Coherent double-resonance effects were observed in the form of a modulation of the emission from the $J=0$ to 1 transition subsequent to a 90° pulse, in the presence of a cw signal at the $J=1$ to 2 resonance (24.3 Gc/sec). The modulation is complete (Fig. 2) when the signal is exactly at resonance, but decreases in depth while increasing in frequency with increasing frequency deviation. This effect can be treated simply by assuming that the $90°\ J=0$ to 1 pulse has left $a_0=a_1=1/\sqrt{2}$. The signal at ω_{12} will then modulate a_1 in accordance with Eq. (2a) as applied to the $J=1$ to 2 transition. The radiation at ω_{10} is proportional to a_1, and its time dependence can be put in the form

$$(1+\delta_{12}/\eta_{12})\cos(\omega_{10}-\delta_{12}+\eta_{12})t + (1-\delta_{12}/\eta_{12})\cos(\omega_{10}-\delta_{12}-\eta_{12})t, \quad (6)$$

where Ω_{12} is the transition rate for $J=1$ to 2, and $\delta_{12}=\omega_{12}-(E_2-E_1)/\hbar$. For ω_{12} at resonance, $\delta_{12}=0$ and the modulation frequency is exactly Ω_{12}. This method therefore provides a direct measurement of the induced transition probability, and hence the line strength. Equation (6) represents the beating of two slightly displaced signals. The components are identical with those observed in absorption double-resonance measurements.[4]

Molecular echoes from the 0 to 1 transition were observed by using 0.1-μsec pulses separated by time interval τ of the order 1 μsec. The free ringing signal [Fig. 1(a)] must be quenched for echoes to be observed. The nonuniform Stark field used to accomplish this splits the resonance line over a frequency range of several megacycles, causing a loss of coherence in the emission in times short relative to a collision time. For these conditions, echoes were observed exhibiting a rate of decay twice that of the unmodified emission signal. We could find no evidence of a three-pulse echo[1] indicating that each collision redistributes the energy as well as randomizing the phase of the radiating molecules.

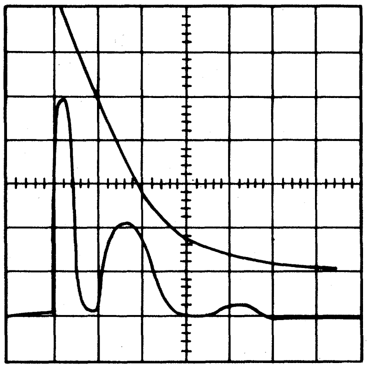


FIG. 2. Coherent emission at $J=0$ to 1 resonance of OCS. Top trace: without signal at $J=1$ to 2 resonance; bottom trace: with signal at $J=1$ to 2 resonance.

---

†Work supported in part by Lockheed Independent Research Fund and U. S. Office of Naval Research.

[1] E. L. Hahn, Phys. Rev. 80, 580 (1950).

[2] R. H. Dicke and R. H. Romer, Rev. Sci. Instr. 26, 915 (1955). In a second paper, R. H. Romer and R. H. Dicke, Phys. Rev. 99, 532 (1955), report the observation of very narrow band components, less than 1 cps of the NH_3 emission at 23.87 Gc/sec. We have found no other reports of the observation of emission and none which use the information contained in the full bandwidth of the relaxation.

[3] H. Feeny, H. Lackner, P. Moser, and W. V. Smith, J. Chem. Phys. 22, 79 (1954).

[4] A. P. Cox, G. W. Flynn, and E. B. Wilson, J. Chem. Phys. 42, 3094 (1965).

STIMULATED RAYLEIGH SCATTERING*

C. W. Cho,† N. D. Foltz, D. H. Rank, and T. A. Wiggins
Department of Physics, Pennsylvania State University, University Park, Pennsylvania

(Received 9 December 1966)

In 1940 Gross observed a broadening of the Rayleigh-scattered light from liquids.[1,2] He attributed this to the finite time required to produce thermal relaxation, the time required being expressed as $\tau=4\pi\eta a^3/kT$, the Debye relaxation time. Here η is the viscosity of the liquid, a is the radius of the liquid molecule, k is the Boltzmann constant, and T is the absolute temperature. A broadening on the Stokes side of a giant-pulse laser line was recently observed by Mash, Morozov, Starunov, and Fabelinskii in certain liquids.[3] They have termed this the stimulated Rayleigh wing and have indicated that the maximum of intensity in this feature should occur at a frequency shift from the laser line of $\Delta\nu$ (in wave numbers), where $2\pi c(\Delta\nu)(\tau)=1$ and τ is the characteristic reorientation time of the liquid. However, it is difficult to determine from their published spectra whether they have observed a true Rayleigh wing or unresolved lines attributable to optical mixing.[4] The phenomenon of a stimulated Rayleigh wing has been discussed by Bloembergen and Lallemand.[5] They have deduced expressions for the nonlinear polarization using a characteristic time which is one-third that of Debye. Bloembergen and Lallemand[5] have observed a broadening of the laser line which they attribute to the stimulated Rayleigh effect. Lallemand[6] has observed the effect of a change in temperature on the width of the stimulated Raman lines in several liquids.

In connection with some observations of optical mixing in liquids, we have observed a sharp line on the low-frequency side of the laser line. For the reasons given below, we believe this to be the stimulated Rayleigh line.

Observations were made using a high-resolution grating spectrograph of resolving power in excess of 300 000 and with reciprocal dispersion of 4 cm^{-1}/cm on the photographic plate. The light from a single-mode giant-pulse ruby laser of power up to 40 MW with a linewidth of 0.025 cm^{-1} and pulse duration of about 10 nsec was focused by a 10-cm focal-length lens into a 10-cm cell containing nitrobenzene or *m*-nitrotoluene. The light transmitted by the cell was focused on the slit of the spectrograph. A polarizer and a quarter-wave plate were inserted between the laser and the focusing lens to prevent reinitiation of laser action in the ruby due to the reflected Brillouin-scattered light.[7] This reduced the possibility of attenuation of the laser energy due to optical mixing.[4]

Figure 1 shows reproductions of the spectra obtained for three temperatures. The line situated between the laser line, which is on the left in each photograph, and the stimulated Brillouin line, the dark line on the right side of each spectrum, is very sharp and has different positions for different temperatures. The frequency shift from the laser line is smaller for lower temperatures.

It is quite clear that this line results from a stimulated effect. It appears only for incident power in excess of 25 MW and the line is very sharp indicating gain narrowing.

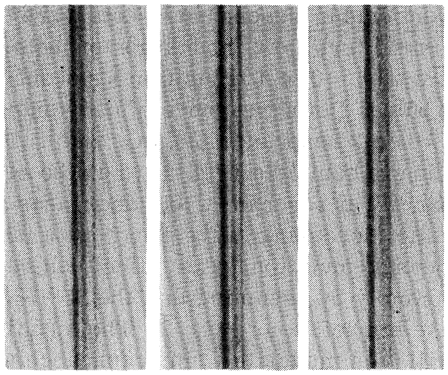

(a) (b) (c)

FIG. 1. Stimulated Rayleigh "Stokes" lines in nitrobenzene at three temperatures: (a), 12°C; (b), 16°C; (c), 31°C. The line at the left in each spectrum is the incident laser line; the second, the stimulated Rayleigh line; the third, the stimulated Brillouin line. The fourth component, which is weak, is at the Brillouin shift away from the stimulated Rayleigh line.

The measured frequency shifts of the stimulated Rayleigh components are indicated in Table I. Also given are the viscosities, the relaxation time and molecular radius computed from the viscosity and measured frequency shift. The constancy of the molecular radius as shown in the last column over a range of more than 100°K indicates the correctness of the interpretation given the observed phenomenon. In addition, the relaxation time of 5×10^{-11} sec measured by Starunov, Tiganov, and Fa-

Table I. Observed frequency shifts of stimulated Rayleigh lines in two liquids at several temperatures. The relaxation time, viscosity, and molecular radius estimated from the relaxation time are also given. The estimated error in measurement of $\Delta\nu$ is ±0.002 cm^{-1}.

T (°K)	$\Delta\nu$ (cm^{-1})	$10^{11}\tau$ (sec)	η (cP)	a (Å)
		nitrobenzene		
285	0.092	5.76	2.40	2.83
285	0.094	5.64	2.40	2.81
286	0.094	5.64	2.35	2.83
286	0.096	5.53	2.35	2.81
288	0.101	5.25	2.26	2.81
290	0.102	5.20	2.17	2.84
293	0.112	4.74	2.01	2.84
299	0.128	4.14	1.80	2.83
304	0.140	3.79	1.65	2.84
390	0.406	1.31	0.60	3.02
		m-nitrotoluene		
299	0.088	6.03	2.08	3.06

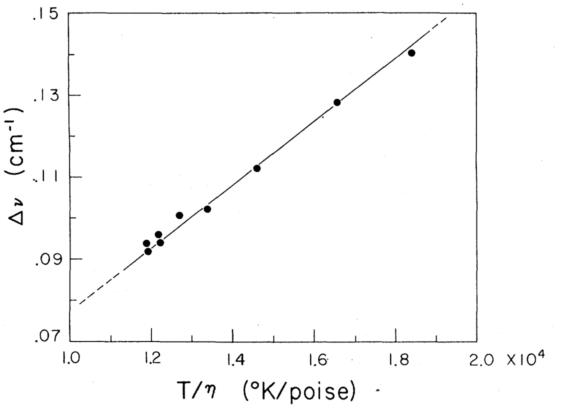


FIG. 2. Plot of the frequency shift of the stimulated Rayleigh line in nitrobenzene as a function of the ratio T/η, where η is the viscosity for the range $T = 285$ to 304°K.

belinskii[8] in nitrobenzene is in agreement with the present result.

To show the dependence of the frequency shift on temperature and viscosity of the liquid, the frequency shifts for nitrobenzene are plotted in Fig. 2 as a function of T/η. The straight line in the figure is drawn through the points so as to have zero intercept at $T/\eta = 0$. The slope of the line was measured to be 7.73×10^{-6} cm^{-1} P/°K. Using the relaxation time given above, the slope would be $3k/8\pi^2ca^3$. From the measured slope, the molecular radius is $2.8_3\times10^{-8}$ cm. This may be compared with the radius of 3.4×10^{-8} cm estimated from the molecular volume.

Table I also gives the results of measurement in *m*-nitrotoluene indicating similar agreement.

In some instances it was possible to observe a weak fourth component. The frequency shift of this component corresponds to that of a stimulated Brillouin shift from the frequency of the stimulated Rayleigh line.

It is apparent from the sharpness of the lines observed, from the requirement on thresholds, from the dependence of the frequency shift on temperature and viscosity, and from the reasonable value of molecular radius deduced that the phenomenon observed is that of stimulated Rayleigh scattering.

The authors wish to thank Dr. A. H. Guenther of the Weapons Laboratory, Kirtland Air Force Base, for the use of the giant-pulse laser system and Dr. R. V. Wick, now of that laboratory, who assisted in the first observation of this effect.

---

*This work was supported by the U. S. Office of Naval Research and the National Science Foundation.

†On sabbatical leave from Memorial University of Newfoundland, St. John's, Newfoundland, Canada.

[1] E. F. Gross, Compt. Rend. Acad. Bulgare 28, 786 (1940).

[2] J. Frenkel, Kinetic Theory of Liquids (Dover Publications, New York, 1955).

[3] D. I. Mash, V. V. Morozov, V. S. Starunov, and I. L. Fabelinskii, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 2, 41 (1965) [translation: JETP Letters 2, 25 (1965)].

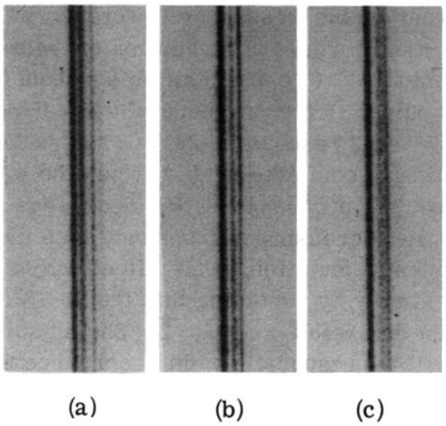
[4] R. V. Wick, D. H. Rank, and T. A. Wiggins, Phys. Rev. Letters 17, 466 (1966).

[5] N. Bloembergen and P. Lallemand, Phys. Rev. Letters 16, 81 (1966).

[6] P. Lallemand, Appl. Phys. Letters 8, 276 (1966).

[7] T. A. Wiggins, R. V. Wick, D. H. Rank, and A. H. Guenther, Appl. Opt. 4, 1203 (1965).

[8] V. S. Starunov, E. V. Tiganov, and I. L. Fabelinskii, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 4, 262 (1966) [translation: JETP Letters 4, 176 (1966)].



(a) (b) (c)

FIG. 1. Stimulated Rayleigh "Stokes" lines in nitrobenzene at three temperatures: (a), 12°C; (b), 16°C; (c), 31°C. The line at the left in each spectrum is the incident laser line; the second, the stimulated Rayleigh line; the third, the stimulated Brillouin line. The fourth component, which is weak, is at the Brillouin shift away from the stimulated Rayleigh line.