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Structure detection in a libration vibration spectrum of water molecules by methods of nonlinear optics

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Abstract. **In exciting water possessing an enhanced optical strength by the radiation of a YAG : Nd^{3+} laser with 20-ps pulses, nonlinear scattering of light was detected in the frequency range of the optical second harmonic. A relationship was established of the signal of the nonlinear scattering with a stimulated Raman scattering (SRS) of the laser radiation in water. Near the SRS threshold, the structure was observed in the spectrum of nonlinear scattering, which is related to intermolecular libration vibrations of water molecules.**

Keywords: *water structure, parametrical interaction in liquids, active spectroscopy of coherent light scattering, optical strength of water.*

10. Introduction

Water is an object that has not been studied completely yet. One reason is the specific feature of pure liquid water molecules to form short-living molecular complexes; a relation between configurations of the complexes determines water properties in particular conditions. Information about the structure of water intermolecular complexes may be obtained from investigations of purely libration, translation, or mixed vibrations of molecules in a low-frequency spectral range. For water, the spectral range of such vibrations is approximately 10–1000 cm^{-1}, which is the operational spectral range for Raman scattering spectroscopy and IR spectroscopy. However, the spectra detected by these methods at the frequencies of intermolecular vibrations related to relative rotations and displacements of water molecules look like separate wide bands having no distinguished structure. This is illustrated in Fig. 1, showing an IR spectrum of water absorption (α is the absorption natural exponent) [1] and a spectrum of spontaneous Raman scattering of light [2]. Such a shape of the spectra is specific for traditional spectroscopy which is used for detecting almost all possible transitions between electron (vibronic) levels of molecules in an equilibrium state.

In contrast to classical spectroscopy of thermal (fluctuation) excitations of molecules, new possibilities are opened by nonlinear spectroscopy, in particular, the spectroscopy of nonlinear light scattering [3]. The specific feature of the nonlinear light scattering spectroscopy is the study of scattering on the coherent excited states of the medium phased by laser radiation [4, 5]. Such investigations performed recently are presented in [6–8] where libration and translational molecule motion was phased by two laser waves possessing different frequencies, where the frequency difference scanned the range of vibration resonances. The parameter detected under such biharmonic excitation was the state of a nonlinear polarisation arising in the medium.

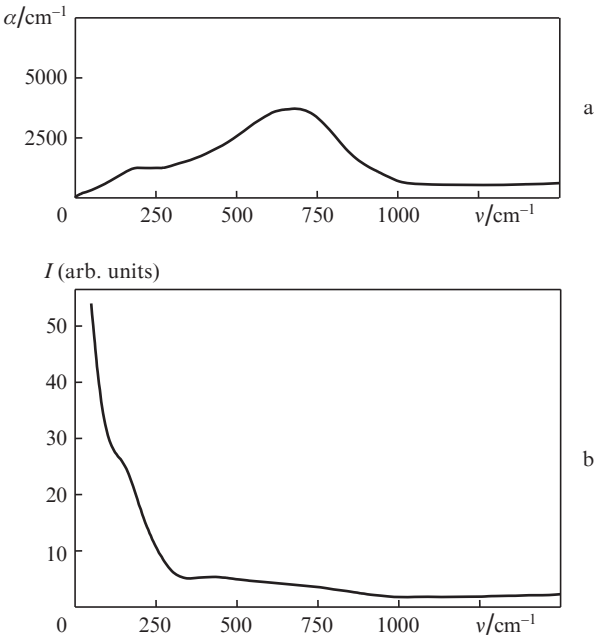

Figure 1. Spectra of IR absorption (a) and spontaneous Raman scattering (b) in water at $T = 25\,^{\circ}C$.

Nevertheless, in contrast to biharmonic pumping, coherent states of molecule vibrations can also be produced in the process of stimulated Raman scattering (SRS) (see Fig. 2a) of the

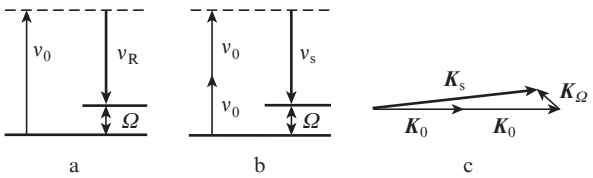

Figure 2. Schemes of possible processes occurring in the field of laser radiation at the frequency ν_0: stimulated Raman scattering of light (a), stimulated hyper-Raman scattering of light (b), and four-photon parametrical interaction of coherent waves (c); ν_s is the Stokes frequency, $\boldsymbol{K}_i$ are the wave vectors of the interacting waves.

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laser radiation itself [9–11]. In this case, as opposed to spectra of thermal scattering (spontaneous Raman scattering), a qualitatively different spectrum of nonlinear light scattering should be observed. It seems that not all possible vibrations of separate molecules can be phased in the process of SRS; hence, the only molecular vibrations which form coherent states in the medium are likely to be manifested in the spectra of nonlinear scattering. If there are coherent molecular vibrations in the vibration coordinate Q at frequency Ω, then in the frequency range of a second optical harmonic of the exciting laser radiation parametrical nonlinear scattering processes may arise such as stimulated hyper-Raman scattering (SHRS) (see Fig. 2b) and four-photon parametric scattering (Fig. 2c) [12, 13].

A process of SHRS is determined by the nonlinear induced polarisation of the medium $P_{NL} = (\partial\beta/\partial Q)E^2Q$, which arises at the Stokes frequency $\nu_s = 2\nu_0 - \Omega$, where the term $\sim\partial\beta/\partial Q$ determines the variation of the hyper-polarisability factor β in the vibration coordinate Q at the frequency Ω of normal molecular vibration; E is the intensity of the exciting field.

In addition to SHRS process, four-photon parametrical scattering may also produce the signal of nonlinear scattering of the laser radiation in the range near its second harmonic with the scattering frequency dependence $\nu_s = 2\nu_0 - \Omega$. The coherent oscillations of molecules in the medium established in the course of SRS of the laser radiation imply the emergence of coherent IR radiation arising at the frequency of molecular oscillations [14]. Under the high intensity of laser radiation and arising coherent IR radiation, a nonlinear parametrical interaction of these waves may occur in the medium. The four-photon parametrical interaction of waves in the medium possessing a third-order nonlinearity is described by the spectral component of the nonlinear polarisation in the case of the laser radiation at frequency ν_0 and a coherent IR radiation at frequency Ω:

$$P(\nu_s) = \chi^{(3)}(-\nu_s, \nu_0, \nu_0, \pm\Omega)E^2(\nu_0)E(\Omega),$$

where ν_s and Ω are the frequencies of the signal and 'idler' waves ($\nu_s > \Omega$ and $\Omega < \nu_0$). The signal frequency in the Stokes range in both processes described is given by the dependence $\nu_s = 2\nu_0 - \Omega$.

The emergence of coherent oscillations in the process of SRS is related to certain conditions. Relatively wide bands of water molecule vibration spectrum and, consequently, a high threshold of SRS require sufficiently intensive exciting radiation to realise the effect. Indeed, first works on SRS observation in water have been performed with ultrashort light pulses of the picosecond range [15–17]. It was stressed that the SRS spectra observed often exhibited an irregular structure varying from shot to shot [18, 19]. A reason for the structure appearance may be a nonstationary excitation of the wide bands of water molecule vibrations. It may also result from the phenomena occurring under a high intensity of the exciting radiation which may lead, for example, to self-focusing or self-modulation of the radiation and to effects related to plasma produced in a water breakdown [20]. Nevertheless, in our previous work [13] we have shown that minimisation of the negative factors while operating near the threshold of SRS in water makes it possible to obtain information about water molecule vibrations by analysing the spectral response of nonlinear scattering at the frequencies close to the frequency of the second optical harmonic for the exciting radiation.

The goal of the present work is to establish a relation between the nonlinear scattering signal in the range of the second optical harmonic of laser radiation with the process of SRS in water, find out the conditions for reproducible detection of the spectral structure of the nonlinear scattering caused by phased libration vibrations of water molecules, and determine the frequencies of characteristic libration vibrations.

11. Experimental setup and method

The scheme for observing the nonlinear scattering is presented in Fig. 3. The exciting radiation of a 1064-nm Nd^{3+}:YAG laser in the form of a single ultrashort pulse with the duration of $\Delta t \approx 20$ ps is focused by the lens L with the focal length $F = 166$ mm to a cell filled with water. The nonlinear scattering was investigated under close-to-threshold conditions. In the experiments, chemically pure cartridge water without gas components was used. Such water, according to our experience [21], possesses a highest optical strength, which makes it possible to neglect the effects related to the plasma breakdown. The signal of nonlinear scattering in the range of the second optical harmonic of laser radiation which propagates along the exciting beam is detected by a photodetector PD1. The filter F1 selects radiation in the spectral range of the second harmonic $2\nu_0 \pm 900$ cm^{-1}. We have found that under the conditions close to the threshold, the divergence of the nonlinear scattering signal is slightly greater than that of the laser radiation, which is an indication that the phase matching in the interacting waves is of collinear type [13].

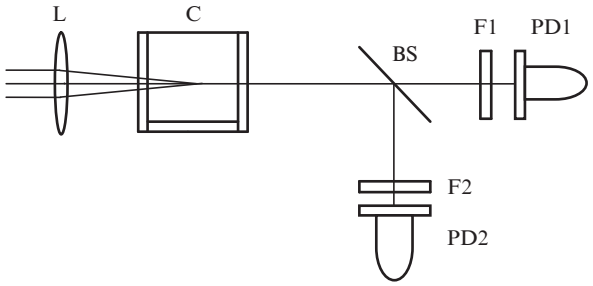

Figure 3. Detection of the four-photon parametrical scattering in water: (L) lens with the focal length $F = 166$ mm; (C) cell with water; (BS) beam splitter; (F1) and (F2) bandpass spectral filters; (PD1) and (PD2) photodetectors.

The experiment schematically shown in Fig. 3 was aimed at establishing a relation between the nonlinear scattering signal and the process of SRS in water. In each shot, in addition to the nonlinear scattering signal we also detected the SRS radiation in water directed forward, which was selected by the filter F2 in the spectral range $\lambda = 1.1–1.9$ μm. The corresponding results are shown in Fig. 4. Dots denote the nonlinear scattering intensity (I_s) in the range of the second optical harmonic versus the SRS intensity of laser radiation (I_R) detected in each shot. The spread of experimental data in the Figure may be related to a non-stationary character of SRS in water. The solid curve is an approximation of these data and, as one can see in Fig. 4, crosses the corresponding zero intensities. This is an indication that there is a unique relation between the nonlinear scattering and SRS in water. From Fig. 4 it follows that the nonlinear scattering only arises in water if there is SRS, which, in turn results in the appearance of coherent vibrations of molecules in the medium.

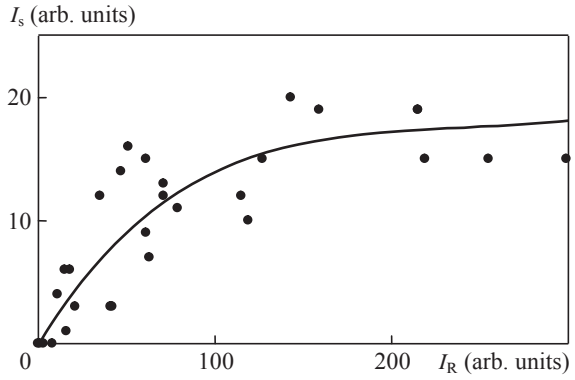

Figure 4. Intensity I_s of the nonlinear scattering signal in water in the range of the second harmonic for laser radiation versus the intensity I_R of arising SRS.

In the present work we for the first time detected the SRS spectrum in water under excitation by the radiation with λ = 1.064 μm in the spectral range of up to 1.17 μm. We succeeded in doing this with a device of low spectral resolution under the pumping above the threshold value of the nonlinear scattering excitation. The corresponding SRS spectrum and microphotogram detected in a single shot are presented in Fig. 5. One can see that SRS in water in this shot arises on libration vibrations with the energy maximum at the frequency of $\sim$580 cm^{-1}.

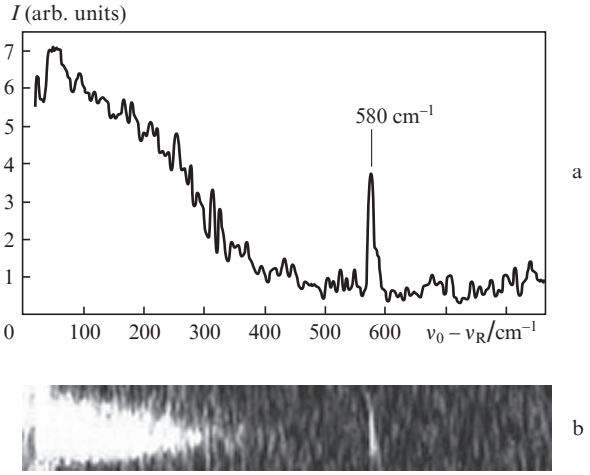

Figure 5. Spectrum of SRS in water under the excitation by neodymium laser radiation (λ =1064 nm, Δt = 20 ps) (a) and image of the radiation passing from a water cell detected in the focal plane of the spectrograph (b). The left part of the image is overexposed by the exciting laser radiation.

The method suggested for studying the nonlinear scattering in the range of the second optical harmonic for the laser radiation [13] is an instrument for investigating the frequencies of the coherent vibrations of molecules in the medium. The coherent vibrations may be formed by well-studied intramolecular or coherent intermolecular vibrations of water molecules. In the present work we pay particular attention to the structure of the intermolecular coherent vibrations which belong to a libration band. For this purpose, we studied the spectral composition of the radiation of the nonlinear scattering in the range of the second optical harmonic which occurs according to the interaction type with the frequency dependence $\nu_s = 2\nu_0 \pm \Omega$, described above (see Figs 2b, c).

The radiation under study was detected by diffraction spectrographs with various spectral resolutions. Figure 6a shows a total spectrum of nonlinear scattering, which was detected in a single shot in the range of the second optical harmonic (λ = 532 nm); the latter is marked by the dash-and-dot line. The intensity of the nonlinear scattering signal corresponds to the ordinate axis and the frequency detuning of the nonlinear scattering frequency from the second harmonic radiation frequency $2\nu_0$ corresponds to the abscissa axis. In Fig. 6, the positive frequency detuning corresponds to the Stokes part of the scattering spectrum.

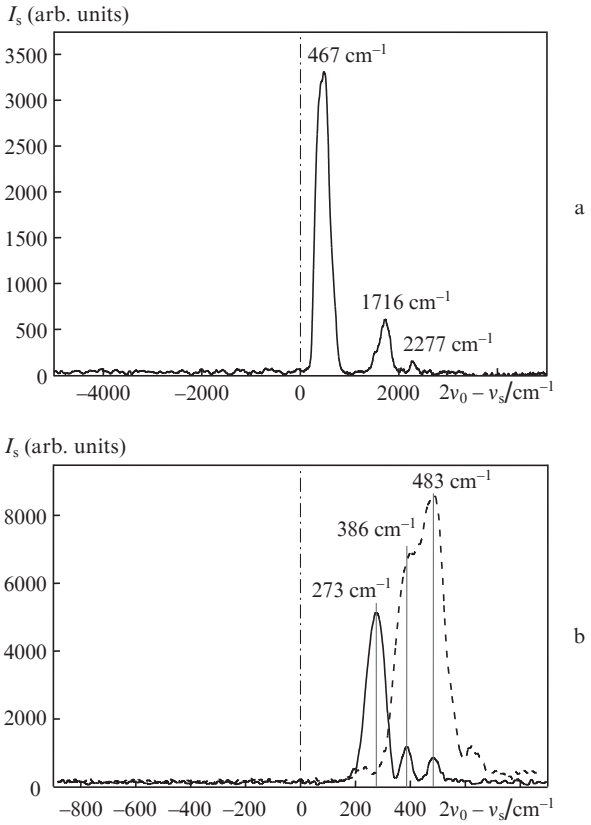

Figure 6. Microphotograms of spectra of the nonlinear scattering of laser radiation in water detected in the range of the second optical harmonic $2\nu_0$ (λ = 532 nm) with the detuning corresponding to the frequency interval of libration vibrations $\Omega = 2\nu_0 - \nu_s$, the spectra were detected in the conditions close to the threshold; (a) total spectrum of the nonlinear scattering detected in a single shot, (b) spectrum of the nonlinear scattering in the range of libration frequencies for two shots with different exciting energies (the spectrum marked by dashed line corresponds to a higher energy).

In the detection scheme (see Fig. 3) with the picoseconds laser excitation at the energy close to the threshold energy for the nonlinear scattering, the spectrum of the latter (see Fig. 6a), according to processed data, only resides in the Stokes range relative to the frequency $2\nu_0$, which corresponds to the wave interaction of the type $\nu_s = 2\nu_0 - \Omega$. Lack of signal in the anti-Stokes part of spectrum we explain by a non-stationary character of excitation and possible asymmetry of phase matching for Stokes and anti-Stokes SRS [13]. In Fig. 6a, well pronounced signals are seen with the maxima at the frequencies

$\Omega = 467$ cm^{-1} (libration band) and $\Omega = 1716$ cm^{-1} (a deformation intramolecular vibration). A weak signal with the maximum at the frequency $\Omega = 2277$ cm^{-1} is also seen in the range of mixed vibrations. It should be stressed that near the threshold there is no signal in the spectrum of nonlinear scattering corresponding to the frequencies of valence vibrations of water molecules in the range $\Omega > 3000$ cm^{-1}.

Figure 6b shows microphotograms of nonlinear scattering spectra in the range of libration frequencies [recorded by a diffraction spectrograph with an enhanced ($\sim$1 cm^{-1}) spectral resolution] for two shots with different excitation energies close to the threshold value. Radiation of nonlinear scattering was studied at the frequency detuning of up to 900 cm^{-1} in both Stokes and anti-Stokes ranges near the range of libration vibrations. One can see from Fig. 6b, that the spectrum of the nonlinear scattering has a structure in the form of separate narrow lines. The structure is reproduced in frequency from shot to shot, namely: the spectral positions of maxima for separate lines are not changed, whereas the intensity ratio in the lines varies. These lines have the spectral width of 30–50 cm^{-1} and partially overlap. Data processing revealed the frequencies of intermolecular vibrations Ω (273, 386, 483 cm^{-1} etc.) in water, which are marked in Fig. 6b.

12. Conclusions

According to the existing understanding of water structure, a libration vibration band is a set of vibrations of water complexes with different contents and, consequently, different frequency spectra. These frequencies as functions of particular types of molecular complexes can only be found by mathematical modelling performed, in particular, in [22] with the structure composition and constants of intermolecular bonds taken into account. The frequencies of the libration vibrations detected in our experiments well agree with data of these modelling calculations.

Thus, the experimental results obtained with the method of nonlinear spectroscopy for the first time revealed the band structure of libration vibrations for water molecules coherently excited in the process of laser SRS. This structure could not be resolved by traditional IR spectroscopy and SRS spectroscopy. It was shown that the best results are obtained under conditions close to the threshold conditions for SRS in water.

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