rho \sim 1 \text{ g/cm}^3$ , because at  $T = 2000 \text{ K}$  the thermal energy was  $kT \sim E_b$ , where  $E_b = 0.17 \text{ eV}$  is the energy of a hydrogen bond; the aggregate state of water under these conditions is not known, so that this state could be called liquid water only in the nominal sense. It is simply known<sup>6</sup> that at  $400^{\circ}\text{C}$  in the density range  $\rho > 0.1 \text{ g/cm}^3$  water does not contain molecules free of the hydrogen bond: only weakened and bent bonds are present.

The third model of the bleaching effect postulating breaking of the hydrogen bonds by laser radiation is not likely to be correct because, according to dielectric relaxation data, the lifetime of a “sessile” molecule in liquid water is  $(5\text{--}8) \times 10^{-12} \text{ s}$  under normal conditions<sup>7,20</sup> and it decreases on increase in temperature. During this lifetime the environment of the molecule changes forming new hydrogen bonds, so that the recovery time of broken hydrogen bonds should be of the same order of magnitude.

Picosecond spectroscopic experiments carried out by Laubereau *et al.*<sup>21</sup> showed that breaking of the hydrogen bonds between ethanol molecules dissolved in  $\text{CCl}_4$  by a resonant interaction with the vibrations of OH group ( $3320 \text{ cm}^{-1}$ ) was followed by restoration of these bonds in a time of the order of 20 ps. Since water has a larger number of neighbors and is characterized by a shorter separation between the molecules than ethanol, the recovery time of the hydrogen bonds should be even less, in agreement with the estimates given above.

### 6. EXPERIMENTAL RESULTS OBTAINED USING $\lambda = 2.79 \mu\text{m}$ LASER RADIATION

It was of interest to determine whether the bleaching of water occurs also at the above wavelength or whether the exposure to this radiation results initially in darkening, as predicted by the fourth model; it also seemed desirable to compare the results obtained using giant pulses with those obtained employing a train of ultrashort pulses and a single ultrashort spike, and to estimate the maximum attainable specific input energies.

We first determined the dependence of the integral transmission of the cell for a giant pulse and a train of ultrashort pulses on the incident energy density (curve 1 in Fig. 8). The optical setup was exactly the same as in Fig. 2. Our photodetectors were liquid-nitrogen-cooled FSG-22 photoresistors with a good sensitivity and a time resolution of 2–3 ns. The quartz cell had a water-filled gap of thickness  $d = 6$

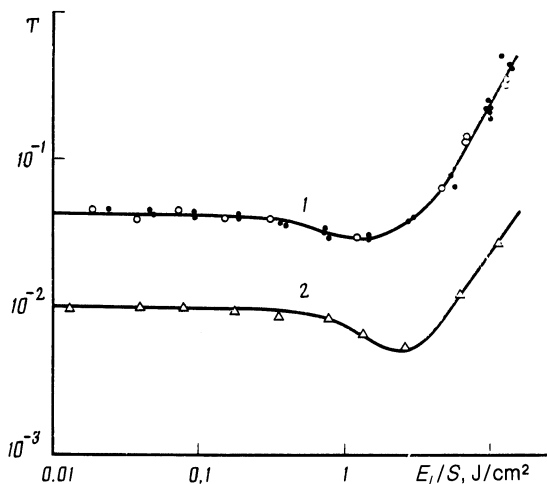


FIG. 8. Dependences of the integral transmission of the cell with water on the incident energy density ( $\lambda = 2.79 \mu\text{m}$ ):  $\bullet$ ) giant pulse,  $\circ$ ) train of ultrashort pulses ( $S = 6.3 \times 10^{-4} \text{ cm}^2$ ,  $d = 6 \mu\text{m}$ ,  $T_0 = 4.5\%$ );  $\Delta$ ) single spike ( $S = 5.7 \times 10^{-5} \text{ cm}^2$ ,  $d = 9 \mu\text{m}$ ,  $T_0 = 1\%$ ).

$\mu\text{m}$  and the initial transmission at the  $\lambda = 2.79 \mu\text{m}$  wavelength was  $T_0 = 4.5\%$ . The area of the laser spot on the cell was  $S = 6.3 \times 10^{-4} \text{ cm}^2$ .

Figure 9a shows the time dependence of the optical density of water at  $\lambda = 2.79 \mu\text{m}$  during irradiation with a giant pulse and with a train of ultrashort pulses of different energies; Fig. 9b shows the profile of the time envelope of the pulse train.

In the case of a single spike (pulse) the experimental conditions were somewhat different. The laser spot area was  $5.7 \times 10^{-5} \text{ cm}^2$ , the cell thickness was  $9 \mu\text{m}$ , and the initial transmission was  $T_0 = 1\%$ . We plotted in Fig. 8 (curve 2) the dependence of the integral transmission of the cell with water on the incident energy density.

Figure 10 gives, by analogy with Fig. 6, all the experimental results obtained using the  $\lambda = 2.79 \mu\text{m}$  laser in the form of a single curve representing the dependence of the relative reduction in the optical density on specific energy per unit volume. We shall now consider the results reported in the present section.

It follows from Fig. 8 that the dependences of the integral transmission are practically the same for a giant pulse

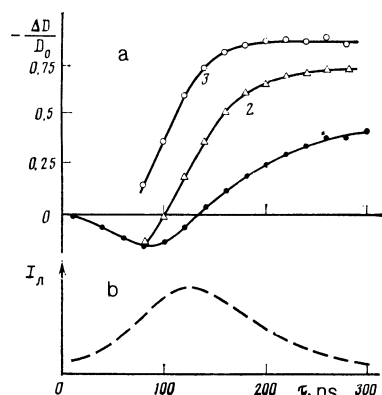


FIG. 9. a) Time dependences of the optical density of water at  $\lambda = 2.79 \mu\text{m}$  in the case of irradiation with trains of the following energies: 3.7 mJ (1), 7.3 mJ (2), 14.4 mJ (3). b) Envelope of the train of pulses.

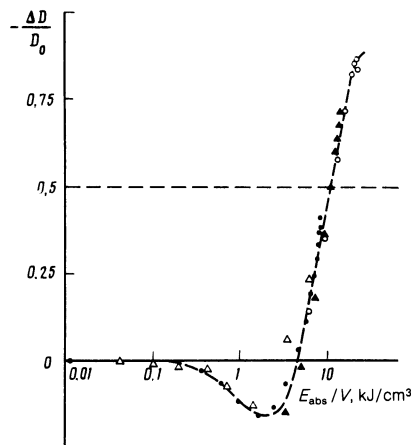


FIG. 10. Dependences of the relative reduction in the optical density of water at  $\lambda = 2.79 \mu\text{m}$  on the specific input energy:  $\bullet$ ,  $\Delta$ ,  $\circ$ ) laser trains of energies 3.7, 7.3, and 14.4 mJ, respectively ( $S = 6.3 \times 10^{-4} \text{ cm}^2$ ,  $d = 6 \mu\text{m}$ ,  $T_0 = 4.5\%$ );  $\Delta$ ) single spike with  $\tau_l = 150 \text{ ps}$  ( $S = 5.7 \times 10^{-5} \text{ cm}^2$ ,  $d = 9 \mu\text{m}$ ,  $T_0 = 1\%$ ).

and a train of ultrashort pulses. This means that there is no dependence on the peak intensity, at least in the range  $I_l \ll 8 \times 10^9 \text{ W/cm}^2$ . Moreover, the dependences of the “instantaneous” transmission on the absorbed energy obtained for trains with different energy and for a single spike fitted the same curve (Fig. 10). Hence, we concluded that in our experiments the absorption coefficient depended only on the specific input energy (and was independent of the time taken to deposit this energy). This would not be true had the bleaching effect occurred mainly because of a reduction in the density caused by bending of the cell walls and transverse expansion (in this case the transmission would continue to rise during the tail of the train without following the changes in the input energy — see Fig. 9). It follows that in our case the change in the absorption was mainly due to the increase in the temperature of the liquid.

We shall now consider the actual dependence of the absorption coefficient on the input energy (we shall use here the specific input energy averaged over the laser spot and over the cell thickness). When the specific input energy was  $1 \text{ kJ/cm}^3$  (Fig. 10), we found that darkening took place: the transmission decreased by a factor of 1.6, corresponding to an increase in the absorption coefficient by  $\sim 15\%$ . A further increase in the input energy began to bleach the cell: at  $10 \text{ kJ/cm}^3$  the optical density decreased twofold and at the maximum input energy of  $22 \text{ kJ/cm}^3$  the transmission reached 75% (corresponding to  $\alpha = 5 \times 10^2 \text{ cm}^{-1}$ ). Further energy supply to the water was quite ineffective, so that in practice  $20 \text{ kJ/cm}^3$  was the maximum input energy which could be achieved in this way.

The observed dependence could therefore be explained by the influence of temperature on the absorption spectrum of water resulting from weakening of the hydrogen bonds. Laser pulses of  $10^{-7}$  and  $10^{-10} \text{ s}$  durations were fast compared with the thermal processes and slow compared with the relaxation of the vibrational energy. In the case of single spikes (pulses) of  $\tau_l = 150 \text{ ps}$  duration and of  $I_l = 7.5 \times 10^{10} \text{ W/cm}^2$  intensity, the results were not affected by the peak intensity of the laser radiation. Consequently, we concluded that  $I_l < I_s$ , where  $I_s$  is the intensity needed for saturation of the vibrational transition in  $\text{H}_2\text{O}$ , described

by Eq. (1). This allowed us also to estimate the relaxation time of the excited vibrational state of water at  $\sim 10^3$  K: its value was  $\tau_{\text{rel}} \sim 3$  ps.

## 7. CONCLUSIONS

1. It was found that water and other liquids containing the OH group and hydrogen bonds were strongly bleached by high-intensity ( $0.1\text{--}100$  J/cm<sup>2</sup>) laser radiation of the  $\lambda = 2.94$   $\mu\text{m}$  wavelength delivered in the form of pulses of  $10^{-7}\text{--}10^{-10}$  s duration. For example, when the energy density of the laser radiation incident on a cell was  $100$  J/cm<sup>2</sup>, the average transmission by the cell rose to 90% from the initial transmission of 0.15%. A characteristic specific input energy at which the absorption per molecule was halved amounted to  $1$  kJ/cm<sup>3</sup> or  $0.2$  eV per molecule.

2. Our experiments indicated that the recovery time of the absorptivity of water was within the range  $100$  ns  $< \tau < 20$   $\mu\text{s}$ . This recovery time was most probably related to the relaxation time of the temperature of the liquid in the cell, which was of the order of microseconds.

3. The dependence of the transmission on the number of the absorbed photons (Fig. 5) indicated that the bleaching process could not be interpreted by the model of a generalized two-level system.

4. The hydrodynamic effects — an increase in the volume of the irradiated liquid during a laser pulse, formation of bubbles, etc. — made no significant contribution to the observed effects in the range of pulse durations and intensities used in our study.

5. The most probable model of the bleaching of water and other liquids is the following: the absorbed laser radiation increases the temperature of the liquid (and the pressure, because  $\rho \approx \text{const}$ ) and this deforms and weakens the hydrogen bonds. The result is a shift of the equilibrium between the strong and weak hydrogen bonds in the direction of weaker ones. The valence absorption band corresponding to the OH group shifts then in the direction of higher frequencies and this is accompanied by a simultaneous reduction in the band intensity. The result is significant bleaching at the  $2.94$   $\mu\text{m}$  wavelength, which under normal conditions is close to the absorption maximum.

6. This hypothesis was confirmed by the darkening of water at  $\lambda = 2.79$   $\mu\text{m}$ . In fact, on increase in temperature the absorption spectrum of water (Fig. 1) showed a shift of its maximum to  $\lambda = 2.79$   $\mu\text{m}$  and a further increase in the input energy shifted it even further toward shorter wavelengths, so that bleaching began. The specific input energy corresponding to halving of the absorption per molecule at  $\lambda = 2.79$   $\mu\text{m}$  was  $10$  kJ/cm<sup>3</sup>.

7. The laser pulses of  $\tau \sim 100$  ps duration used in these experiments were clearly far too long for the observation of the dynamic breaking of the hydrogen bonds or for saturation of the absorption resulting in the transition to the first vibrational level. Our estimate of the vibrational relaxation times of water gave a value  $0.1$  ps  $< \tau_{\text{rel}} < 3$  ps.

8. Interaction with the erbium laser radiation in the form of nanosecond or picosecond pulses created in water extremal thermodynamic states which were inaccessible by other methods:  $p \sim 50$  kbar,  $T \sim 5 \times 10^3$  K. In spite of the fact that the initial absorption was less than at  $\lambda = 2.94$   $\mu\text{m}$ , we found that the  $\lambda = 2.79$   $\mu\text{m}$  radiation made it possible to reach approximately twice the maximum input energy because the bleaching effect was less. Dynamic spectroscopy of hydroxyl-containing liquids at such extremal states should provide additional information on the structure of the liquid and on the dynamics of the H bonds.

9. Since  $3\text{-}\mu\text{m}$  lasers are now becoming important in medicine, particularly in laser surgery, one should bear in mind that the bleaching effect may increase the depth of penetration of laser radiation in interactions with living tissues.

<sup>1</sup>V. M. Zolotarev, V. N. Morozov, and E. V. Smirnova, *Optical Constants of Natural and Technical Media* [in Russian], Khimiya, Leningrad (1984).

<sup>2</sup>G. V. Yukhnevich, *Infrared Spectroscopy of Water* [in Russian], Nauka, Moscow (1973).

<sup>3</sup>V. I. Malyshev, *Usp. Fiz. Nauk* **63**, 323 (1957).

<sup>4</sup>G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco (1960).

<sup>5</sup>G. N. Zatssepina, *Physical Properties and Structure of Water* [in Russian], Moscow State University (1987).

<sup>6</sup>B. Z. Gorbunov and Yu. I. Naberukhin, *Zh. Strukt. Khim.* **16**, 703 (1975).

<sup>7</sup>W. A. P. Luck, in *The Hydrogen Bond* (ed. by P. G. Schuster, G. Zundel, and C. Sandorfy), Vol. 3, *Dynamics, Thermodynamics, and Special Systems*, North-Holland, Amsterdam (1976), p. 1367; E. Whalley, *ibid.* p. 1425.

<sup>8</sup>Kh. S. Bagdasarov, V. I. Zhekov, L. A. Kulevskii *et al.*, *Kvantovaya Elektron. (Moscow)* **7**, 1959 (1980) [*Sov. J. Quantum Electron.* **10**, 1127 (1980)].

<sup>9</sup>A. D. Zweig, M. Frenz, V. Romano, and H. P. Weber, *Appl. Phys. B* **47**, 259 (1988).

<sup>10</sup>E. V. Zharikov, N. N. Il'ichev, S. P. Kalitin *et al.*, *Kvantovaya Elektron. (Moscow)* **13**, 973 (1986) [*Sov. J. Quantum Electron.* **16**, 635 (1986)].

<sup>11</sup>L. I. Andreeva, K. L. Vodop'yanov, S. A. Kaïdalov *et al.*, *Kvantovaya Elektron. (Moscow)* **13**, 499 (1986) [*Sov. J. Quantum Electron.* **16**, 326 (1986)].

<sup>12</sup>K. L. Vodop'yanov, L. A. Kulevskii, P. P. Pashinin *et al.*, *Kvantovaya Elektron. (Moscow)* **14**, 1219 (1987) [*Sov. J. Quantum Electron.* **17**, 776 (1987)].

<sup>13</sup>K. B. Eisenthal, in *Ultrashort Light Pulses: Picosecond Techniques and Applications* (ed. by S. L. Shapiro), Springer-Verlag, Berlin (1977), p. 275.

<sup>14</sup>K. L. Vodop'yanov, L. A. Kulevskii, V. G. Mikhalevich, and A. M. Rodin, *Zh. Eksp. Teor. Fiz.* **91**, 114 (1986) [*Sov. Phys. JETP* **64**, 67 (1986)].

<sup>15</sup>M. H. Rice and J. M. Walsh, *J. Chem. Phys.* **26**, 824 (1957).

<sup>16</sup>M. P. Vukalovich, S. L. Ryvkin, and A. A. Aleksandrov, *Tables of Thermophysical Properties of Water and Water Vapor* [in Russian], Izd. Standartov, Moscow (1969).

<sup>17</sup>K. L. Vodop'yanov, M. E. Karasev, L. A. Kulevskii *et al.*, *Pis'ma Zh. Tekh. Fiz.* **14**, 324 (1988) [*Sov. Tech. Phys. Lett.* **14**, 143 (1988)].

<sup>18</sup>K. L. Vodop'yanov, L. A. Kulevskii, P. P. Pashinin, and A. M. Prokhorov, *Zh. Eksp. Teor. Fiz.* **82**, 1820 (1982) [*Sov. Phys. JETP* **55**, 1049 (1982)].

<sup>19</sup>Yu. I. Naberukhin, *Zh. Strukt. Khim.* **25**, (2), 60 (1984).

<sup>20</sup>D. Eisenberg and W. Kauzmann, *Structure and Properties of Water*, Oxford University Press (1969).

<sup>21</sup>H. Graener, T. Q. Ye, and A. Laubereau, *J. Chem. Phys.* **90**, 3413 (1989).

Translated by A. Tybulewicz