

# A change in the refractive properties of water irradiated by a 2.94- $\mu\text{m}$ erbium laser

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**Abstract.** A decrease in the refractive index of water in its transparency region caused by irradiation by high-power 100-ps pulses from a 2.94- $\mu\text{m}$  erbium laser is found and measured. The possible reasons for this phenomenon are discussed.

During the development and study of an erbium laser operating on the  ${}^4I_{11/2} - {}^4I_{13/2}$  transition in the region from 2.7 to 2.9  $\mu\text{m}$ , bleaching of water caused by the  $\text{Er}^{3+}$ : YAG laser radiation at 2.94  $\mu\text{m}$  was found [1] and studied [2–9]. The transmission of a five micron thick water layer increased from  $10^{-3}$  to 0.9 [2], depending on the irradiation intensity, which was, however, strongly related to the energy deposited to the unit volume of water. Note that the energy input in the experiments could achieve  $40 \text{ kJ cm}^{-3}$ , which is 16 times greater than the energy required for complete evaporation of the irradiated water.

In [2], the dependence of the pressure in a liquid layer on the input energy was also measured. This pressure achieved 20 kbar for the input energy equal to  $40 \text{ kJ cm}^{-3}$ . Estimates showed that the temperature of water during such irradiation could increase up to several thousands degrees. At such high temperatures, the intense thermal radiation can appear in the spectral region overlapping with the absorption bands of water in the normal state.

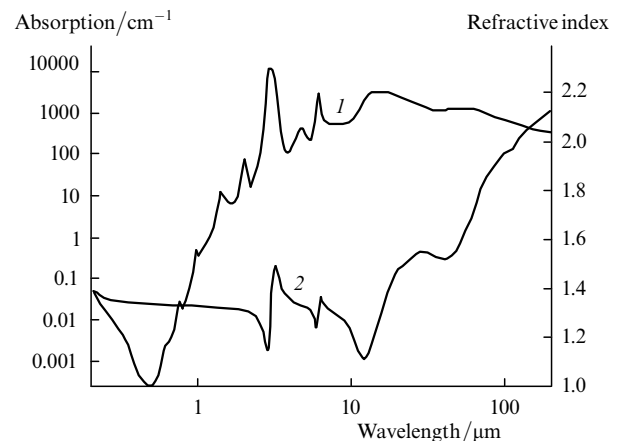
To estimate the lower bound of the temperature of water, a special experiment was performed [8]. A lithium fluoride cell containing water was irradiated by giant 100-ns pulses from an erbium laser at 2.94  $\mu\text{m}$ , and the irradiated region was projected to a FSG-22 Ge–Au photodetector using a KRS23 glass lens with the focal distance  $f = 120 \text{ mm}$ . An InAs plate of 3 mm thickness was placed in front of the input window of the photodetector, which served as a band filter to cut off radiation with the wavelength shorter than 3.5  $\mu\text{m}$ . The long-wavelength boundary of the emission spectrum was determined by absorption of a LiF substrate for  $\lambda > 7 \mu\text{m}$ .

When the input energy was increased up to  $10 \text{ kJ cm}^{-3}$ , a weak but quite distinct signal was observed in the oscilloscope screen, which was related to the IR radiation from a

cell with water. Knowing the sensitivity of the detection unit, the solid angle of the radiation collection, and the absorption spectrum of liquid water in the region between 3.5 and 7  $\mu\text{m}$ , we can estimate the lower bound of the liquid temperature that is required to obtain the IR radiation signal. We estimated the temperature of water heated by a radiation pulse from an erbium laser using Kirchhoff's law and the absorption spectrum of water in the spectral range from 3.5 to 7.0  $\mu\text{m}$  obtained in [10]. This temperature was estimated as 3000 K [8].

Thus, during irradiation for  $\sim 100 \text{ ns}$ , water is brought to the supercritical region in the phase  $pT$  diagram. The aggregate state of water in the supercritical region has not been adequately studied so far, although it has been investigated in many papers under stationary conditions [3, 11–21], in shock tubes [22–26], and upon laser irradiation [27–40].

We decided to continue these studies taking into account the high rate and high energy input to the most intense absorption band of water (Fig. 1).



**Figure 1.** Dependences of the absorption coefficient (1) and the refractive index (2) on the wavelength for water under normal conditions [10].

Using the method of two-exposure holographic interferometry and the shadow method, we have studied [5, 41] the dynamics of the state of water in the region of irradiation by giant 100-ns pulses from an erbium laser at 2.94  $\mu\text{m}$  by simultaneously probing the region by the second harmonic 10-ns pulses from a neodymium laser at 0.53  $\mu\text{m}$  with a variable delay with respect to the pulse from an erbium laser.

The most important result of these studies is, in our opinion, the observation of a decrease in the refractive index of

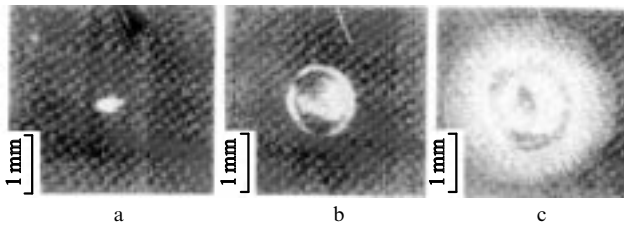
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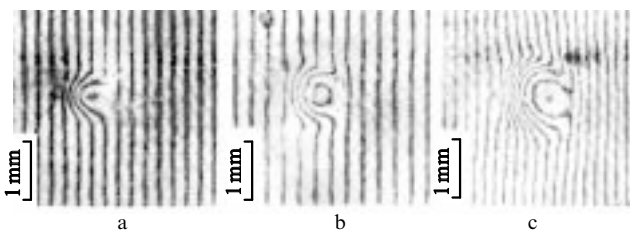
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water in a cell at a wavelength of  $0.53 \mu\text{m}$  during the time that did not exceed the duration of pulses from an erbium laser, i.e., for  $\sim 100 \text{ ns}$ , the water density being constant during this time (Fig. 2). Note that the refractive index  $n$  decreased from 1.33 for water in the normal state to 1.1, which shows that the properties of water substantially changed after intense irradiation by an erbium laser.



**Figure 2.** Shadowgraphs of a cell with water (the water layer thickness is  $5 \mu\text{m}$ ) obtained for delays of the probe pulse equal to 60 (a), 120 (b), and 450 ns (c).

The question about the constant density of water in the irradiated region is of a paramount importance for the interpretation of the experimental results. The ratio of the radius of a Gaussian beam (radius of the irradiated region) to the sound velocity in water defines the characteristic time of a substantial change in the density. This time is  $\sim 100 \text{ ns}$ . The maximum decrease in the refractive index in interferograms presented in papers [5, 41] was achieved within 60 ns after the onset of the erbium laser pulse (Fig. 3). However, it has been repeatedly assumed in discussions that the shift of the interference bands observed in the irradiated cell was caused by a decrease in the water density due to the water mass removal from the irradiated region rather than by a decrease in the refractive index of water. It is important to note that a change in the refractive index  $n$  of water from 1.33 to 1.1 corresponds to the three-fold change in the first-order susceptibility  $\chi^{(1)}$  (which appears nontrivial), and this fact should be explained.



**Figure 3.** Interferograms of a cell with water (the water layer thickness is  $5 \mu\text{m}$ ) for the same delays of the probe pulse as in Fig. 2.

To solve the question about a change in the water density, which supposedly reduces the refractive index of water almost to unity, we performed similar experiments but using the excitation ( $2.94 \mu\text{m}$ ) and probe ( $0.588 \mu\text{m}$ ) pulses of duration  $\sim 100 \text{ ps}$ . It is obvious that in this case no mass removal from the irradiated region or bending of cell walls can occur, i.e., the water density remained constant a much longer time than the pulse duration.

An  $\text{Er}^{3+}$  laser operated in the regime of active longitudinal mode locking. A single spike was separated using a

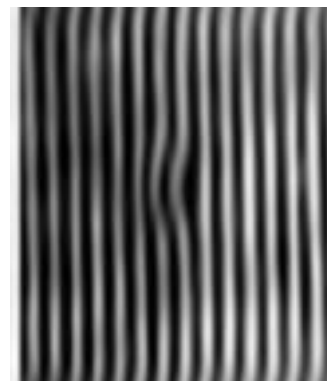
third electrooptic crystal placed inside the cavity. The energy of a single spike was  $0.7\text{--}1 \text{ mJ}$ , its duration was  $\tau = 100 \text{ ps}$ , and the repetition rate was  $1.5 \text{ Hz}$ .

The laser beam was split into two beams with a beamsplitter. One of the beams with the energy  $0.5\text{--}0.6 \text{ mJ}$  was focused to a cell with water, and the second beam with the energy  $0.2\text{--}0.4 \text{ mJ}$  was used for consecutive three-step generation of the fifth harmonic at  $0.588 \mu\text{m}$ , which was used as a probe beam. Three lithium niobate crystals served as nonlinear elements. The frequency conversion was performed according to the scheme  $\omega + \omega \rightarrow 2\omega$ ,  $2\omega + 2\omega \rightarrow 4\omega$ ,  $4\omega + \omega \rightarrow 5\omega$ . The efficiency of conversion to the fifth harmonic (in intensity) achieved several percent with respect to the beam intensity at the fundamental frequency.

The 50-ps pulses of the fifth harmonic were directed through an optical delay line to a Mach-Zehnder interferometer with a cell with water placed in one of its arms. To decrease the path difference for obtaining the sharpest interference pattern, plane-parallel glass plates of the appropriate thickness were inserted into the second arm of the interferometer. The required density of the interference fringes was obtained by tilting a beamsplitter cube. The energy of the fifth harmonic was sufficient to obtain interferograms with a magnification of  $7\times$  on the Aerofoto-42 film.

To determine the sign of a change in the refractive index, a thin plane-parallel plate of thickness  $t$  was inserted into one of the interferometer arms. When this plate was rotated around a vertical axis through the angle  $\varphi$ , its optical thickness  $L$  changed as  $t/\cos \varphi$ . The minimum path difference was achieved for  $\varphi = 0$ . When the plate was rotated, the density of interference fringes increased toward the greater refractive index. This test allows one to determine unambiguously the sign of a change in the refractive index.

The radiation of an erbium laser was focused with a CaF lens with the focal distance  $f = 70 \text{ mm}$  on a cell with water. The thickness of the water layer was  $10 \mu\text{m}$ . The radius  $w$  of a Gaussian laser beam in a cell was  $60 \mu\text{m}$ . The delay between the exciting and probe pulses was  $2 \text{ ns}$ . Fig. 4 shows the interferogram of a cell at this moment of time. The shift of the interference pattern was 0.5 of the fringe at the center of the laser caustics in the direction of its decrease. The density of the input energy in this case was  $20 \text{ kJ cm}^{-1}$ . The region of water heated by laser radiation has no time to change its vol-



**Figure 4.** Interferogram of a cell with water (the water layer thickness is  $10 \mu\text{m}$ ) irradiated by a 100-ps pulse from an  $\text{Er}^{3+} : \text{YAG}$  laser at  $2.94 \mu\text{m}$ . The interferogram was obtained at the wavelength  $0.588 \mu\text{m}$  of the fifth harmonic of an  $\text{Er}^{3+} : \text{YAG}$  laser emitted synchronously with the fundamental frequency.

ume during the delay time. The change in the refractive index estimated by relating the change in the optical length to the entire cell thickness is  $\Delta n = -0.05$ . In reality the optical thickness changes by  $\sim 3 \mu\text{m}$ , so that  $\Delta n = -(0.1 - 0.2)$ .

It was assumed in papers [11, 17] that the behaviour of the absorption line observed with increasing temperature can be explained by the dissociation of hydrogen bonds between water molecules. It seems that strong heating of water by short pulses from an erbium laser really results in the dissociation of hydrogen bonds (the dissociation energy of hydrogen bonds is  $5 \text{ kcal mol}^{-1}$  ( $1.2-3 \text{ kJ cm}^{-3}$  [11]) and in the change in the interaction between water molecules, the distance between them being virtually unchanged. The change in the water structure and in the interaction between water molecules cause a change in the polarizability of molecules and a decrease in the refractive index observed in experiments. Therefore, the linear susceptibility  $\chi^{(1)}$  substantially changes (approximately by a factor of three). However, additional theoretical calculations and experiments should be performed to confirm this hypothesis.

We have tried to find possible explanations for this experimental effect, which is nontrivial in our opinion. It seems that the water bleaching observed in our experiments is explained by the fact that intense irradiation by an erbium laser results in the disappearance of the resonance absorption line of water.

Note, however, that the water bleaching can also be caused either by the saturation effect, when the population difference of the energy levels involved in the resonance transition is changed but the dipole moment (or the oscillator strength  $f$ ) remains invariable, or by the shift of the absorption band (from the resonance radiation frequency) when the dipole moment does not vanish either. However, in both these cases, the refractive index could not tend to unity. It seems that strong water bleaching accompanied by a noticeable decrease in the refractive index in the transparency region is explained by substantial structural transformations of water caused by high-power short laser pulses.

We can assume that the structural transformations are related to the rapid vibrational-rotational relaxation, because it seems that the VT relaxation in a nonexpanding liquid is impossible. In turn, the increase in the rotational energy should result in the dissociation (at least partial) of hydrogen bonds, which are characterised by the spatial directivity and therefore weaken upon rapid rotation or librations of water molecules relative to each other. We can use some analogy with the problem on the internal rotation [42, 43] for the potential of the type

$$U(\chi) = \frac{U_0}{2} (1 + \cos 3\chi) \quad (0 < \chi < 2\pi)$$

described in a textbook. When  $\chi = 0$  (rotation is absent), the potential  $U(0) = U_0$ . When a molecule rotates, the averaging should be performed over  $\chi$  within the entire interval  $[0, 2\pi]$ . In this case, the potential decreases by half:

$$U_\chi = \frac{1}{2\pi} \frac{U_0}{2} \int_0^{2\pi} (1 + \cos 3\chi) d\chi = \frac{U_0}{2}.$$

In contrast to the simplest potential presented above, the potential for hydrogen bonds will exhibit narrower peaks in the rotation angle scale because of the spatial directivity of the hydrogen bonds. The distance between these peaks

exceeds their angular size. All this in turn should cause a further decrease in the potential averaged over rotations, but in space rather than in the plane, resulting in a weakening of the hydrogen bond.

It seems that the dissociation of hydrogen bonds should result in the disappearance of the  $3400\text{-cm}^{-1}$  absorption band and the rise of the  $3650\text{-cm}^{-1}$  absorption band, i.e., the dissociation should be manifested in the spectra in the same way as upon diluting water with a nonpolar solvent  $\text{CCl}_4$  [44]. Of course, the absorption band can be additionally shifted due to the interaction with the environment in the different aggregate state.

The decrease in the refractive index can also be explained by the appearance of transient absorption bands near the probe wavelength of  $0.59 \mu\text{m}$ , resulting in the interference measurements in the region of anomalous dispersion of the refractive index.

The decrease in the refractive index almost to unity should obviously reduce the coefficient of reflection from the water surface upon normal incidence of light.

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