

Remote nonlinear polarization Raman spectroscopy

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A new method of remote Raman spectroscopy has been demonstrated experimentally. In this method, the signal level is more than 10^6 times the level of the signal corresponding to spontaneous Raman scattering. The divergence of the measured light is 2×10^{-4} . The method can be used to study the vibrational spectra of transparent media at large distances.

1. A new method of nonlinear Raman spectroscopy has been demonstrated in the experiments reported here. This is a remote spectroscopy of the Kerr effect induced by a Raman-scattering resonance (RKRS) in which spectroscopic information about the medium under study is embodied in changes in the intensity of an intense, coherent, monochromatic wave which is propagating precisely opposite the pump wave incident on the medium. As in the ordinary spectroscopy of the optical Kerr effect induced by a Raman resonance,^{1,2} we measure the change in the polarization of a probe wave of frequency ω_1 while scanning the difference ($\omega_1 - \omega_2$) between the frequencies of the pump waves near Ω_R , the frequency of the Raman resonance under study.

A distinction from Refs. 1 and 2 is that the probe wave arises in the medium under study as a result of a stimulated Brillouin scattering of one of the incident waves [in our case, the wave $\mathbf{E}_1(\omega_1)$], so that the measurements are taken remotely. However, in contrast with the remote version of coherent anti-Stokes scattering which was proposed and implemented in Refs. 3 and 4, where the geometry of the interaction of all the waves is rigidly fixed, and the angles between the vectors are tens of degrees, in our case the pump waves, with wave vectors \mathbf{K}_1 and \mathbf{K}_2 , can intersect in the medium under study at any angle (including zero), and the signal that is measured, $\mathbf{K}_{\text{IRKRS}}$, propagates in a direction making an angle of 180° with \mathbf{K}_1 . This method can thus be used to carry out remote measurements at large distances, limited only by the need to exceed the threshold for stimulated Brillouin scattering of one of the pump waves in the medium under study.

2. The method of remote spectroscopy of a Kerr effect induced by a Raman-scattering resonance described by us in this letter was proposed theoretically in Ref. 5.

The experimental apparatus is shown in Fig. 1. The pump waves are the second harmonic of a single-frequency laser (1) and a dye (rhodamine G) laser (5) ($\lambda_1 = 532$ nm, $550 \text{ nm} \leq \lambda_2 \leq 585$ nm; power levels $P_1 \cong P_2 \cong 1$ MW; $\tau_{\text{pulse}} = 20$ ns; spectral width $\Delta\nu_2 \cong 1 \text{ cm}^{-1}$ for the dye laser). The pump waves are focused by a spherical mirror at an angular separation $\cong 1^\circ$ in the liquid under study, which is held in an open cell (9). The linear polarization of wave \mathbf{E}_1 is sharpened by a calcite wedge (6); wave \mathbf{E}_2 is either linearly polarized (with an angle $\varphi = 60^\circ$ between the unit polarization vectors of waves \mathbf{E}_1 and \mathbf{E}_2) or circularly polarized. A photomultiplier

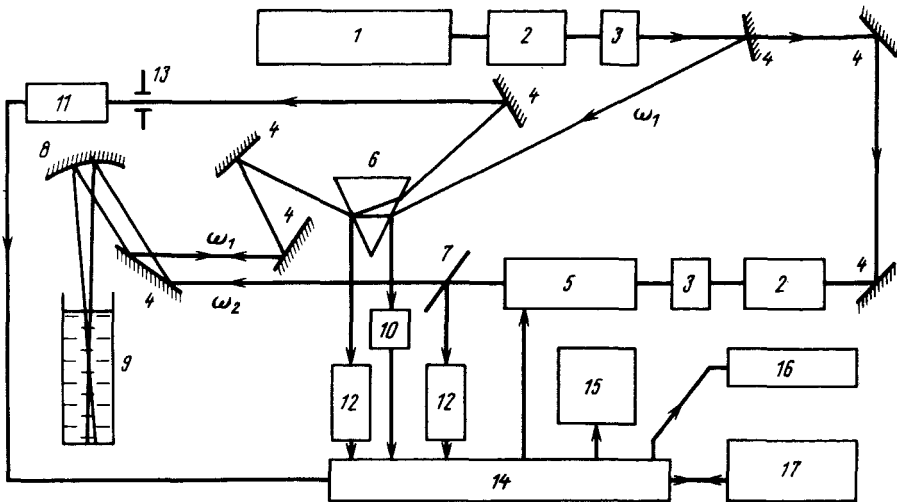


FIG. 1. The experimental apparatus. 1—Single-frequency laser; 2—Nd:YAG amplifiers (the pulse repetition frequency is $f = 10$ Hz); 3—DSDA-crystal second-harmonic oscillators; 4—rotating mirrors; 5—dye laser; 6—calcite wedge; 7—glass plate; 9—cell; 10—photodiode (to trigger the measurement system); 11, 12—FEU-79 photomultiplier; 14—CAMAC bus; 15—graphics display; 16—chart recorder; 17—DVK-2 microcomputer.

(11) measures the intensity of the depolarized part of the wave, E_{1de} , which is deflected by calcite wedge 6 and separated from the incoherent light by a system of diaphragms and mirrors. At the same time, photomultipliers (12) measure the intensities of waves E_{1de} and E_2 in each laser pulse. All the signals are processed by a computer (17), which also controls the frequency scanning of the dye laser and generates curves for a graphics display (15) and a chart recorder (16).

Measurements were taken in ethanol, acetone, distilled water, and sea water. Waves E_1 and E_2 are focused in the liquids through the exposed surface. The wave E_{1de} propagates in the direction opposite E_1 and in the presence of E_2 becomes elliptically polarized. The properties of its elliptic polarization, as in the ordinary optical Kerr effect induced by a Raman resonance,^{1,2} depend on the precision of the tuning of $(\omega_1 - \omega_2)/2\pi c$ to Ω_R , the frequencies of the Raman-active molecular resonances of the medium. The calcite wedge deflects the depolarized part of the wave, E_{1de} . In all cases, the photomultiplier detects the intense signal at the frequency ω_1 , which is attenuated beforehand by a factor of more than 10^6 to avoid damage to the photomultiplier. The measured signal disappears completely when wave E_2 is blocked; i.e., it arises as a result of the four-wave process $\omega_1 = \omega_2 - (\omega_2 - \omega_1)$. The RKRS signal can easily be seen on a sheet of paper placed in front of diaphragm 13; it appears as a bright green spot $\cong 4$ mm in diameter. When the condition $(\omega_1 - \omega_2)/2\pi c \cong \Omega_R$ is satisfied, the brightness of the RKRS signal seen on the paper increases sharply.

3. In the case of a linear polarization of the pump waves, the following expression can be derived^{1,2} for the intensity of the wave E_{1RKRS} , under the condition that the

Raman-scattering line has a Lorentzian shape:

$$I_{1\text{RKRS}} \sim \left| \frac{2}{3} + \frac{(1-\rho) \overline{\chi_{1111}^{(3)R}} / \chi_{1111}^{(3)NR}}{-i-\Delta} \right|^2 I_2^2 I_{1\text{de}}, \quad (1)$$

where ρ is the degree of depolarization of the Raman-scattering line, $\overline{\chi_{1111}^{(3)R}}$ is the peak value of the resonant contribution to the cubic susceptibility $\chi_{1111}^{(3)}$ of the medium, $\chi_{1111}^{(3)}$, $\chi_{1111}^{(3)NR}$ is the nonresonant part of the susceptibility, $\Delta = (\omega_1 - \omega_2 - \Omega_R) / \Gamma$, Γ is the half-width of the Raman-scattering resonance, and $I_{1\text{de}}$ and I_2 are the intensities of waves $E_{1\text{de}}$ and E_2 . In the case of a circularly polarized E_2 wave we have^{1,2}

$$I_{1\text{RKRS}} \sim \left| \frac{(1-3\rho) \overline{\chi_{1111}^{(3)R}} / \chi_{1111}^{(3)NR}}{-i-\Delta} \right|^2 I_2^2 I_1; \quad (2)$$

in other words, the nonresonant pedestal associated with $\chi_{1111}^{(3)NR}$ is suppressed. Figure 2 shows the RKRS spectra of the Raman line of ethanol with a frequency $\Omega_R / 2\pi c = 920 \text{ cm}^{-1}$ in the cases of (a) a linear polarization of the pump waves and (b) a

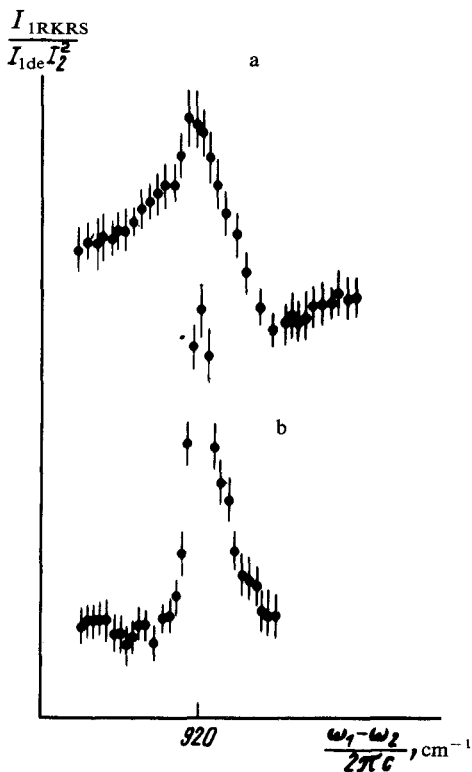


FIG. 2. RKRS spectrum of ethanol (the line $\Omega_R / 2\pi c = 920 \text{ cm}^{-1}$). a—Both pump waves are linearly polarized, $\widehat{e}_1 e_2 = 60^\circ$; b—the wave $E_2(\omega_2)$ is circularly polarized.

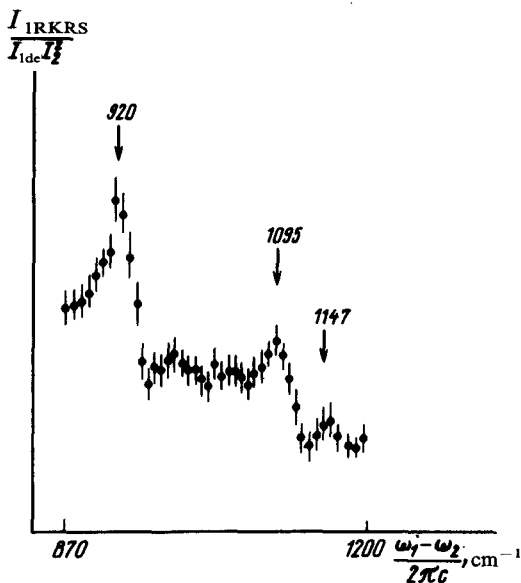


FIG. 3. Panoramic RKRS spectrum of ethanol. The pump waves are linearly polarized. $\widehat{e}_1 \widehat{e}_2 = 60^\circ$.

circular polarization of E_2 . We see that in the remote geometry the spectrum of the optical Kerr effect induced by Raman scattering can be seen clearly; the relative error of the measurements is less than 20% (50 pulses are accumulated at each spectral point). In case b, there is a substantial suppression of $\chi_{1111}^{(3)NR}$. A numerical simulation of the curves in Fig. 2 yields the spectroscopic properties of the 920- cm^{-1} Raman line of ethanol (it must be noted here that $\chi_{1111}^{(3)NR}$ for the RKRS is not the same as $\chi_{1111}^{(3)NR}$ in coherent anti-Stokes spectroscopy because of the contribution made to cubic susceptibility, $\chi_{1111}^{(3)NR}$, of the medium by the slow orientational motions of the molecules²): $\overline{\chi_{1111}^{(3)R}} / \chi_{1111}^{(3)NR} = 0.75 \pm 0.1$; $\Gamma = 7 \pm 1 \text{ cm}^{-1}$.

Figure 3 shows a representative panoramic RKRS spectrum of ethanol over the interval 870–1200 cm^{-1} ; the arrows show the lines with the frequencies $\Omega_R / 2\pi c = 920 \text{ cm}^{-1}$, $\Omega_R / 2\pi c = 1095 \text{ cm}^{-1}$, $\Omega_R / 2\pi c = 1147 \text{ cm}^{-1}$.

In summary, these experiments have demonstrated the possibility of carrying out remote measurements by methods of nonlinear polarization Raman spectroscopy in a collinear geometry of the interacting waves. In this case, all of the well-known advantages of coherent anti-Stokes spectroscopy and other methods of four-photon Raman spectroscopy are extended to remote measurements: the high signal level, the high spectral resolution, the absence of an effect of fluorescence of the medium under study (a particularly important advantage in the probing of natural waters), and the possibility of an interference resolution of the structure of the bands formed by the superposition of many Raman lines. The net result is to open up some wide opportunities for applications of this new method.

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