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Four-photon parametric light scattering of ultrashort laser pulses in water in case of weak self-phase modulation

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***Abstract*.** **The hyper-Raman scattering (HRS) of light in water is detected reliably by the active spectroscopy method of coherent light scattering, in particular, by the method of four-photon parametric light scattering in a medium in which HRS is a 'signal' wave in the parametric process involving simultaneously two high-power laser photons and IR photons of an 'idler' wave. Hyper-Raman scattering by libration vibrations of water molecules, which virtually cannot be detected by conventional methods of Raman scattering, was observed.**

Keywords: *parametric interaction in liquid, active spectroscopy of coherent light scattering, optical strength of water.*

1. Introduction

Water is a unique object of nonlinear optics. It has a low SRS gain ($G_R = 7 \times 10^{-5}$ cm MW^{-1} for the 3435-cm^{-1} line [1], a low nonlinear refractive index ($n_2 = 1.4 \times 10^{-13}$ CGSE units [2]) and a high enough optical breakdown threshold $I > 1$ TW cm^{-2} [3]. This allows one to study water in strong light fields and observe multiphoton parametric processes during the propagation of picosecond laser pulses. The most spectacular effect observed in water is the generation of synchronous directional broadband radiation (picosecond supercontinuum).

At present this effect is interpreted in two different ways. It is assumed that such radiation appears either due to the self-phase modulation of a radiation pulse propagating in water or due to four-photon parametric scattering of laser radiation. The generation of a supercontinuum according to the first mechanism occurs mainly for subpicosecond intense laser pulses upon a strong modulation of the refractive index of water, often under conditions of a strong self-focusing of radiation, and is characterised by a continuous diffuse spectrum of scattered radiation [4]. The generation of radiation according to the second mechanism assumes the coherent interaction of pump and scattered waves under the phase-matching conditions of the type $2\boldsymbol{K}_0 = \boldsymbol{K}_s + \boldsymbol{K}_i$, where $\boldsymbol{K}_0$, $\boldsymbol{K}_s$ and $\boldsymbol{K}_i$ are the wave vectors of laser radiation detected in the visible region of 'signal' and 'idler' radiation [5], respectively. In this case, the efficient conversion can be realised at lower radiation intensities due to parametric conversion over a large interaction length of pump and scattered waves. Therefore, in the case of four-photon parametric conversion, the phase-matching condition for all the waves involved in scattering plays an important role.

In this paper, we studied the properties of four-photon parametric scattering of picosecond laser pulses in water by using single ~20-ps, few millijoule pulses from a Nd^{3+} : YAG laser.

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2. Experimental

Figure 1 shows the principal scheme of our experimental setup. The resonator of a master oscillator was formed by two mirrors M1 and M2, fold mirror M3, and a polarisation prism. Highly reflecting mirror M1 ($R = 1.0$) had the radius of curvature of 2.5 m. The use of such a mirror provided stable lasing at the TEM_{00q} mode. Reflector M2 was a cell with a passive plane-mirror ($R = 1$) Q switch. The initial vertical polarisation of laser radiation was provided by a DKDP crystal polarisation prism. A single

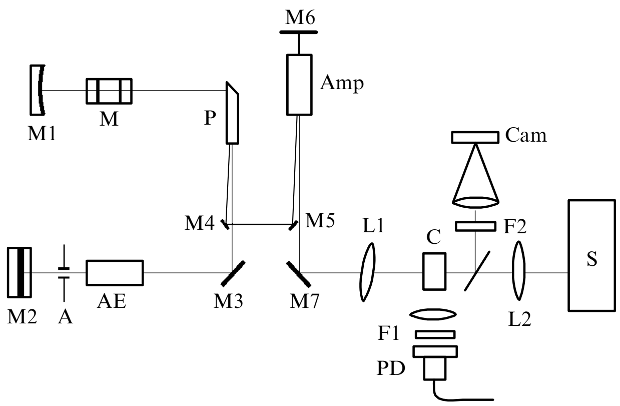


Figure 1. Scheme of the setup for recording parametric interaction of light in water: (AE) Nd^{3+} : YAG active element (of diameter 4 mm and length 73 mm); (M1) highly reflecting mirror ($R = 1.0$); (P) polarisation prism; (M) electrooptical DKDP crystal modulator; (A) 2.5-mm aperture; (M3 – M7) fold mirrors ($R = 1.0$); (Amp) Nd^{3+} : YAG amplifier (of diameter 6 mm and length 80 mm); (L1) focusing lens ($F = 70$ mm); (L2) lens focusing radiation emerging from a cell; (F1) filter transmitting only laser radiation at 1.064 μm; (F2) filter transmitting radiation in the range from 300 to 800 nm; (Cam) camera; (PD) photodiode; (S) spectrograph; (C) cell with water.

ultrashort light pulse was separated from a pulse train by means of an electrooptical modulator. When a high-voltage electric pulse of duration equal to the pulse repetition period in a pulse train of the laser was applied to the modulator, the polarisation plane of laser radiation rotated through an angle 90°. This radiation was coupled out through the polarisation prism from the resonator and was directed by means of fold mirrors M4 and M5 to a double-pass amplifier. The stable generation of $\sim$ 20-ps pulses was achieved in the regime in which the moment of the gain saturation in the active medium coincided with the moment of the passive Q switch bleaching (the so-called second lasing threshold regime) [6].

The maximum energy of the output laser pulse after amplification was 10 mJ. The output beam diameter was 1 mm. This radiation was directed by lens L1 with the focal distance $F_1 = 70$mm to a cell of length 40 mm. Lens L1 could be tilted by a small angle to the optical axis, which introduced small astigmatism to the incident beam. Such off-axial aberration of the lens causes the beam deformation. This is accompanied by the distortion of the axial symmetry of the beam and the increase in its divergence, which inevitably, as shown in [7], leads to the increase in the self-focusing threshold. Thus, by changing the tilt angle of the lens, we could vary the threshold self-focusing conditions for incident radiation. The spectrum of laser radiation transmitted through the cell was controlled with a spectrograph.

We investigated water of different compositions purified from impurities: distilled water containing air and water stored in preliminarily evacuated ampoules, which did not contain gases. These two samples considerably differed in the intensity of weak radiation scattering. The intensity of light scattered in distilled water containing air is approximately 20 times higher than that in water in ampoules. This is explained by the presence of bubston clusters (stable particles consisting of individual gas nanobubbles – bubstons [8]) in water purified from impurities.

We measured the optical strength of water and determined the spectral and angular distribution of the signal wave in the range from 300 to 800 nm during four-photon parametric interaction in water.

The optical breakdown is a process resulting in the optical damage of a material in the intense laser radiation field. At present there exist two methods for studying the optical breakdown in liquids [9]. The first method is based on the investigation of scattering by inhomogeneities produced during the breakdown in water. This method is used, as a rule, to study the optical breakdown caused by laser pulses of duration shorter than 10 ps. The second method for measuring the optical breakdown threshold is based on the detection of light flashes appearing in the beam track (the so-called flash model). In this paper, we determined the breakdown of water by the light scattering signal (at an angle of 90°) at the laser excitation wavelength. This signal was detected with a photodiode.

The breakdown threshold proved to be considerable dependent on the concentration of gas in water. In distilled water containing air and, as a result, a great amount of bubston clusters, the optical breakdown threshold for ultrashort pulses was $W_{\rm th} = 0.07$ mJ. On the contrary, in the case of ampoule water containing a considerably smaller amount of bubston clusters, the optical breakdown threshold was rather high ($W_{\rm th} = 0.9$ mJ). In both cases, when the ultrashort pulse energy exceeded $W_{\rm th}$, a breakdown flash was observed. Therefore, the optical breakdown in water has the seed nature. Water with a lower content of gas had the greater strength with respect to the optical breakdown. All further studies were performed with this water.

3. Four-photon parametric scattering of picosecond laser pulses in water

The effect of nonlinear parametric interaction can be clearly observed in ampoule water having a higher optical breakdown threshold. The four-photon parametric interaction of waves in a medium with the third-order nonlinearity is described by the spectral component of nonlinear polarisation

$$P(\nu_{\rm s}) = \chi^{(3)}(-\nu_{\rm s}, \nu_0, \nu_0, \pm\nu_{\rm i})E^2(\nu_0)E(\nu_{\rm i}),$$

where ν_0 is the laser radiation frequency and $\nu_{\rm s}$ and $\nu_{\rm i}$ are the frequencies of the signal and idler waves ($\nu_{\rm s} > \nu_{\rm i}$ and $\nu_{\rm i} < \nu_0$). In the case when three photons interact at the input, a fourth photon can be emitted due to parametric frequency conversion, i.e. $\nu_{\rm s} = 2\nu_0 \pm \nu_{\rm i}$. The nonlinear conversion processes can proceed efficiently under the so-called phase-matching conditions when $\boldsymbol{K}_{\rm s} = 2\boldsymbol{K}_0 \pm \boldsymbol{K}_{\rm i}$. This relation is satisfied for the two types of interaction between collinearly propagating coherent waves (Fig. 2).

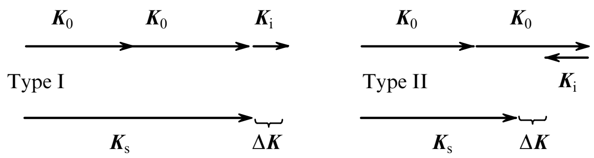


Figure 2. Possible types of interaction of coherent waves.

In the first type of interaction ($\nu_{\rm s} = 2\nu_0 + \nu_{\rm i}$), the signal frequency $\nu_{\rm s}$ is located in the anti-Stokes region with respect to the second-harmonic frequency of laser radiation $\nu_{\rm s} > 2\nu_0$. In this case, the phase mismatch is $\Delta\boldsymbol{K} = 2\boldsymbol{K}_0 - (\boldsymbol{K}_{\rm s} - \boldsymbol{K}_{\rm i})$, i.e. the modulus is $\Delta K/2\pi = 2\nu_0(n_0 - n_{\rm s}) + \nu_{\rm i}(n_{\rm i} - n_{\rm s})$, where n_0, $n_{\rm s}$ and $n_{\rm i}$ are the refractive indices at the laser, signal, and idler frequencies of the interacting waves, respectively, and frequency ν is expressed in inverse centimetres.

In the case of interaction of the second type ($\nu_{\rm s} = 2\nu_0 - \nu_{\rm i}$), the signal frequency $\nu_{\rm s}$ is located in the Stokes region with respect to the second-harmonic frequency of laser radiation $\nu_{\rm s} < 2\nu_0$. In this case, $\Delta\boldsymbol{K} = 2\boldsymbol{K}_0 - (\boldsymbol{K}_{\rm s} + \boldsymbol{K}_{\rm i})$ and $\Delta K/2\pi = 2\nu_0(n_0 - n_{\rm s}) + \nu_{\rm i}(n_{\rm s} - n_{\rm i})$.

Figure 3 shows the frequency dependences of the refractive index of water and of the modulus of the phase mismatch $\Delta K/2\pi$ for collinear four-photon interaction of the first and second types. The processing of the experimental results showed that the collinear interaction considered above was achieved by focusing radiation by a lens with the focal distance $f = 70$ mm at pulse energies below 1 mJ. The self-focusing effect was suppressed by tilting the lens to the optical axis. As a result, the detection regime of four-photon parametric scattering in water was selected so that the self-phase modulation and self-focusing of the laser beam were absent up to the pulse energy $W \approx 1$ mJ. In this case, the spectral width of transmitted laser radiation at 1.064 μm did not exceed $\Delta\nu \approx 1.5$ cm^{-1}. The regime selected in such a way corresponded to the conditions of weak self-phase modulation of ultrashort laser pulses.

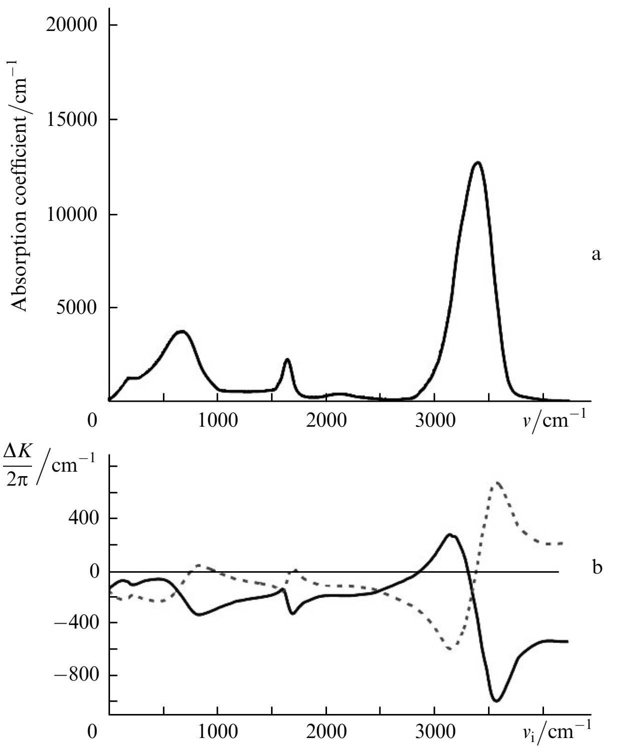


Figure 3. Frequency dependences of the refractive index of water at 25 °C (a) and of the phase mismatch of type I (solid curve) and type II (dashed curve) four-photon parametric interaction (b).

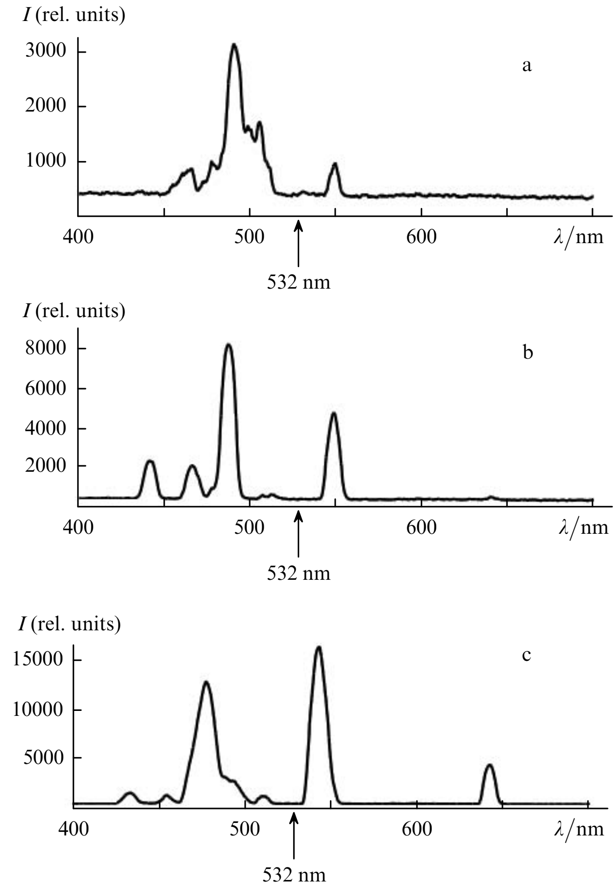


Figure 4. Spectra of four-photon parametric scattering in water at the energies W of the exciting light pulse (the case of collinear interaction) equal to 0.3 (a), 0.6 (b), and 0.9 mJ (c).

At high laser pulse energies, the distortion of the transverse intensity distribution of the beam propagated through a cell with water was observed. The beam self-focusing at laser pulse energies $W > 1$ mJ was accompanied by additional noncollinear four-photon parametric scattering.

The four-photon parametric scattering spectra were recorded with a minispectrometer. All visible radiation emerging from the cell along the laser beam was focused by lens L2 on the input slit of the spectrograph.

Figure 4 shows the spectra of three flashes produced by low energy (up to 1 mJ) light pulses at 1.064 μm at the moment of collinear interaction. Note that the parametric scattering spectrum is located at both sides of the 532-nm second-harmonic wavelength of incident radiation.

It follows from Fig. 4a that at the lowest excitation energies the parametric scattering spectrum is mainly located in the short-wavelength spectral region with respect to the second-harmonic wavelength. This spectral region corresponds to the first type of four-photon parametric interaction at which the signal-wave frequency is located in the anti-Stokes region with respect to the second-harmonic frequency of laser radiation $\nu_s = 2\nu_0 + \nu_i$. Conversion of this type can be realised in the presence of coherent IR radiation in the form of an idler wave. The matter is that when the laser pulse intensity is $\sim 10^{11}$ W cm^{-2}, a four-photon parametric scattering signal is recorded in water in the presence of SRS which can be produced by the 1.064-μm fundamental radiation beam [1]. In this case, as shown in [10], IR radiation can appear which serves as a seed for a coherent idler wave in type I four-photon parametric interaction. Note that the spectrum of this radiation in the anti-Stokes region ($\nu_s > 2\nu_0$) is different for different flashes. This fact and also the asymmetry of the parametric scattering spectrum observed in the Stokes and anti-Stokes regions are probably manifestations of the SRS nonstationarity in the field of picosecond light pulses. In this case, as a rule, the intensity distribution of forward and backward SRS radiation becomes asymmetric.

It seems that the formation of radiation in the anti-Stokes region can be explained only by type I four-photon parametric interaction ($\nu_s = 2\nu_0 + \nu_i$). On the contrary, as follows from Fig. 4, the spectrum of type II four-photon parametric interaction ($\nu_s = 2\nu_0 - \nu_i$) in the Stokes region ($\nu_s < 2\nu_0$) is well reproducible. This suggests that the seed of radiation in the Stokes region has a regular nature. The seed can be hyper-Raman scattering (HRS) at the Stokes frequency $\nu_s = 2\nu_0 - \Omega$, where Ω is a molecular vibrational frequency of water. The diagram of HRS, determined by the third-rank tensor $(\partial\beta_{ijk}/\partial q)$, by a molecular vibration with the coordinate q and frequency Ω is presented in Fig. 5. According to the selection rules [11], the HRS spectrum has the large information content. The alternative selection rules

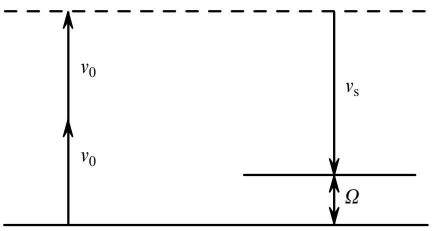


Figure 5. Diagram of the HRS of light in a medium with a molecular vibration at the frequency Ω ($\nu_s = 2\nu_0 - \Omega$).

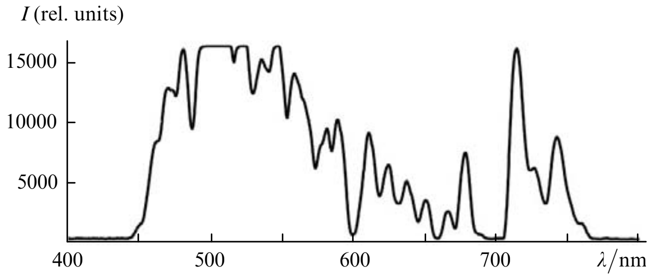
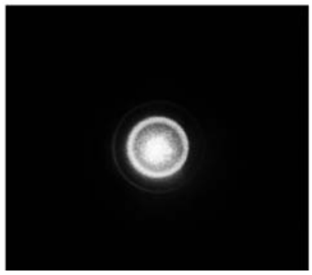


Figure 6. Spectrum of nonlinear scattering of light in water for the laser pulse energy $W = 1.6$ mJ.

a



b

Figure 7. Far-field four-photon parametric scattering patterns for 20-ps, 1.064-μm laser pulse energies 0.6 (a) and 1.6 mJ (b).

do not act in this spectrum and, in addition, molecular vibrations that are inactive both in Raman and IR absorption spectra can be manifested.

The processing of four-photon parametric scattering spectra in the Stokes region observed upon excitation of water by 0.1 – 1.0-mJ pulses showed that radiation appears first at the frequency shifted from the second-harmonic frequency by $\Omega = 480 \pm 30$ cm^{-1} (Fig. 4a). This frequency is close to the frequency of intermolecular librations of water molecules observed in the spontaneous Raman spectrum [12]. Aside from this line, the line shifted from the second-harmonic frequency by $\Omega = 3220 + 30$ cm^{-1} is observed in the Stokes region (Figs 4b, c). This frequency corresponds to an intermolecular vibration of water molecules. Note that the intensity of usual spontaneous Raman lines corresponding to the fundamental vibrations of water molecules (symmetric with $\Omega_1 = 3247$ cm^{-1} and anti-symmetric with $\Omega_2 = 3435$ cm^{-1}) exceeds that of the spontaneous Raman line corresponding to a libration vibration at $\Omega \approx 500$ cm^{-1}. In our case, the inverse relation is observed, which can be caused by the specificity of four-photon parametric interaction according to which the signal-wave intensity should be proportional to the intensity of the IR idler wave. Water strongly absorbs IR radiation at $\lambda \approx 3$ μm, and therefore the four-photon parametric interaction involving the idler wave a $\nu_i \approx 3300$ cm^{-1} should be strongly attenuated. This circumstance can explain the fact that the intensity of four-photon parametric scattering at $\Omega \approx 500$ cm^{-1} is greater than that at $\Omega \approx 3300$ cm^{-1}.

Thus, the processing of the spectra in the Stokes spectral region ($\nu_s < 2\nu_0$) shows that four-photon parametric collinear interaction leads to the efficient amplification of the HRS signal. In this case, the HRS radiation is the signal wave for the parametric process ($\nu_s = 2\nu_0 - \nu_i$).

At high laser pulse energies $W > 1$ mJ, the laser beam experienced self-focusing in water. In this case, a change in the laser beam cross section was accompanied by the appearance of additional noncollinear four-photon parametric scattering. As a result, the number of lines in the nonlinear scattering spectrum considerable increased (Fig. 6).

Together with recording the spectra of nonlinear scattering along the laser beam direction, we also recorded the far-field parametric radiation intensity distribution with a camera (Fig. 1). Filter F2 suppressed the fundamental 1.064-μm laser radiation. Figure 7 shows the far-field parametric radiation patterns in the visible region for two energies of a laser pulse incident on a cell with water.

4. Conclusions

We have studied the spectra of collinear four-wave interaction for different 1.064-μm laser radiation intensities. The two types of parametric interaction of the waves involved in scattering have been found. The anti-Stokes four-photon parametric scattering in water was observed for the first time.

The spectroscopy of four-photon parametric scattering of light is promising for studying both molecular and intermolecular vibrations in condensed media. By using this method, we recorded hyper-Raman scattering by libration vibrations of water molecules, which virtually cannot be detected by conventional Raman scattering methods.

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