

Saturation studies of H₂O and HDO near 3400 cm⁻¹ using intense picosecond laser pulses

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The effect of significant decrease of water absorptivity for the intense picosecond laser radiation at $\lambda = 2.79$ and $2.94 \mu\text{m}$ being near the center of the OH stretching mode absorption band was discovered. In case of pure water a thermal mechanism dominated: A very fast temperature rise led to weakening of H-bonds and consequently to the absorption band shift towards higher frequencies. As a result, a considerable (up to 10 times) decrease in the optical density at the laser frequency was obtained. In the second case of HDO diluted in D₂O the temperature effects were eliminated and a pure spectroscopic saturation of the $\nu = 0$ to $\nu = 1$ vibrational transition was displayed. The saturation intensity as high as $I_s = 2.5 \cdot 10^{11} \text{ W/cm}^2$ in this case gives the value of energy relaxation time of the OH excited state to be in the range $0.3 \text{ ps} < T_1 < 0.6 \text{ ps}$. The width of the homogeneously broadened component of the fundamental OH band in HDO spectrum is evaluated to be $\geq 40 \text{ cm}^{-1}$.

I. INTRODUCTION

This work was an attempt to understand in more detail the mechanism of significant water bleaching under the influence of strong laser field near $3 \mu\text{m}$.¹⁻³ In Ref. 1, for example, liquid water (and ethanol) served as bleachable absorber of $2.94 \mu\text{m}$ radiation within the laser resonator, producing intense giant pulses. A thermal mechanism of the bleaching was later suggested³ and a conclusion was made that the role of the vibrational transition saturation was negligible; Very fast population relaxation times in water ($T_1 < 3 \text{ ps}$) were predicted.

In Ref. 4-6 it was shown that by intense picosecond light pulses in the infrared, it is possible to saturate the $\nu = 0$ to $\nu = 1$ transition of the OH stretching mode and with a pump-probe method to measure the time of vibrational energy relaxation T_1 . It was experimentally found that T_1 (OH) both in liquid and in solid phases is dramatically influenced by the participation of the OH group in the H-bond, leading not only to large spectral shift to lower frequencies and integral absorption rise, but also to more than one order of magnitude decreasing of T_1 . The following lifetimes T_1 were found: 204 ps for OH at the SiO₂/vacuum interface, 150 ps for OH bound to SiO₂ surface in CCl₄ solution, and 109 ps for OH in the bulk of fused silica.⁴ On the contrary, T_1 was measured to be: 5 ps for H-bonded OH groups of ethanol oligomers (solvent CCl₄)⁵ and 5 ps for H-bonded OH groups in PVB/PVA polymers.⁶ In Ref. 7, the population lifetime for physisorbed bulk water bound to the surface of colloidal SiO₂ was found to be $< 2 \text{ ps}$, because the resonance light intensity was not enough to noticeably populate the upper vibrational level.

Evidently, in liquid water small population lifetimes should be expected due to the high mobility of molecules,

big number of H bonds per molecule, and rich middle infrared spectrum to assume vibrational energy transfer mechanism to lower ($\omega/2$) frequencies. This mechanism⁸ may exist in H-bonded systems due to nonlinear coupling of high- and low-frequency vibrations and anharmonicity of the latter.

The simple enough technique for nonlinear transmission measurements can be productive for studying such fast systems as liquid water; Middle Infrared (i.r.) light intensities of 10^{11} - 10^{12} W/cm^2 , used in our experiment, seem to be proper for the sufficient population of $\nu = 1$ OH vibrational states of liquids with small energy relaxation times T_1 . The upper state population should manifest itself in the absorption decrease at the frequency of the excitation.

II. EXPERIMENTAL

We used two types of erbium-activated garnet lasers emitting at wavelengths of 2.94 and $2.79 \mu\text{m}$. The former was an erbium-activated yttrium erbium garnet Y₃Al₅O₁₂:Er³⁺ laser.⁹ The emission wavelength of it: $2.94 \mu\text{m}$ (3406 cm^{-1}) is located at the maximum of the stretching fundamental absorption band of liquid water at room temperature (absorption coefficient $\alpha = 1.28 \cdot 10^4 \text{ cm}^{-1}$). The emission wavelength of the second laser: $2.79 \mu\text{m}$ (3580 cm^{-1}), with an active element consisting of erbium-activated yttrium scandium gallium garnet,¹⁰ was located in the high frequency wing of the same absorption band of water (Fig. 1) and the absorption coefficient $\alpha = 5.16 \cdot 10^3 \text{ cm}^{-1}$ was 2.5 times less than at the band center.

These lasers were operated at a repetition frequency of 1 Hz in two regimes: train of ultrashort pulses generated by active mode locking, when the laser emitted a series of

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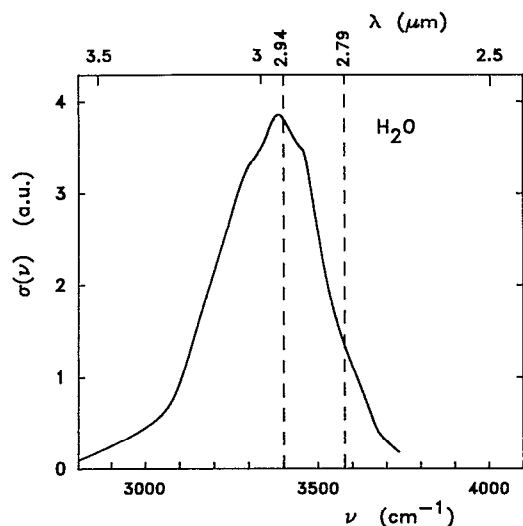


FIG. 1. Infrared absorption spectrum of H₂O at 30 °C.

ultrashort pulses of 110 ± 10 ps duration separated by an interval of 7 ns with an envelope of 130–160 ns duration and delivering an energy of 10–20 mJ for the whole train; a single spike separated from a train by electrooptic methods and then amplified to produce a single pulse of 110 ± 10 ps duration and up to 2 mJ energy. The pulse duration measurements were carried out with the 4ω frequency of the laser light ($\lambda \approx 0.7 \mu\text{m}$) using streak camera.

The laser beam with the Gaussian spatial distribution of the intensity (TEM₀₀ mode) was directed to a quartz cell containing the investigated liquid. The thickness of the cell in the case of pure water was controllably varied in the range of 1–10 μm and amounted to 100 μm in the case of HDO solution in D₂O. The energy of the radiation incident on the cell varied by attenuating glass plates. Selection of the focusing lens made it possible to vary the laser spot on the cell within the range of $S = 3.7 \cdot 10^{-5} - 1.3 \cdot 10^{-2} \text{ cm}^2$. Pyroelectric photodetectors were used to record the energy of the incident and transmitted radiation.

III. H₂O

First we carried out experiments with 2.94 μm radiation. Fig. 2(1) shows the dependence of the relative reduction in the optical density $D = -\ln T$ of water at the 2.94 μm wavelength

$$-\frac{\Delta D}{D_0} = \frac{\ln(T/T_0)}{\ln(1/T_0)}$$

on E_{abs}/V , representing specific absorbed laser energy averaged over the cell thickness and the transverse dimensions of the laser spot. Further on it will be clear why we have chosen this value as an argument rather than the laser energy fluence or intensity. Here T_0 and T are small signal and final transmissions correspondingly; T is defined sim-

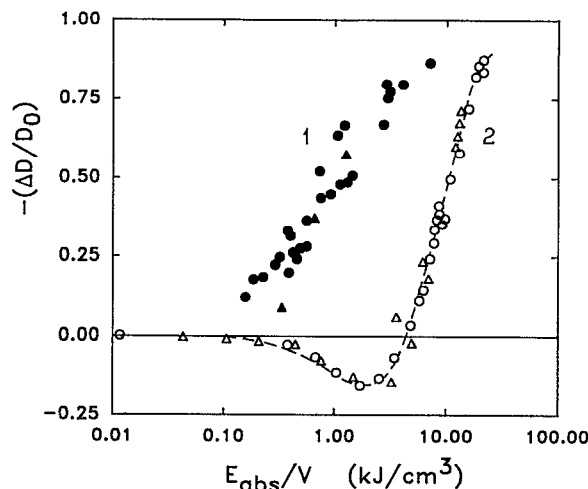


FIG. 2. Dependencies of the relative change in the optical density of water on the specific absorbed laser energy; closed circles and triangles—trains of pulses and single pulses at $\lambda = 2.94 \mu\text{m}$; open circles and triangles—trains of pulses and single pulses at $\lambda = 2.79 \mu\text{m}$.

ply as a ratio of transmitted and incident laser energies. For each cell thickness the dependence of the transmission vs incident laser energy was measured at different values of the laser spot area. Experimental points represent results for different cell thicknesses (1.6–5 μm) and, correspondingly different initial transmissions (12%–0.15%). Both trains of pulses and single pulses were used. One can see from Fig. 2(1) that an increase in the energy of the incident radiation at $\lambda = 2.94 \mu\text{m}$ resulted in the monotonic increase of the transmission. It should also be noted that the degree of bleaching of water became quite considerable: The transmission T of the 5 μm thick cell increased from the initial value $T_0 = 1.5 \cdot 10^{-3}$ to $T_{\text{max}} = 0.9$, i.e., by almost three orders of magnitude, at incident energy fluence of $\approx 100 \text{ J/cm}^2$, corresponding to $E_{\text{abs}}/V = 10 \text{ kJ/cm}^3$. The optical density decreased here by a factor of ≈ 10 .

Clearly, the dependencies obtained for a train [Fig. 2(1)] 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. On the one hand, the observation that in the case of a single spike right up to the maximum value of the laser peak intensity $I_{\text{max}} = 2.6 \cdot 10^{10} \text{ W/cm}^2$ the peak intensity had no effect (only the energy fluence was important), the observation that led us to the conclusion that the laser radiation intensities were insufficient to reach spectroscopic saturation of the transition between $v = 0$ and $v = 1$ vibrational levels of the water molecule: $I \ll I_s$, where $I_s = \hbar\omega/2\sigma T_1$ is the saturation intensity; Here σ is the absorption cross section per OH bond in water ($1.95 \cdot 10^{-19} \text{ cm}^2$). It thus follows that the energy relaxation time for water should be at least $T_1 < 3 \text{ ps}$.

We attribute the bleaching effect in this experiment to the spectrum evolution due to the temperature rise in the water layer. The change of HDO absorption spectra near

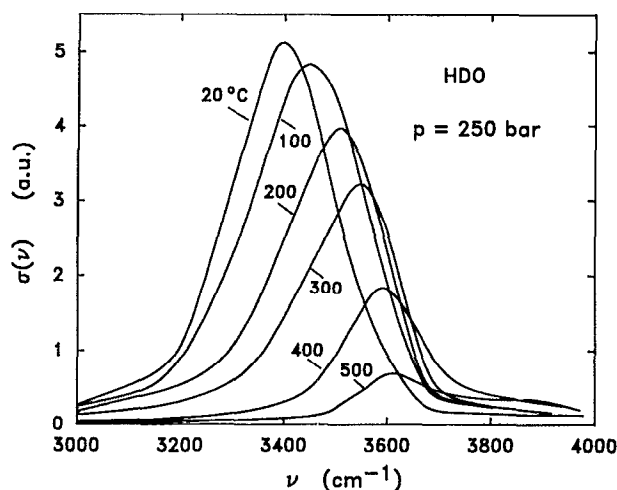


FIG. 3. Change of the ν_3 HDO absorption spectra with temperature at a constant pressure $p = 250$ bar (from Ref. 11).

3400 cm^{-1} with temperature at a constant pressure of 250 bar,¹¹ for example, is shown in Fig. 3. The high frequency shift of the absorption band with temperature and simultaneous reduction in the band intensity occurs due to weakening of the H bonds. A characteristic specific input energy at which the optical density was halved amounted in our experiment to 1 kJ/cm^3 , corresponding to temperature rise of 235°C : This is in good correspondence with Fig. 3. Thus, within the experimental errors the bleaching effect at different experimental conditions (cell thicknesses, beam spots, and pulse durations) is the function of the specific energy input, which is just proportional to a temperature rise. At higher input energies, however, the temperature rise is accompanied by the increasing of the pressure: at the energy input of 10 kJ/cm^3 $T \approx 2000^\circ\text{C}$ and $p \approx 20 \text{ kbar}$.^{2,3} Taking into account the pressure increase, the evolution of spectrum with temperature should not go so fast as in Fig. 3, because the role of the pressure, at least up to 40 kbar, from the viewpoint of the absorption band shift is opposite to that of the temperature.¹²

The idea of the predominant temperature effect proved correct by the experiments with the $\lambda = 2.79 \mu\text{m}$ laser [Fig. 2(2)]. As before, the trains of pulses and single spikes fitted the same curve, showing that the transmission is the function of the input energy. The initial darkening of the water layer occurred because on increase in temperature the absorption spectrum first showed a shift of its maximum towards $2.79 \mu\text{m}$ (Fig. 3). Eventually, the normal bleaching of the water layer started. The recovery time of this transmission change was determined by heat diffusion from water layer and characterized by the time of the order of microseconds.³

IV. HDO IN D₂O

To eliminate temperature effects we have used the HDO solution (1 vol. %) in D₂O. The absorption band near 3400 cm^{-1} is similar to that of the H₂O, but characterized by symmetrical contour¹³ with a full width of

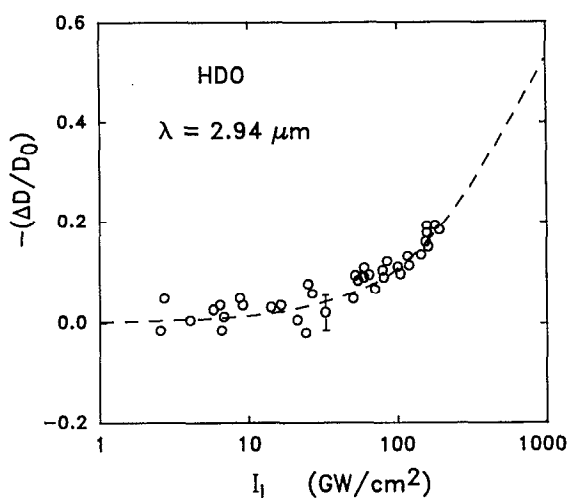


FIG. 4. Absorption saturation curve of HDO in D₂O. The broken curve—theoretical corresponding to $I_s = 250 \text{ GW/cm}^2$.

$\Delta\nu = 250 \text{ cm}^{-1}$. Single spikes of $2.94 \mu\text{m}$ laser radiation were used with 110 ps duration and close to Gaussian temporal and spatial distribution. The pulse energy varied in the interval 0–0.75 mJ. The area of the laser spot in the focus of 5 cm lens was $3.7 \cdot 10^{-5} \text{ cm}^2$. A cavity of $100 \mu\text{m}$ thickness was used with weak signal transmission of HDO at $2.94 \mu\text{m}$ of 48%.

A saturation curve (the relative decrease of optical density of the cell vs peak laser intensity) is shown in Fig. 4. One can see that the saturation really starts at the laser intensities higher than 100 GW/cm^2 .

The broadening of the OH stretching band in water is inhomogeneous and is a consequence of the random nature of hydrogen bonds: Each group of molecules is characterized by its own H-bond strength and appropriate spectral shift towards lower frequencies.¹⁴ The width of each homogeneously-broadened component of the band is determined by the energy and phase relaxation times T_1 and T_2 ; T_2 is connected with the fluctuations of H bonds in time and coupling of the OH vibrations with low frequency intermolecular vibrations. The question of correlation of the widths of homogeneous and inhomogeneous contours for the liquid water stretching i.r. band still remains open.

The upper limit of the energy relaxation time T_1 can be derived, however, from our experiment taking the formula for absorption saturation for a homogeneously broadened line, i.e. implying that all the molecules take part in the absorption process. As the relaxation time is expected to be much smaller than the laser pulse duration we can admit that α is a function of the instant I value and use the steady state formula:¹⁵

$$\alpha = \frac{\alpha_0}{1 + I/I_s}, \quad (1)$$

where α_0 is a small signal absorption and

$$I_s = \hbar\omega/2\sigma T_1 \quad (2)$$

is a saturation intensity.

The broken line represents the best fitted curve corresponding to the dependence given by (1) with $I_s = 250$ GW/cm². Nonuniformity of laser radiation in space and time was taken into account: We computed the fitting curve of the energy transmission change vs peak laser intensity $I(0,0,0)$ integrating the dependence

$$dI = \frac{\alpha_0 I(t, r, z)}{1 + I(t, r, z)/I_s} dz$$

over t , r , and z ; Here r and z are transverse and longitudinal coordinates. Experimentally found absorption cross section for HDO molecule at the band maximum was $\sigma = 2.25 \cdot 10^{-19}$ cm². So we get from (2) $(T_1)_{\max} = 0.6 \pm 0.2$ ps.

The lower limit of T_1 can be derived regarding the opposite case of strongly inhomogeneous broadening of the absorption contour taking the homogeneous envelope arising only from the lifetime broadening

$$g(\nu - \nu_0) = \frac{2T_1}{1 + 4\pi^2(\nu - \nu_0)^2 T_1^2}$$

with a full width $\Delta\nu_h = 1/\pi T_1$.

If $\Delta\nu$ is the full width of the inhomogeneous band, only about $\Delta\nu_h/\Delta\nu$ part of the molecules should be vibrationally excited to cause the absorption saturation and the saturation intensity becomes smaller by this factor. More exactly, for the Gaussian shape of the whole band

$$I_s = \frac{\hbar\omega}{2\sigma T_1^2 \Delta\nu} \sqrt{\frac{\ln 2}{\pi}}$$

The steady state dependence of α vs I in the case of inhomogeneously broadened line is given by the formula:¹⁵

$$\alpha = \frac{\alpha_0}{\sqrt{1 + I/I_s}} \quad (3)$$

and for small rate of saturation $\alpha \approx \alpha_0/(1 + I/2I_s)$. Taking $2I_s = I_0 = 250$ GW/cm², we get in our case $(T_1)_{\min} = 0.27 \approx 0.3 \pm 0.1$ ps. From the uncertainty principle it follows that the minimum width of the homogeneous contour should be

$$\Delta\nu_h = 1/\pi T_1 = 40 \text{ cm}^{-1}$$

To check the applicability of our technique for measuring the population relaxation time we used another liquid: 0.6 mol/l (3.5 vol. %) solution of ethanol in CCl₄ at the same experimental conditions. At this concentration the H bonds between ethanol molecules are formed, manifesting themselves in a wide absorption band with the maximum at 3300 cm⁻¹. The cell thickness was 100 μm, initial transmission (2.94 μm)–53%. From Fig. 5, representing the saturation curve for ethanol irradiated with 2.94 μm picosecond pulses, one can see that much stronger saturation than in the case of HDO takes place. At the maximum $I = 180$ GW/cm², the optical density is decreased 3.5 times. The theoretical curve corresponding to α vs I dependence in the form (1) rather than (3) fits the best experimental data with I_s value of 21 GW/cm². Using experimentally found $\sigma = 1.84 \cdot 10^{-19}$ cm² (2.94 μm) per

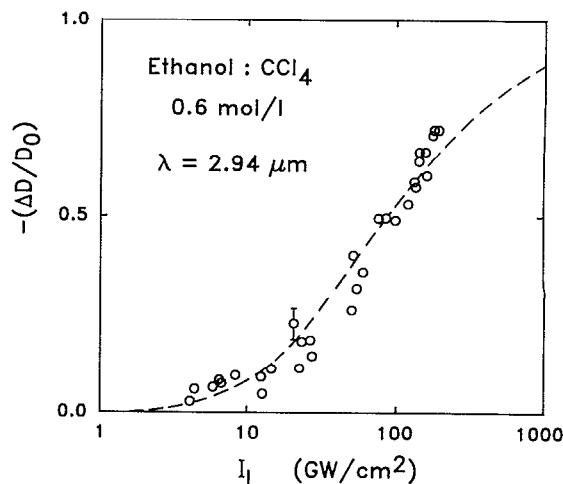


FIG. 5. Absorption saturation curve of ethanol in CCl₄. The broken curve—theoretical for $I_s = 21$ GW/cm².

ethanol molecule at this concentration we find from (2) the population relaxation time of the H-bonded ethanol molecule (absorption recovery time) to be 9 ± 3 ps which is consistent with 20 ± 5 ps measured by pump and probe technique in Ref. 5.

We consider that coherent nonlinear effects (such as stimulated Raman or Brillouin scattering) play negligible roles in our experiments because of a very small (< 100 μm) thicknesses of the cell. A simplified two level system was used here based on the balance of the absorbed and transferred into heat power. This model regards only the recovery time of the molecule to its initial absorbing state after the excitation to the $\nu = 1$ vibrational level and does not regard the intermediate states (with broken H bonds, for instance). The future application of tunable i.r. short pulse (< 1 ps) pump-probe methods will probably provide more detailed information about the phenomena observed.

V. CONCLUSION

Two mechanisms are responsible for water nonlinear transmittance for the intense laser radiation near 3400 cm⁻¹: temperature effect and spectroscopic saturation, differing in the characteristic recovery times by seven orders of magnitude.

In the first case (pure water), the absorbed laser radiation essentially increased the temperature of the liquid which followed up the changes in the laser radiation intensity due to very fast (at least $< 10^{-11}$ s) relaxation of the vibrational excitation in water. This leads to the weakening of H bonds, absorption band shift to higher frequencies, and a reduction in the band intensity. The result is significant bleaching at the laser wavelength, initially being near the center of the band. In pure water this effect should dominate for laser pulse durations more than 1 ps.

In case of HDO solution in D₂O, temperature effects were eliminated and the saturation of the OH vibrational transition had been shown with the saturation intensity as high as $I_s = 2.5 \cdot 10^{11}$ W/cm². The value of the population

relaxation time was found to be $0.3 < T_1 < 0.6$ ps at room temperature. This value is in correspondence with the estimates of other works for liquid water: $T_1 < 2$ ps⁷, $T_1 < 3$ ps³.

The lower limit for the homogeneously broadened component of the HDO absorption band near 3400 cm^{-1} was found to be $\Delta\nu_h \geq 40\text{ cm}^{-1}$.

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