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Origin of low-frequency spectrum structure of four-photon scattering in liquid water

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Abstract. A multipeak structure of four-photon scattering spectrum in the range from -2 to $+2\,\mathrm{cm}^{-1}$ has been found experimentally in liquid water. The theoretical interpretation relates these spectral features to an interference of strictional and orientational contributions to the scattered signal.

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The spectrum of intrinsic excitations of liquid water is investigated in detail and interpreted rather authentically in a high-frequency ($\geq 100\,\mathrm{cm}^{-1}$) range [1]. Such investigation is more difficult in the low-frequency range due to the complex statistics of short-range order fluctuations. These fluctuations result in, first, new lines arising inherent only in such excitation structures, and, second, broadening and mutually overlapping lines of classical origin.

One of the most promising spectroscopy techniques is a method of four-photon polarization spectroscopy, which allows new information on the structure and properties of liquid water and other liquids with strong intermolecular interactions to be gained [2–6]. In particular, with the help of this method in water and some water solutions, temperature and concentration deformations of a narrow part of the Rayleigh wing spectra are found, which modified nonmonotonically nearly thermodynamic anomalies at temperatures of 0, 4, 36, and 76 °C [2–4]. Also a regular set of lines of collective modes has been found in the range from 10 to $90\,\mathrm{cm}^{-1}$ [5, 6]. In the present work we measured the four-photon spectra of liquid water in the range from -2 to $+2\,\mathrm{cm}^{-1}$ and recorded their multipeak structures.

1 Theory

In four-photon polarization spectroscopy, the process $\omega_S = \omega_p - (\omega_p - \omega_S)$ is realized, where the difference $\omega_p - \omega_S$ is scanned in the vicinity of studied resonances (in our case around the Brillouin doublet and the Rayleigh wing). A measured parameter is the polarization of the ω_S wave, determined by a nonlinear source proportional to the third-order susceptibility of the medium.

Nonlinear spectroscopy uses the high intensity of optical beams. Therefore, to describe a valid signal, one has to consider not only the interaction of pumping and reference waves but also the specific amplification of signal and reference waves in the pump field, owing to the stimulated scattering of the pumping wave. Furthermore, in the studied low-frequency band, when a frequency difference $\Omega = \omega_p - \omega_S$ of pumping and reference waves is less than $10\,\mathrm{cm}^{-1}$, the strongest mechanisms of optical nonlinearity are strictional and orientational interactions (Kerr effect). In the experiment [2–5], the signal and reference waves coincide in frequency and direction, representing different polarization components of a single wave packet.

Variation in these waves under action of the counter propagating pump beam (with frequency ω_p and amplitude $A_j^{(p)}$) is described by equations for slow amplitudes $A_j^{(S)}$ ($j = 1, 2$) of the field at frequency ω_S, in which light-induced variations $\delta\varepsilon$ of the dielectric constant [7] are related to the above two mechanisms of nonlinearity:

$$\frac{\mathrm{d}A_j^{(S)}}{\mathrm{d}z} = \frac{1}{2}\left\{\frac{2G_B\Omega_B\Gamma_B}{2\Omega_B\Gamma_B - i(\Omega_B^2 - \Omega^2)} A_k^{(S)} A_k^{(p)*} A_j^{(p)} + \frac{3G_R\Gamma_R}{2(\Omega - i\Gamma_R)}\left[A_k^{(S)} A_k^{(p)} A_j^{(p)*} + A_k^{(p)} A_k^{(p)*} A_j^{(S)} - \frac{2}{3} A_k^{(S)} A_k^{(p)*} A_j^{(p)}\right]\right\} \quad (1)$$

Here G_B and G_R are the maximum increments of amplification due to Brillouin and Rayleigh wing scattering for a linearly polarized pump wave of unit intensity:

$$G_B = \frac{\omega_p \Omega_B \rho(\partial\varepsilon/\partial\rho)^2}{4c^2 n_0^2 \nu_a^2 \Gamma_B}; \quad G_R = \frac{16\pi^2 B_K}{3n_0 c};$$

Γ_B and Γ_R are the half-widths of spontaneous scattering lines; $\Omega_B = 2\omega_p n_0 \nu_a / c$ is the frequency shift of Brillouin scattering (ν_a and c/n_0 are the speeds of sound

and light in medium); and ρ, ε, and B_K are the density, dielectric, and Kerr constants of a medium, respectively.

In conditions of the proposed experiment $\left|A_j^{(S)}\right|^2 \le I_p \exp(-G_{B,R} I_p l)$, where I_p is the intensity of pump wave. Input ($z = 0$) boundary conditions in the area of overlapped pump and reference beams are $A_1^{(S)}(0) = \sqrt{I_0}$ ($\sqrt{I_0}$ is the input amplitude of linearly polarized reference wave) and $A_2^{(S)}(0) = 0$.

For the pumping wave of circular polarization $\left(A_1^{(p)}/A_2^{(p)} = i\right)$, the solution to system (1) at these conditions gives the signal wave intensity $I_2 = \left|A_2^{(S)}(l)\right|^2$ on the exit from an interaction volume:

$$I_2(\Omega) = \frac{I_0}{4}\left|\exp\left[\frac{3\Gamma_R G_R I_p l}{2(\Omega - i\Gamma_R)}\right] - \exp\left[\frac{\Gamma_R G_R I_p l}{4(\Omega - i\Gamma_R)} + \frac{\Omega_B \Gamma_B G_B I_p l}{2\Omega_B \Gamma_B - i(\Omega_B^2 - \Omega^2)}\right]\right|^2, \quad (2)$$

where $I_p = \left|A_1^{(p)}\right|^2 + \left|A_2^{(p)}\right|^2$ is the pump wave intensity.

If the amplification on the length of interaction is weak, the signal intensity (2) is an even function of frequency deviation $I_2(-\Omega) = I_2(\Omega)$. If the exponents in (2) are comparable to 1, the dependence of signal intensity on Ω becomes asymmetrica. The solid curve in Fig. 1 shows the spectral dependence (2) calculated for parameters of liquid water [8]. Compared to other liquids, the stimulated Brillouin scattering increment ($G_B \approx 5 \times 10^{-3}$ cm/MW) in water is much lower, while the Kerr constant ($B_K \sim 4 \times 10^{-7}$) is rather high; therefore for water $G_B/G_R \sim 2$. Hence, the two nonlinear mechanisms give comparable contributions in the investigated frequency range. Adapted for comparison to the experiment (averaged by the window $\Delta\Omega \sim 0.1\,\mathrm{cm}^{-1}$), the plot of formula (2) is also shown in Fig. 1 (dashed curve).

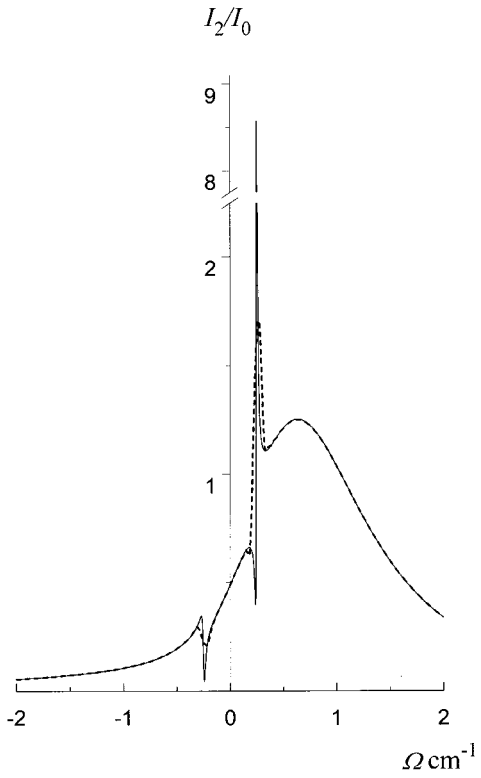

Fig. 1. Theoretical plot of signal wave intensity as a function of frequency difference $\Omega = \omega_p - \omega_S$ with total Rayleigh wing amplification $G_R I_p l = 1.3$ and $G_B I_p l = 3.3 (\Omega_B = 0.25\,\mathrm{cm}^{-1},\ \Gamma_B = 6 \times 10^{-3}\,\mathrm{cm}^{-1},\ \Gamma_R = 1\,\mathrm{cm}^{-1})$. The solid line is for monochromatic waves; dashed line is averaged by the window $\Delta\Omega = 0.1\,\mathrm{cm}^{-1}$

2 Experiment

The experiment was conducted according to a scheme, the measuring part of which is shown in Fig. 2. For a master oscillator, we used a pulsed Nd^{3+}:YAG laser. The laser beam after two-cascade amplification and conversion to the second and third harmonics was used for pumping of a dye laser with Coumarin-7 solution, oscillating in the range of 485–545 nm. The dye laser linewidth that determinet the spectral resolution was $0.1\,\mathrm{cm}^{-1}$ at a pulse energy of 10 mJ and a pulse duration of 10 ns. For the pump wave, we used the second harmonic of the master laser ($\lambda = 532$ nm, pulse energy of 30 mJ), which together with the dye laser allowed us to tune frequency difference $\omega_p - \omega_S$ in the range from -450 to $+1830\,\mathrm{cm}^{-1}$.

The signal at frequency ω_S was selected with the help of a polarization analyzer (Glan prism) and a spatial filter, which cut noncoherent illumination from pump waves and then was detected by a photomultiplier. Further, after amplification and digitizing, the signal was recorded in a computer for statistical processing.

Figure 3 shows the four-photon spectra of twice distilled water, received with a spectral resolution of 0.4 (Fig. 3a) and $0.15\,\mathrm{cm}^{-1}$ (Fig. 3b). The comparison of experimental and theoretical spectra (Fig. 3 and 1) reveals their qualitative and approximate quantitative similarity. The two spectra contain sharp peaks in the low-frequency range, corresponding to the Brillouin resonances, and much more flat maxima (or only one maximum) related to the stimulated Rayleigh wing scat-

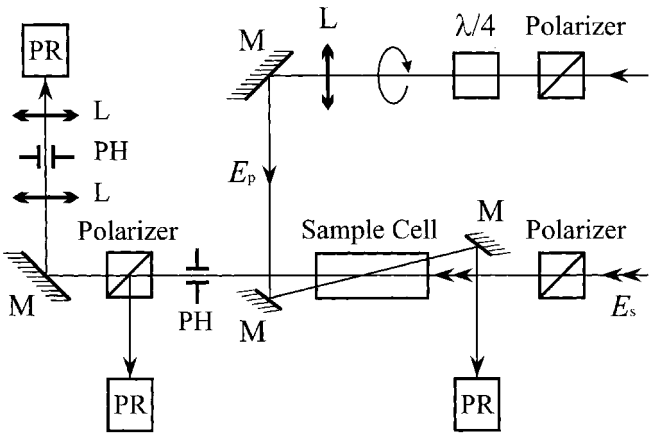

Fig. 2. Schematic representation of the optical arrangement of the experimental setup. L, lenses; M, mirrors; PH, pinholes; PR, photoreceivers

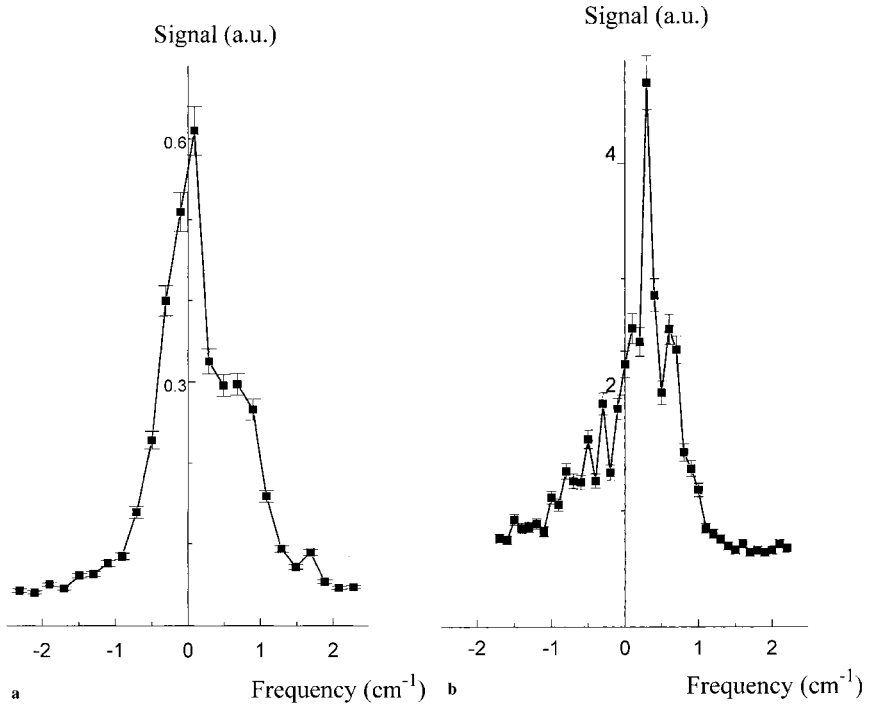

Fig. 3. Four-photon spectra of twice distilled water with the spectral resolution 0.4 (a) and 0.15 cm^{-1} (b)

tering and the interference of Kerr and Brillouin scattering channels.

3 Discussion

The performed experiment confirms the interference mechanism proposed above that forms the fine structure of low-frequency scattering in water. This mechanism can be used in four-wave experiments for measurement of some parameters, which are hardly measurable in other schemes. In particular, it concerns the temperature derivatives of the Kerr constant B_{K} and orientational relaxation time Γ_{R}^{-1}, which strongly depend on the short-range order in liquid water. With decreasing temperature, water molecules form more and more hydrogen bonds. Since Rayleigh wing scattering is provided by rotations of the molecular cluster ensemble, a whole spectrum of relaxation times $\Gamma_{\mathrm{R}}^{-1}(N) \propto N^{2/3}$, where N is the number of molecules in a cluster, is broadened. The maximum of cluster distribution, over the size $r(\sim N^{1/3})$, is shifted on cooling to the greater r. The effective Γ_{R} thus decreases, and this reduction, evidently, can be rather precisely measured with the help of the above described scheme. It is important that the Γ_{R} reduction, up to the values characteristic of ice and probably of supercooled water, changes the four-photon spectrum not only quantitatively but also qualitatively.

Figure 4 shows the results of function (2) calculations for $\Gamma_{\mathrm{R}} \ll \Omega_{\mathrm{B}}$. Additionally, we take into account the typical (for condensed media) background noninertional nonlinearity (relaxation time $\ll 3 \times 10^{-12}$ s). This contribution is described by insertion of the component $4\pi i\omega n_2 c^{-2} n_0^{-1} A_k^{(\mathrm{S})} A_k^{(\mathrm{p})} * A_j^{(\mathrm{p})}$, where n_2 is the factor of nonlinearity of a refraction parameter $n \approx n_0 + n_2 E^2$ (scalar nonlinearity) in the right part of (1). The characteristic dip in Fig. 4 arising near zero frequency difference, which is observed also

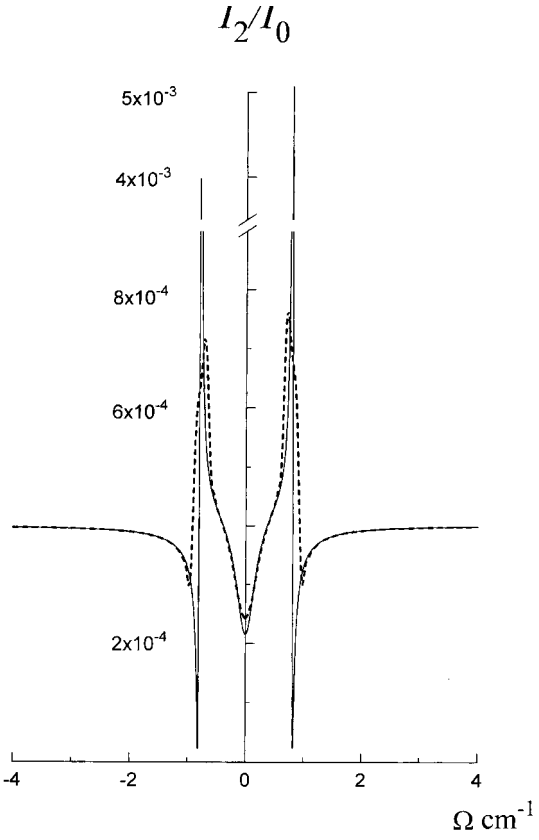

Fig. 4. Theoretical plot of signal wave intensity for $\Gamma_{\mathrm{R}} \ll \Omega_{\mathrm{B}}$($\Gamma_{\mathrm{R}} = 0.2\ \mathrm{cm}^{-1}$, $\Omega_{\mathrm{B}} = 0.8\ \mathrm{cm}^{-1}$, $\Gamma_{\mathrm{B}} = 5 \times 10^{-3}\ \mathrm{cm}^{-1}$) and nonresonant nonliarity $4\pi\omega n_2 c^{-2} n_0^{-1} I_{\mathrm{p}} l = 4 \times 10^{-2}$; total amplifications $G_{\mathrm{R}} I_{\mathrm{p}} l = 10^{-2}$ and $G_{\mathrm{B}} I_{\mathrm{p}} l = 0.25$. Solid curve is for monochromatic beams and dashed line is averaged by the window $\Delta\Omega = 0.3\ \mathrm{cm}^{-1}$

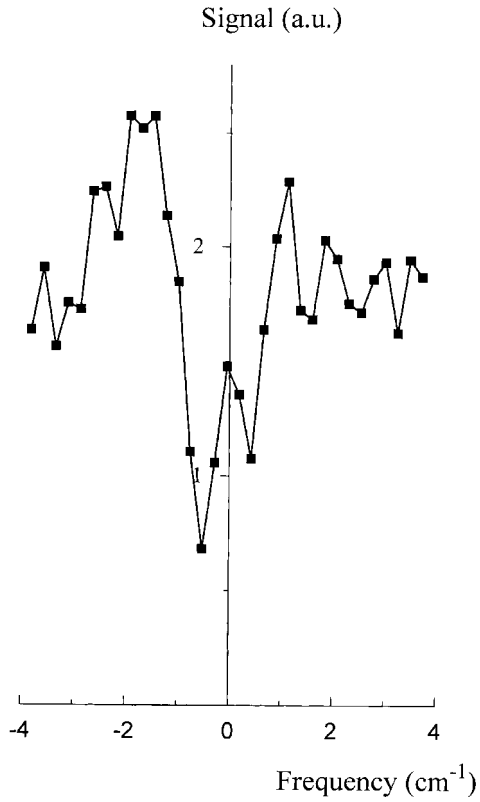

Fig. 5. Four-photon spectrum of ice

in the experimental spectra of ice (Fig. 5), can be related to destructive interference of orientational and background nonlinearity for circular pumping wave polarization. This spectral dip increases the accuracy of the reconstructed values of I_R and G_R/G_B by the experimental data. This means, obviously, that four-photon spectroscopy is a promising optical method for investigating the temperature variability the intrinsic structure of liquid water.

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