

Four-wave polarized Rayleigh-line-wing spectroscopy

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A new method for detecting anisotropy relaxation—four-wave polarized spectroscopy of the Rayleigh line wing—is proposed. This new method has been implemented experimentally. An anomalous behavior of the spectra is found at temperatures of 3 °C and 35.5 °C.

In this letter we propose and report the experimental implementation of a new method for studying the relaxation of the anisotropy of centrally symmetric media; four-wave polarized Rayleigh-line-wing spectroscopy. The method consists of measuring the dispersion of the intensity of the depolarized component of the wave at the frequency $\omega_2 = \omega_1 - (\omega_1 - \omega_2)$ as the frequency difference between pump waves, $\omega_1 - \omega_2$, is scanned near a zero frequency. This method is one version of four-wave modulation spectroscopy (involving a modulation of the dielectric constant through an optical nonlinearity), which has previously been used only to obtain spectra of molecular vibrations,^{1,2} of (Mandel'shtam-) Brillouin scattering,³ and of the unshifted Rayleigh line.⁴

Another purpose of this study was to learn about the deformation of the spectra obtained in the application of this new method to liquid water over the temperature

range 2–40 °C. We have observed anomalous changes in the shape of the spectra at temperatures of 3 °C and 35.5 °C.

The method proposed here for obtaining spectra of the Rayleigh line wing is essentially one of the detecting methods of the polarization state perturbed by a non-linear source of the wave at the frequency ω_2 .

$$P_i^{(3)}(\omega_2) = 6\chi_{ijke}^{(3)}(\omega_2; \omega_1, \omega_2, -\omega_1)E_j^{(1)}E_k^{(2)}E_e^{(1)*} \quad (1)$$

in the four-wave mixing $\omega_2 = \omega_1 - (\omega_1 - \omega_2)$. Here $\chi^{(3)}$ is the cubic susceptibility of the medium; $E^{(1)}$ and $E^{(2)}$ are the electric field intensities; and the difference $\omega_1 - \omega_2$ is scanned over the Rayleigh line wing. The following expression can be derived for the intensity of the signal at the frequency ω_2 from transparent media in the case in which the Brillouin resonances and the wing of the Rayleigh line have a Lorentzian shape and for a circular polarization of the wave at frequency ω_1 :

$$I_s(\omega_2) \propto \left| \frac{\bar{\chi}^B}{i + (\omega_1 - \omega_2 + \Omega_B) / \Gamma_B} + \frac{\bar{\chi}^B}{i + (\omega_1 - \omega_2 - \Omega_B) / \Gamma_B} + \frac{(1 - 3\beta)\bar{\chi}^R}{i + (\omega_1 - \omega_2) / \Gamma_R} \right|^2 I_1^2 I_2 l^2, \quad (2)$$

$$\bar{\chi}^B = \frac{1}{64\pi^2 D} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T \beta_s (2 - \gamma) \frac{\Omega_B}{\Gamma_B} L^4,$$

$$\bar{\chi}^R = \frac{N_0 [(\alpha_{11} - \alpha_{22})^2 + (\alpha_{22} - \alpha_{33})^2 + (\alpha_{33} - \alpha_{11})^2] L^4}{90 kT \Gamma_R}$$

Here l is the length of the region in which waves $E^{(1)}$ and $E^{(2)}$ intersect; β_s is the adiabatic compressibility; $\gamma = C_p/C_v$; ρ is the density; β is the degree of depolarization of the scattering; ϵ is the dielectric constant; L is a correction for the internal field; α_{11} , α_{22} , and α_{33} are the diagonal components of the polarizability tensor of the molecules; k is the Boltzmann constant; T is the temperature; and $\bar{\chi}^B$ and $\bar{\chi}^R$ are the peak values of the Brillouin susceptibility and the Rayleigh-line-wing susceptibility, respectively. Expression (2) ignores the contribution from scattering by the thermal lattice (the central Rayleigh peak) since for optically transparent media this contribution is much smaller (by two or three orders of magnitude) than the four-wave signal from Brillouin scattering.²

In the case of liquids with a strong intermolecular interaction (water, aqueous salt solutions, and aqueous acid solutions) the third term in (2) should consist of several terms, corresponding to different anisotropy fluctuation mechanisms. This circumstance should be manifested in $I_s(\omega_2)$ as characteristic deformations of the spectrum, so that it should become possible to distinguish and study the contributions made to the signal from the individual anisotropy relaxation processes.

The experimental apparatus consisted of a Nd:YAG laser, three Nd:YAG laser

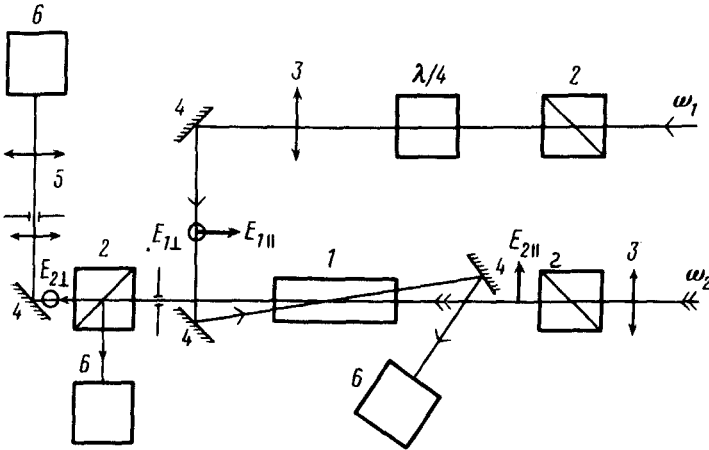


FIG. 1. The optical layout of the experiments. 1—Cell holding the substance under study; 2—polarizers (Glan prisms); 3—lenses; 4—mirrors; 5—spatial filter; 6—photodetectors.

amplifiers, and a dye (Coumarin 7) laser, pumped by the third harmonic from a Nd:YAG laser. The output from the dye laser was tunable over the interval 480–550 nm. Circularly polarized light at the second harmonic of the driving laser ($\lambda_1 = 532$ nm) and the linearly polarized light from the dye laser (ω_2) were brought into spatial coincidence in a cell holding the substance under study. The signal corresponding to the four-wave polarized Rayleigh-line-wing spectroscopy was distinguished from background light by a polarizer and a spatial filter and then detected by a photodetector (Fig. 1). The signal was then read out by a microcomputer, which simultaneously measured the energy of the pump waves with the frequencies ω_1 and ω_2 controlled the scanning of the frequency of the dye laser, and carried out a statistical analysis of the detected signal.

As in other types of four-wave spectroscopy, the level of the signal in this method is significantly greater than the level in spontaneous scattering; in our experiments, the signal level amounted to 10–10 photons per pulse at the spectral peak.

The experiments were carried out in distilled, degassed water. The spectra were recorded over the temperature interval 2.5–39 °C at steps of 0.5 °C.

Figure 2a shows spectra of the water at temperatures of 2.5–4.5 °C. The spectra are made up of a superposition of two maxima: a narrow one near $(\omega_1 - \omega_2)/2\pi c = 0$, caused by the scattering of the E_{11} wave at the frequency ω_1 by the isotropic grating of the pressure and the density (four-wave excitation of Brillouin scattering), and a broader maximum corresponding to the contribution to the detected signal E_{21} of the anisotropy relaxation, consisting of the four-wave Rayleigh-line-wing spectrum. We see that at $T = 3$ °C the central component of the Rayleigh line wing narrows and shrinks in amplitude.

Figures 2b and 3 show spectra of the water in the temperature intervals 7–23° and 33.7–37 °C. We see that as the temperature is raised from 7 °C to ≈ 20 °C, there is a

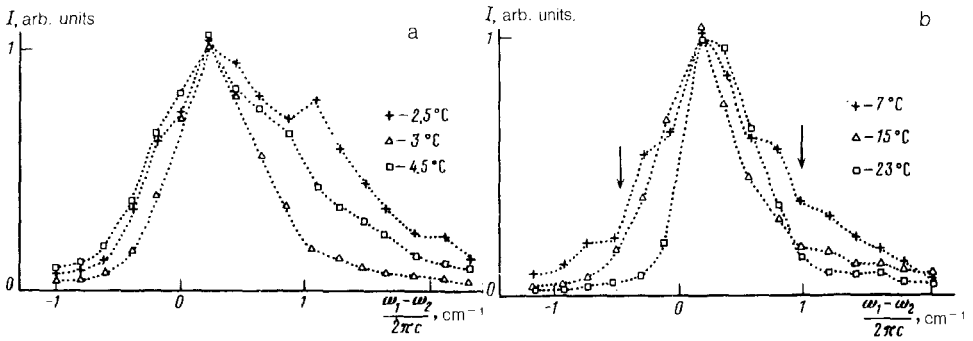


FIG. 2. Four-wave Rayleigh-line-wing spectra of liquid water. The spectra have been normalized to the peak of the Brillouin line. a— $T = 2.5, 3.0, 4.5^\circ\text{C}$; b— $T = 7.0, 15.0, 23^\circ\text{C}$.

fivefold decrease in the amplitude of the signal corresponding to the component of the Rayleigh line wing. Near 35.5°C we see an increase in the amplitude and a broadening of the central component of the Rayleigh line wing of water. Each of the temperatures at which we see anomalies in the behavior of the signal corresponds to a special point for liquid water (the density maximum and the C_p maximum).

The overall spectra in Figs. 2 and 3 are asymmetric. To the left of the maximum (at $\omega_2 > \omega_1$) there is a dip (this dip was recorded separately; this region of frequency deviations is not shown in Figs. 2 and 3). The presence of this dip is evidence of the incomplete suppression of the nonresonant part of the susceptibility, $\chi^{(3)NR}$. The frequency position of the dip is evidence that on the whole the Rayleigh line wing has a degree of depolarization $\beta > 1/3$. The spectral shape of the signal observed at certain temperatures (e.g., $T = 7^\circ\text{C}$) is evidence that the spectrum of the narrow part of the Rayleigh line wing is formed by the superposition of several lines differing in width. Experimentally, this circumstance is manifested in a characteristic slope change on the wing of the spectrum, marked by the arrow.

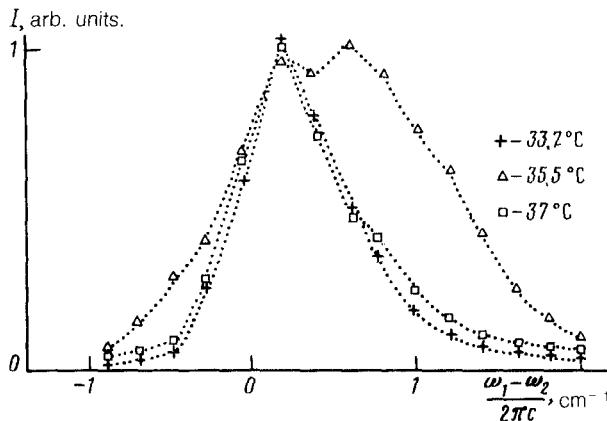


FIG. 3. Four-wave Rayleigh-line-wing spectra of liquid water. The spectra have been normalized to the peak of the Brillouin line. $T = 33.7, 35.5, 37^\circ\text{C}$.

In summary, we have proposed and reported an experimental implementation of a new method for detecting the anisotropy relaxation of liquids and gases: four-wave Rayleigh-line-wing spectroscopy. This new method is distinguished by a high signal level, which exceeds the corresponding level in spontaneous scattering by five to six orders of magnitude. This new method is also distinguished by the possibility of separately studying different physical relaxation mechanisms, since the corresponding contributions to the detected signal, which interfere with each other, are manifested in the spectrum as characteristic features. In the spectroscopy of the spontaneous Rayleigh-line-wing scattering, these contributions cannot be distinguished. The strong temperature dependence of the spectra in this new method opens up the possibility of a contactless and accurate determination of the temperature of the water, including measurements at a distance.

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