Electrostrictive and Thermal Stimulated Rayleigh Spectroscopy in Liquids

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(Received 22 June 2001; published 15 November 2001)

We have observed the spectrum of electrostrictive stimulated Rayleigh scattering in a liquid and created a transition to stimulated thermal Rayleigh scattering with the addition of an absorbing liquid. With the proper amount of absorption, the electrostrictive and thermal contributions to the scattering exactly cancel, resulting in no stimulated Rayleigh scattering. An absorption coefficient of 0.000 12 cm^{-1} is sufficient to cancel the electrostrictive Rayleigh scattering in Freon 113.

DOI: 10.1103/PhysRevLett.87.233902 PACS numbers: 42.65.Es, 33.20.Fb, 39.30.+w, 42.50.Vk

Rayleigh scattering involves the scattering of light by nonpropagating entropy or thermal fluctuations. These fluctuations produce spatial variations in refractive index and hence light scattering. When the incident light is sufficiently intense, stimulated Rayleigh scattering occurs.

In this Letter we describe the use of tunable Rayleigh gain spectroscopy in electrostrictive and predominantly absorptive liquids. We show that electrostrictive and thermal effects can cancel each other, resulting in no stimulated Rayleigh scattering, in agreement with theory [see Eq. (1) below] [1]. Complete cancellation of a stimulated scattering process has not been observed previously to our knowledge. Cancellation of stimulated Raman scattering due to Stokes/anti-Stokes coupling has been observed [2], but this cancellation occurs only at a specific phase-matching angle. The combination of electrostrictive and absorptive effects leads to the reduction of the stimulated Brillouin gain over a part of the spectral profile [3], but with a proportional increase in gain over a different portion of the spectral profile.

Two primary mechanisms can produce the coupling between light and medium for stimulated Rayleigh scattering—electrostriction and light absorption. For stimulated electrostrictive Rayleigh scattering, the thermal fluctuations are produced indirectly as a result of the electrostrictive density fluctuations, and the process is relatively weak. In absorptive media, thermal fluctuations are produced directly by absorption of light, leading to much larger gains for stimulated thermal Rayleigh scattering. A third mechanism, the electrocaloric effect, can cause stimulated Rayleigh scattering through direct coupling of the electric field and temperature. This effect is negligible in most circumstances [4].

Stimulated electrostrictive Rayleigh scattering is much more difficult to observe than stimulated thermal Rayleigh scattering [5,6] and stimulated Rayleigh wing scattering [7,8] (scattering by fluctuations in the orientation of anisotropic molecules). Early experiments in gases [9] and liquids [10,11] resulted in spectrally shifted scattered light that was attributed to pure stimulated Rayleigh scattering. Later work using gain spectroscopy resulted in partially resolved peaks from electrostrictive stimulated Rayleigh scattering in a gas [12]. We measured the stimulated Rayleigh peak in a liquid using stimulated gain spectroscopy. The Rayleigh peak is spectrally resolved and isolated from the stimulated Brillouin peak, allowing confirmation that the electrostrictive stimulated Rayleigh scattering matches the anticipated line shape.

In gain spectroscopy, the amplification or gain of the scattered light produced by a strong pump light beam is monitored using a second probe light beam. The spectral variation in gain for the probe beam is given by the imaginary part of a complex Lorentzian function [1]:

$$g_{\mathrm{RL}} = [g^a_{\mathrm{RL}}(\max) - g^e_{\mathrm{RL}}(\max)] \frac{4\nu/\Delta\nu_{\mathrm{RL}}}{1 + (2\nu/\Delta\nu_{\mathrm{RL}})^2}, \tag{1}$$

where $\Delta\nu_{\mathrm{RL}}$ is the spontaneous Rayleigh linewidth, $g^e_{\mathrm{RL}}(\max)$ and $g^a_{\mathrm{RL}}(\max)$ are the maximum values for the electrostrictive and the absorptive gain factors, respectively, and $\nu = \nu_s - \nu_p$ is the difference between the frequencies ν_s of the probe (or scattered) beam and ν_p of the pump beam.

The experimental apparatus used to measure the frequency dependence of the gain factor is illustrated in Fig. 1. Ray trajectories are represented by dotted lines. We use the light from an injection-seeded, homebuilt, single-mode Nd:YAG laser [13] at 1064 nm to provide the pump radiation. We operate this laser at 10 Hz with a full width at half maximum pulse duration of about 29 ns, which results in a Fourier transform limited spectral bandwidth of about 15 MHz. The probe light is provided by a tunable single-mode diode laser (Environmental Optical Sensors, Inc., model 2010) with a linewidth smaller than 300 kHz in 50 ms.

The spatial filters serve to suppress higher order transverse spatial modes. Furthermore, the spatial filter in the probe beam trajectory, together with the two optical isolators, prevents pump light from reaching the resonator of the tunable laser, which would otherwise cause frequency and amplitude fluctuations on the probe beam. Inside the cell, the counterpropagating ($\sim$180° crossing angle) pump and probe beams are overlapped at their focal points to obtain an optimal gain signal. The beam spot sizes at the focus are approximately 385 and 260 μm ($1/e^2$ beam radius) for the pump and probe beams, respectively.

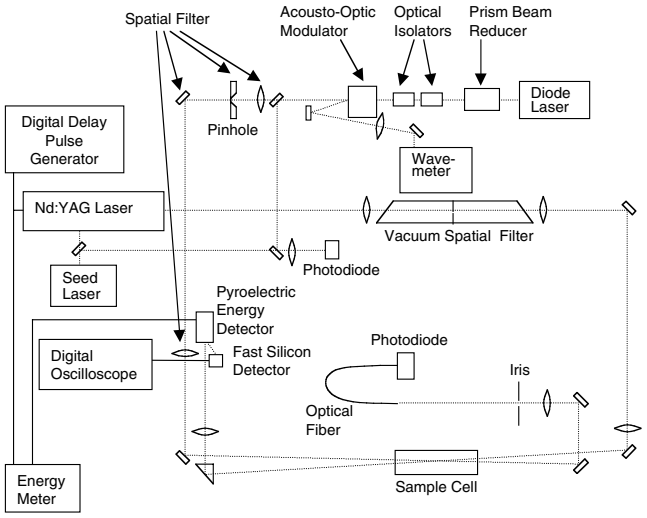

FIG. 1. Experimental apparatus for stimulated Rayleigh gain spectroscopy in liquids.

Detection is performed using an InGaAs photodiode with a transimpedance amplifier. The output signal is split with a bias tee into a high frequency portion, which is the gain signal for the ~29 ns pulse, and a low frequency part, which monitors the probe beam power. The energy of the Nd:YAG beam is measured with a pyroelectric energy detector. The measured gain signals are divided by the probe and pump beam powers to compensate for fluctuations in the laser powers. A fast silicon detector is used to measure the pulse duration of the pump beam. Portions of the seed laser and probe laser are mixed on a second InGaAs photodiode to directly measure the relative frequency between the two lasers for measurements on the Rayleigh peak. For Figs. 4 and 5 below, the probe wavelength was measured using a wave meter.

Because the time constants for Rayleigh scattering are typically longer than the laser pulse width, transient effects are important [14,15]. We eliminate these transient effects by measuring the time-integrated gain signal, a method that was used previously for stimulated Brillouin scattering [16]. Using the transient expressions for stimulated electrostrictive and thermal Rayleigh scattering [17] and following the analysis used for stimulated Brillouin scattering [16], is may be easily shown that the time-integrated gain signal spectrum provides a simple measurement of the convolution of the laser and Rayleigh line shapes.

We used Freon 113 (1,1,2-trichlorotrifluoroethane from Aldrich Chemical Co., 99.8%, <0.005% water) to observe stimulated electrostrictive Rayleigh scattering because it does not absorb light at 1064 nm. Most liquids containing hydrogen atoms have optical absorption at 1064 nm due to overtone or combination vibrational bands.

We used pump beam energies of about 5 mJ in a 30 ns pulse to observe the pure electrostrictive signal in Freon 113. This corresponds to a power of about 10^8 times larger than the ~1 mW of probe beam power available at the sample cell. To enable measurement of spectra linear in the gain coefficient, the gain signals were approximately 1% of the probe beam power. Thus even a small fraction of scattered pump light can completely overwhelm the electrostrictive gain signal. This effect is exacerbated by the fact that the pump and probe beams have nearly identical frequencies in the region of the Rayleigh peak. Thus, a heterodyne signal between the probe beam and scattered pump light is also present at the detector used to measure the gain signal. This heterodyne process provides an effective amplification of the scattered pump light since the detected heterodyne signal is proportional to the square root of the product of the pump and probe powers. Thus the 1% gain signal is only as big as the heterodyne signal from a scattered pump light power of 10^{-4} of the probe beam power, or 10^{-12} of the pump beam power.

The influence of scattered pump light was reduced by using very clean windows and Freon, by tilting the sample cell to direct reflections from the windows away from the detector, blocking all stray reflections and other scattered light with black screens, making the pump and probe beams of approximately the same diameter, spatially filtering the pump and probe beams to remove higher order transverse spatial modes, and spatially filtering the probe beam before the detector using an iris, lens, and multimode fiber. However, we could not reduce the scattered light below the level produced by spontaneous Rayleigh scattering of the Freon in the volume determined by the overlap between the pump and probe beams. This spontaneous Rayleigh scattering is the dominant noise source for our measurements. We reduced the influence of the heterodyne signal from spontaneous Rayleigh scattering by averaging the measured gain over many laser shots (typically 60 shots for the stimulated Rayleigh measurements). Because the pump and probe beams are not phase locked, the heterodyne signal should average to zero. We could not use the Nd:YAG laser to amplify the probe beam before the liquid cell because that would limit the gain observation time sufficiently to introduce transient effects, which would distort the line shapes.

The solid curve at the top of Fig. 2 shows the measured electrostrictive Rayleigh gain signal in Freon 113. The width of the Rayleigh peak is broadened considerably by the spectral linewidth of the pulse laser. The dashed curve shows the result of fitting the line shape of Eq. (1), convolved with the Gaussian spectral profile of the pump laser. The linewidth of the Rayleigh peak, calculated [1] using known properties of the Freon [18], is 4 MHz. The linewidth of the pump laser was fixed at the Fourier transform limited width determined from the pulse duration (15 MHz). The contribution of the probe laser linewidth is negligible. Measurements were performed at a 5 Hz repetition rate to eliminate contributions of the 10 Hz frequency dither used to lock the Nd:YAG laser to the seed laser. The fit is good considering the only free parameter is the peak height.

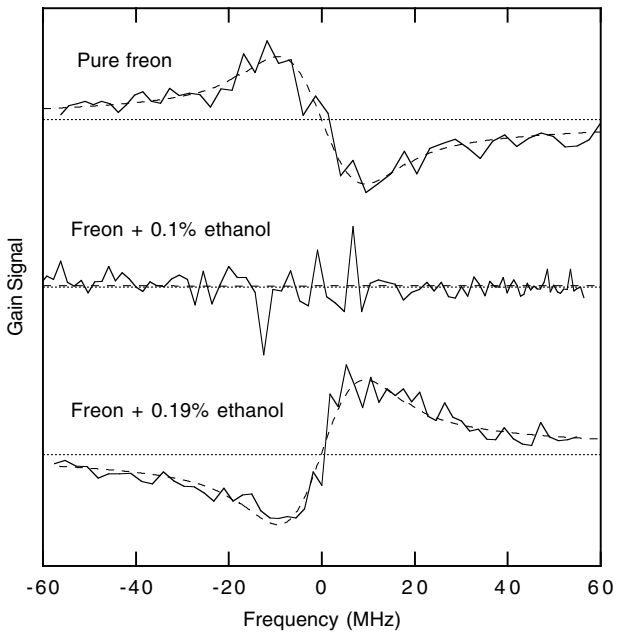

FIG. 2. Measured stimulated Rayleigh gain signal (solid curves) and fitted profile (dashed curves) in pure Freon 113 (top), Freon with 0.1% ethanol (middle), and Freon with 0.19% ethanol (bottom) as a function of the frequency difference between the probe and pump lasers.

To produce some absorption in the Freon, we used ethanol, which mixes with Freon and has moderate absorption at 1064 nm. The Freon and ethanol both comprise a pair of single-bonded carbon atoms, but differ in the atoms surrounding the carbons. After adding 0.10% (volume percentage) of ethanol, the electrostrictive and absorptive gains have the same value and cancel each other out [see Eq. (1)]. The curve measured for this condition is shown in the middle of Fig. 2. The Rayleigh gain signal (solid curve) shows no Rayleigh peak, and the curve fitting (dashed curve) produces a flat line. The small variations in the measured gain signal are due to the heterodyne signal from scattered pump light. After doubling the amount of ethanol in Freon 113, we obtain a gain signal that has about the same height as in pure Freon, but is inverted. The measured gain signal for 0.19% of ethanol is shown at the bottom of Fig. 2 (solid curve); the dashed curve is the fitted profile.

We measured the absorption coefficient for different volume percentages of ethanol in Freon. The absorption coefficient displays a linear dependence on the percentage of ethanol, rising from zero in pure Freon to 0.117 cm^{-1} for pure ethanol. This measurement shows that a very small absorption coefficient (0.000 12 cm^{-1}) is sufficient to cause the cancellation of the electrostrictive Rayleigh scattering at 0.1% ethanol.

For small amounts of ethanol in Freon the physical properties (apart from the absorption) are changed only little. Theory [1] predicts a linear growth of the maximum absorptive gain factor $g^a_{\mathrm{RL}}(\mathrm{max})$ with the absorption coefficient, whereas the maximum electrostrictive gain factor $g^e_{\mathrm{RL}}(\mathrm{max})$ does not depend on the absorption. Measurements of the gain signal were performed for various amounts of ethanol in Freon, and the height of the Rayleigh peak was determined from fits as in Fig. 2. The results are shown in Fig. 3 for small percentages of ethanol. We display peak height rather than peak area as the area of the Rayleigh peak is infinite [Eq. (1) behaves as $1/\nu$ for large ν]. As expected, the height displays a linear dependence on the absorption coefficient [or $g^e_{\mathrm{RL}}(\mathrm{max}) - g^a_{\mathrm{RL}}(\mathrm{max})$]. The height has a negative value for $g^a_{\mathrm{RL}}(\mathrm{max}) = 0$ in pure Freon, becomes zero for $g^a_{\mathrm{RL}}(\mathrm{max}) = g^e_{\mathrm{RL}}(\mathrm{max})$, corresponding to 0.1% of ethanol, and has positive values for $g^a_{\mathrm{RL}}(\mathrm{max}) > g^e_{\mathrm{RL}}(\mathrm{max})$.

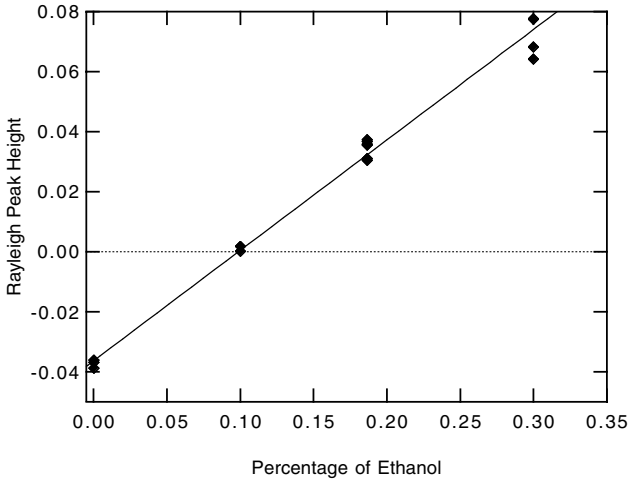

FIG. 3. Measured heights of the fitted Rayleigh peak in a mixture of Freon 113 and ethanol.

When the probe laser is scanned over a larger frequency range, stimulated Brillouin scattering is observed. The

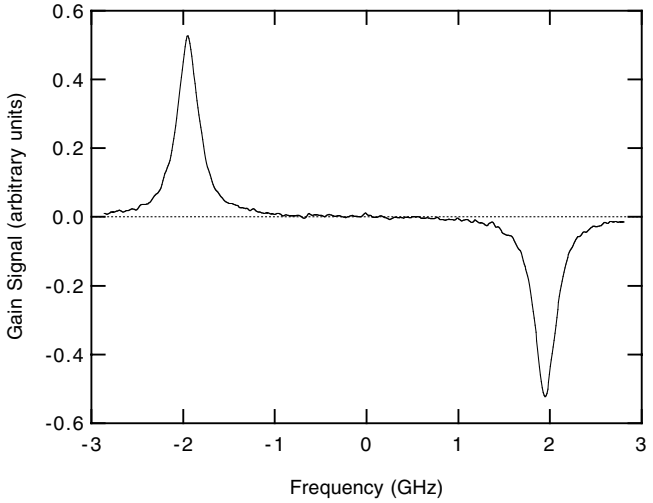

FIG. 4. Measured stimulated Brillouin gain signal in pure Freon 113 as a function of the frequency difference between the probe and pump lasers. The stimulated Rayleigh gain signal of Fig. 2 is too small to be seen in this figure.

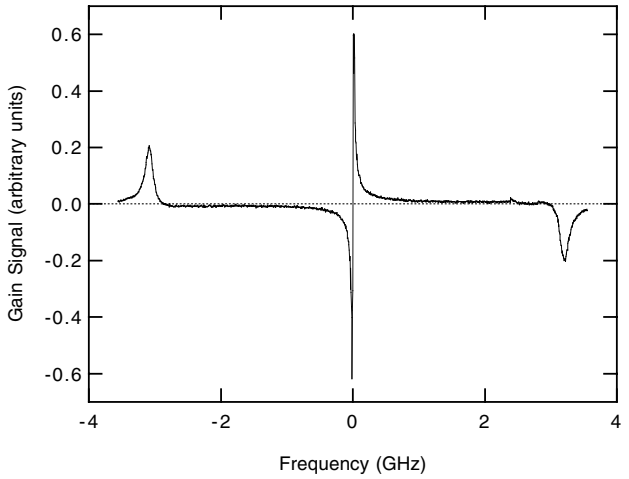

FIG. 5. Measured stimulated Brillouin gain signal in ethanol as a function of the frequency difference between the probe and pump lasers. Absorption produces a large stimulated thermal Rayleigh peak and stimulated thermal Brillouin scattering, which causes asymmetry of the stimulated Brillouin peaks.

shapes of the stimulated electrostrictive and thermal Brillouin scattering peaks are described by the real and imaginary parts of the complex Lorentzian profile, respectively [1]. Only stimulated electrostrictive Brillouin scattering is observed in pure Freon 113 (Fig. 4). Gain and loss peaks are observed at the left and right of Fig. 4, respectively. The gain and loss peaks correspond to the transfer of energy from the pump laser to the probe laser and vice versa. The stimulated electrostrictive Rayleigh scattering, which is typically about 100 times smaller than the stimulated electrostrictive Brillouin scattering, is too small to be seen in Fig. 4.

The modest absorption coefficient of ethanol at 1064 nm ($0.12\ \mathrm{cm}^{-1}$) is sufficient to cause very large stimulated thermal Rayleigh scattering in ethanol, which is now much larger than the stimulated Brillouin scattering peak (Fig. 5). Stimulated thermal Brillouin scattering, which, like the Rayleigh peak, is described by the imaginary part of the complex Lorentzian, causes asymmetry of the Brillouin peaks in ethanol.

We reported an experimental investigation of stimulated Rayleigh scattering in liquids by tunable Rayleigh gain spectroscopy. We observed the electrostrictive Rayleigh peak in a liquid (Freon 113). By adding small amounts of ethanol, we increased the absorption coefficient to the point where electrostrictive and absorptive gain cancel. For a further increase of the absorption, the peak inverts from its original form. In agreement with theory, a linear relationship between the height of the peak and the absorption coefficient was observed.

This work was supported by the Air Force Office of Scientific Research under Contracts No. F49620-97-C-0002 and No. F49620-01-C-0020. E. M. J. was supported by the Research Experiences for Undergraduates Program of the National Science Foundation.

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