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Brillouin Scattering in Liquids at 4880Å

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Abstract—An argon ion laser has been used as a source of 4880Å radiation to study Brillouin scattering in liquids. Hypersonic velocities were measured in benzene, carbon disulfide, carbon tetrachloride, chloroform, methylene chloride, methylene iodide, toluene, and water at a scattering angle of 89° 45′. The width of the Brillouin line for monochromatic excitation was found to be approximately 0.007 cm^{-1} in toluene and 0.011 cm^{-1} in methylene chloride. However, line broadening in benzene, carbon disulfide, chloroform, and methylene chloride was found to be less than 0.002 cm^{-1}. Depolarization factors of the Brillouin lines were measured in carbon disulfide, benzene, and toluene. The wing structure of the Rayleigh lines and depolarization of the Rayleigh wings were also measured in benzene, carbon disulfide, and toluene. Widths of the Rayleigh wings were approximately 6.8 cm^{-1} in benzene, 6.7 cm^{-1} in carbon disulfide, and 8.5 cm^{-1} in toluene. From measurements of Brillouin scattering intensity, approximate values of the electrostrictive coupling constants of the other seven liquids were calculated relative to those of carbon disulfide.

INTRODUCTION

BEFORE the advent of the laser, Brillouin spectra were obtained with either a Hg or a Zn light source. Recently several groups have demonstrated the suitability of the CW He–Ne laser as a source of illumination for obtaining linear Brillouin spectra in liquids and solids [1]–[5], and stimulated Brillouin scattering has been obtained with the Q-switched ruby laser [6]–[12]. The high-intensity, narrow-beam divergence, and monochromaticity of the laser make it an excellent source for such work. Furthermore, if the shape of the laser excitation line is known, broadening of the Brillouin components can be measured [2], [3], [5] and, hence, phonon lifetimes can be calculated. The CW argon-ion (Ar^+) laser appears especially suited to linear Brillouin experiments which involve the measurement of line shapes, since relatively high intensities of the 4880Å line may be obtained in a single mode. This is in addition to the order of magnitude advantage of the Ar^+ laser over the He–Ne laser provided by the ν^4 dependence of the scattering intensity and by the greater sensitivity of photomultiplier tubes and films in the region of 4880Å.

Another slight advantage of the spectral region of the Ar^+ laser is that the Brillouin shift is one third greater at 4880Å than at 6328Å. This allows velocity of sound measurements to be extended to higher phonon frequencies.

The present paper reports the results of several Brillouin and Rayleigh scattering experiments performed in liquids using a CW Ar^+ laser with a power output of approximately 0.07 mW. The spectral advantages of the Ar^+ laser are great enough that this rather modest power is sufficient to perform such experiments.

EXPERIMENTAL APPARATUS

The laser consisted of a 14-cm by 0.12-cm bore, water cooled, quartz discharge tube in a cavity 30 cm long. The laser cavity had mirrors with a 120-cm radius of curvature. The threshold current was 0.8 amperes when 0.5-mm Hg of Ar was used as the active medium.

The experimental arrangement was similar to that of Chiao and Stoicheff [2] for the hypersonic velocity measurements. The scattered light was observed at 89°45′ through a pressure scanning, Fabry–Perot interferometer. A spacer of 8.501 mm was used to resolve the Brillouin components from the central Rayleigh scattered line, and spacers of 8.501 mm, 16.00 mm, and 42.00 mm were used to observe line broadening. The measured finesse of the interferometer was approximately 15. A photomultiplier detection system having a time constant of 0.5 second was used in conjunction with a grating monochromator.

For measurement of the Rayleigh wings, the Fabry–Perot interferometer was eliminated from the above system.

All experimental samples were of either spectroscopic or reagent grade purity. Those of reagent grade purity were filtered through 10-micrometer fritted disks before observing the Brillouin spectra.

HYPERSONIC VELOCITY MEASUREMENTS

The shift in frequency of a photon scattered by a phonon, the Brillouin shift, is given by [13]

$$\Delta\nu = \nu_s = (2nv/\lambda_0)\sin(\theta/2) \tag{1}$$

where ν_s, the frequency of the phonon, is the same as the Brillouin shift, n is the index of refraction of the medium, v is the velocity of sound in the medium, Θ is the angle of observation of the scattered light with respect to the incident beam, and λ_0 is the wavelength of the incident radiation. The velocity of sound at a frequency equal to $\Delta\nu$, in the Gc/s range for liquids, can therefore be obtained by measuring the Brillouin shift. The hypersonic velocity observed in eight liquids is shown in the fourth column of Table I. The fifth column of this table gives ultrasonic velocities taken from the literature. Values of hypersonic velocity for these liquids exist in the literature [1]–[4], but a direct comparison is misleading because of the temperature and frequency dependence of the velocity. Assuming small dispersion and only weak temperature dependence,

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TABLE I
HYPERSONIC VELOCITY AND FREQUENCY OF PHONONS OBTAINED FROM BRILLOUIN SHIFTS

Liquid	Room Temperature °C	Phonon frequency at 89°45′ scattering angle (10^9 c/s)	Hypersonic velocity (m/s)	Ultrasonic velocity (m/s)
Benzene	25.0	6.75	1546 ± 13	1304*
Carbon disulfide	25.0	5.93	1236 ± 23	1158**
Carbon tetrachloride	24.7	4.70	986 ± 42	923*
Chloroform	24.1	4.60	1112 ± 6	987*
Methylene chloride	24.1	4.33	1028 ± 17	1077*
Methylene iodide	24.1	5.07	986 ± 10	965*
Toluene	24.7	5.85	1354 ± 19	1324**
Water	24.7	5.66	1466 ± 37	1492**

* From R. T. Lagemann, D. R. McMillan, Jr., and W. E. Woolf, "Temperature variation of ultrasonic velocity in liquids," *J. Chem. Phys.*, vol. 17, pp. 369–373, April 1949. These values have been extrapolated so that they are at the same temperature as the values in column two.

** From Herzfeld [24], p. 362. These values were not obtained at the same temperatures as the present measurements.

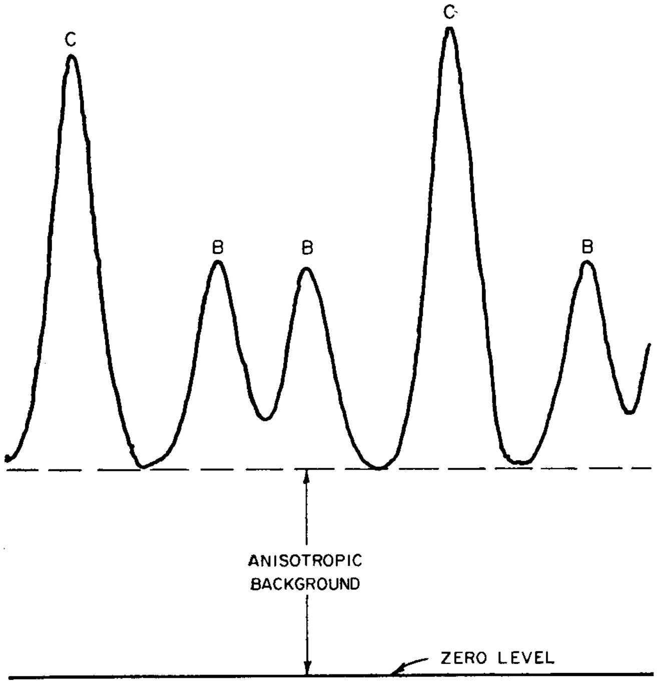

Fig. 1. Brillouin scattering in benzene with 8.501-mm etalon. "C" denotes the central unshifted line; "B" denotes the Brillouin components.

our velocities agree well with those of Benedek et al. [1], Chiao and Stoicheff [2], and Rank et al. [4] in cases where a comparison is possible.

The standard deviation in the measurements of the hypersonic velocity varies from less than 1 percent for chloroform to more than 4 percent for carbon tetrachloride. These figures are calculated from the results of several measurements of Brillouin shifts, and do not include possible error in the measurement of the scattering angle. This latter error was estimated to be approximately ±15′. The precision of measurement of the Brillouin shifts was mainly limited by nonlinearities in the scan and uncertainties in the measurement of fringe centers. Further contributions to the error could have resulted from drifting of the laser frequency, since no special stabilization was provided. A typical result is shown in Fig. 1. The linewidth in this illustration is mainly instrumental.

LINE BROADENING

Broadening of the Brillouin components arises from "damping" of thermal phonons, and is intimately connected with the viscosity coefficients of the medium. Assuming the predominance of a single relaxation mechanism for thermal phonons in the liquids of these experiments, the intensity of Brillouin scattered radiation for a monochromatic exciting line is expected to be of the form

$$I(\omega) = (I_0\Gamma/2\pi)/[(\omega - \omega_0)^2 + (\Gamma/2)^2] \qquad (2)$$

where I is the intensity at angular frequency ω, I_0 is the total intensity, and ω_0 is the angular frequency at the center of the line. The width of this Lorentzian line at half maximum Γ is a measure of the damping of the hypersonic phonons. From this figure, a relaxation time τ, in this case equivalent to the phonon lifetime, can be obtained immediately, since $\tau = 1/\Gamma$.

Broadening of the Brillouin line was observed in the present case by using higher resolving power of the Fabry–Perot interferometer. With 8.501-mm and 16.00-mm etalons, the Brillouin line of toluene for monochromatic excitation was found to be approximately 0.007 cm^{-1} wide at half maximum. The corresponding measurement for methylene chloride was approximately 0.011 cm^{-1}. The recorded fringe pattern for toluene is shown in Fig. 2. Brillouin line broadening was detected in several other liquids, but the traces were rather noisy, and these were not measured.

To arrive at a figure for the Brillouin linewidth, it is necessary to make corrections for the width of the laser line, the effect of an approximately 3° angular aperture of observation, and the "instrumental" linewidth of the rest of the optical detection system. Under the assumption that all the lines are Lorentzian, the observed linewidth is the sum of the widths of the separate contributions. This is a good approximation if the laser is operated in a single mode and if the angular aperture is small, but it is less precise for multimode laser operation. If one makes this assumption and further assumes no broadening of the center component of the Brillouin triplet (composed of Rayleigh and Tyndall scattered light), then it can be shown that the true width of the Brillouin line for monochromatic excitation is merely the observed width of the Brillouin line minus the sum of the observed width of the central component and the width of the angular aperture. The angular aperture appears because the Brillouin line is broadened by this effect, but the center component is not. This method

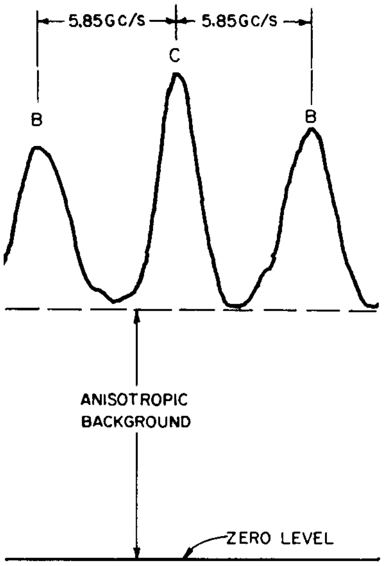

Fig. 2. Line broadening in toluene. The Rayleigh linewidth is instrumental.

was used to arrive at linewidths even though the laser was in multimode operation during the toluene measurement. The linewidth quoted for toluene is therefore in error by perhaps 50 percent. The linewidth for methylene chloride was obtained using single-mode laser operation at 0.016 mW and is, therefore, more accurate.

From the Brillouin linewidths the lifetimes of the phonons responsible for Brillouin scattering at 89°45′ in toluene and methylene chloride are calculated to be approximately 7.6×10^{-10} seconds and 4.8×10^{-10} seconds, respectively.

Polarization Effects

Light scattering in liquids which arises from three causes is considered in the present experiments: 1) pressure waves propagating at the speed of sound scatter light into the two Brillouin components, 2) entropy fluctuations produce the Rayleigh components, 3) optical anisotropy of the molecules produce a broad background centered about the Rayleigh line. Using a method similar to Cummins and Gammon [5], depolarization factors for each of the above scattering phenomena have been measured in three highly anisotropic liquids: carbon disulfide, benzene, and toluene. A polarization analyzer was placed between the liquid scatterer and the interferometer so that it passed light whose electric vector was perpendicular to the plane of scattering, parallel to the plane of scattering, and the analyzer was then removed. These data are identified by the subscripts $\perp$, $||$, and T, respectively. For incident light polarized perpendicular to the scattering plane, the ratio of the scattered light intensity polarized in the plane of scattering to that polarized perpendicular to this plane is the depolarization factor $\rho_\perp = I_{||}/I_\perp$. At the center of the Brillouin line there were no indications of Brillouin components in the $||$ direction greater than 3 percent of the $\perp$ component in toluene, 2 percent of the $\perp$ component in CS_2, and 1 percent of the $\perp$ component in benzene. Fig. 3 shows results for CS_2.

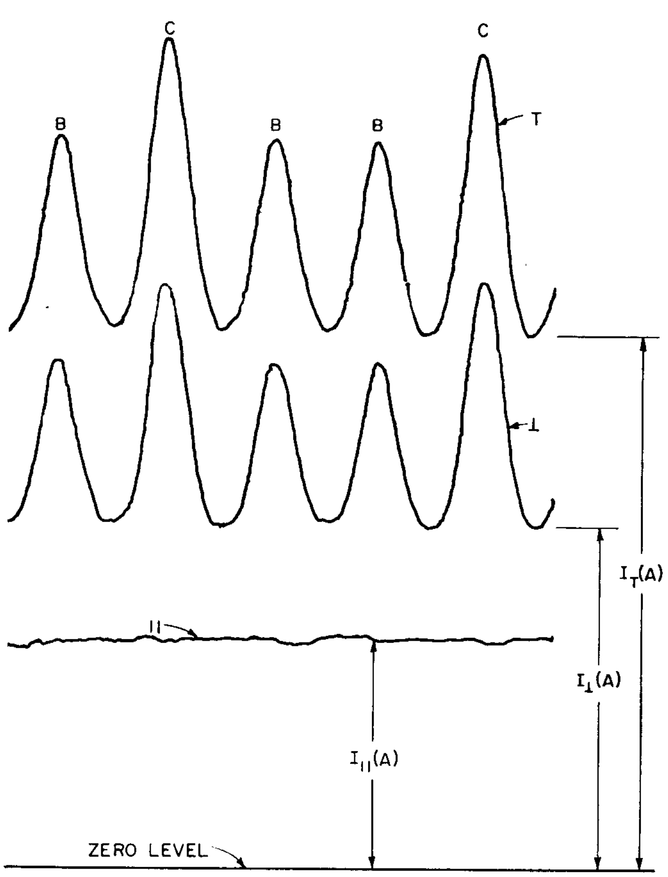

Fig. 3. Superimposed spectra of CS_2. T = no analyzer, $\perp$ = analyzer perpendicular to scattering plane, $||$ = analyzer parallel to scattering plane. Incident light was polarized $\perp$. In order to allow comparison of intensities the traces have been normalized to the same base line.

The depolarization factor for incident unpolarized light ρ_u is more commonly reported than ρ_v. The two are related by

$$\rho_u = 2\rho_\perp/(1 + \rho_\perp). \tag{3}$$

For the Brillouin components, therefore, it is found that $\rho_{u(B)} \leq 0.06$ for toluene, ≤ 0.04 for CS_2, and ≤ 0.02 for benzene.

Depolarization at the center of the Rayleigh line was also measured for these liquids in the same way. The results were $\rho_{u(R)} \leq 0.06$ for toluene, ≤ 0.04 for CS_2, and ≤ 0.06 for benzene. A horizontal Rayleigh component was observed in benzene which was about 3 percent of the vertical Rayleigh component, but it was thought to be caused by Tyndall scattering.

The scattering from anisotropic fluctuations gives rise to a broad background under the Rayleigh and Brillouin spectra that is also depolarized to some degree. This will be treated more fully in the section on Rayleigh wings, but at this point, in Table II, measurements of the depolarization factors are shown for light scattered by optical anisotropy, $\rho_{\perp(A)}$ and $\rho_{u(A)}$. These determi-

TABLE II

Depolarization Factors for Light Scattered by Optical Anisotropy and by Brillouin Processes.*

Liquid	$\rho_{\perp(A)}$	$\rho_{u(A)}$	$\rho_{\perp(A+B)}$	$\rho_{u(A+B)}$
Carbon disulfide	0.69	0.81	0.39	0.56
Benzene	0.58	0.73	0.23	0.37
Toluene	0.54	0.70	0.23	0.37

* Depolarization was measured at the center of the Brillouin line in each case.

nations were made by comparing ordinates at the center of the Brillouin lines. The results agree within 10 percent with the results of Cummins and Gammon [5] for benzene.

For historical reasons one sometimes sees depolarization factors reported for light which is scattered by both Brillouin and anisotropic processes. Table II gives these depolarization factors for incident light polarized ⊥ to the scattering plane $\rho_{\perp(A+B)}$ and for unpolarized incident light $\rho_{u(A+B)}$, obtained from measurement of the appropriate intensities at the center of the Brillouin line. Results of Cummins and Gammon [5] for benzene are not comparable since they have integrated over a frequency range of the order of the Brillouin linewidth. All of the results in this section were corrected for polarization effects of the detection system.

Rayleigh Wings

The background below the Brillouin spectra as seen in Figs. 1–3 is due to fluctuations in the orientation of the molecules in the liquid (optical anisotropy), and may be looked upon as highly damped rotational Raman scattering. This background shows itself under less resolution as wings on the Rayleigh lines, and has been observed in benzene by several authors [14]–[17]. Birus has reported seeing such broadening in water, ethyl alcohol, and toluene [16]. Brandmüller has written a lengthy paper on the Rayleigh wing, and concluded from his data on many molecules that the intensity of scattering from liquids is proportional to the optical anisotropy of the molecule [17]. Scattering from a highly anisotropic molecule like benzene therefore results in an intense wing as compared to a highly isotropic molecule such as carbon tetrachloride.

A Fastie–Ebert monochromator with 10-micrometer slits, giving an instrumental line width of approximately 0.15 Å, was used to obtain traces of the Rayleigh wings in CS_2, benzene, and toluene. The traces for CS_2 analyzed for polarization are shown in Fig. 4. The width at half maximum of that part of the line due to the Rayleigh wings was approximately 6.7 cm^{-1} in CS_2, approximately 6.8 cm^{-1} in benzene, and approximately 8.5 cm in toluene. The Rayleigh wings have very low intensity in carbon tetrachloride, chloroform, water, and ammonia, and a measurement of the linewidth was not possible in these liquids.

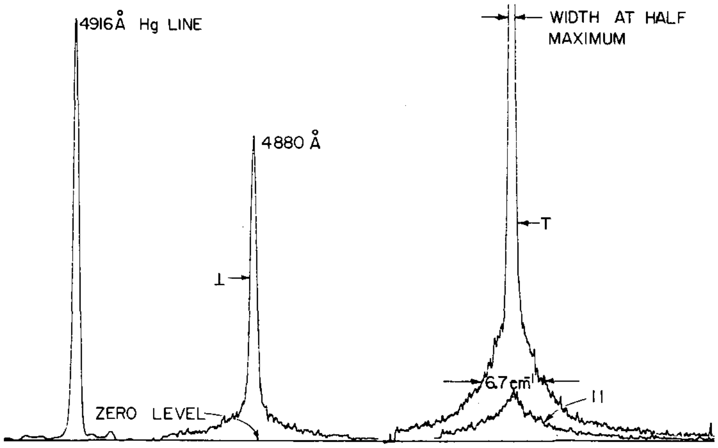

Fig. 4. Rayleigh wings in CS_2. Actual data taken with no polarization analyzer (T), with analyzer parallel to the scattering plane (||), and with analyzer perpendicular to the scattering plane (⊥). Incident light was polarized perpendicular to the scattering plane. The wings are the source of the anisotropic background in Figs. 1–3. The 4916-Å line of Hg is shown to indicate resolution.

A theory of the Rayleigh wings has been written by Leontovich [22]. A theory of rotational Raman scattering by polyatomic molecules has been given by Placzek and Teller [21], and for the rotation of molecules in liquids by Debye [23].

Electrostrictive Constants

The cross section for Brillouin scattering is given by [18]

$$\sigma_B = (8\pi^3/3)(\gamma_s^2/B_s)kTV/\lambda_i^4 \tag{4}$$

where γ_s is the adiabatic electrostrictive constant, B_s is the adiabatic bulk modulus, T is the temperature of the medium, k is Boltzmann's constant, V is the volume of the interaction region, and λ_i is the wavelength of the incident radiation. Therefore, from the ratio of the scattered Brillouin light intensity for two different liquids, the ratio of the electrostrictive constants may be obtained. For similar experimental conditions the relative electrostrictive constants for two liquids obtained from (4) are

$$\gamma_{s2}/\gamma_{s1} = (B_{s2}I_2/B_{s1}I_1)^{1/2}. \tag{5}$$

Since the liquids used in this experiment show dispersion in the hypersonic region [3], [6], [19], γ_s and B_s must be regarded as functions of frequency in this range. The relative electrostrictive constants are therefore only approximate, since for a single scattering angle different phonon frequencies are involved in the Brillouin scattering process for each liquid [see (1)]. The line-broadening experiments also indicate that in the case of toluene damping of the phonons occurs, so that Brillouin scattering intensities measured at the line centers can only be approximate.

Table III lists the Brillouin scattering cross sections and the electrostrictive constants of seven liquids relative to those of CS_2. These ratios are estimated to be accurate to ±15 percent.

TABLE III
Relative Electrostrictive Constants of Liquids Derived from Brillouin Intensities

Liquid	I_l/I_{CS_2} (Relative Brillouin intensities of scattered light compared to CS_2)	$\gamma_{liquid}/\gamma_{CS_2}$
Carbon disulfide CS_2	1	1
Benzene C_6H_6	0.37	0.64
Carbon tetrachloride CCl_4	0.25	0.45
Chloroform $CHCl_3$	0.47	0.67
Methylene chloride CH_2Cl_2	0.37	0.52
Methylene iodide CH_2I_2	0.97	1.28
Toluene C_7H_8	0.29	0.49
Water H_2O	0.05	0.24

CONCLUSION

The versatility of a low power CW Ar^+ laser to investigate Brillouin and Rayleigh scattering in liquids has been demonstrated. In particular, approximately 0.016 mW of power in a single mode is sufficient, because of the spectral advantages of the Ar^+ laser, to measure the width of Brillouin lines by conventional techniques. The same laser operating at approximately 0.07 mW has been used to measure hypersonic velocities, depolarization of scattered light, relative electrostrictive constants, and has been used to investigate the structure of the Rayleigh line.

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REFERENCES

[1] G. B. Benedek, J. B. Lastovka, K. Fritsch, and T. Greytak, "Brillouin scattering in liquids and solids using low-power lasers," *J. Opt. Soc. Am.*, vol. 54, pp. 1284–1285, October 1964.

[2] R. Y. Chiao and B. P. Stoicheff, "Brillouin scattering in liquids excited by the He-Ne maser," *J. Opt. Soc. Am.*, vol. 54, pp. 1286–1287, October 1964.

[3] R. Y. Chiao, "Brillouin scattering and coherent phonon generation," Ph.D. thesis, Mass. Inst. Tech., Cambridge, pp. 1–138, 1965.

[4] D. H. Rank, E. M. Kiess, U. Fink, and T. A. Wiggins, "Brillouin spectra of liquids using a He-Ne laser," *J. Opt. Soc. Am.*, vol. 55, pp. 925–927, August 1965.

[5] H. Z. Cummins and R. W. Gammon, "Rayleigh and Brillouin scattering in benzene: depolarization factors," *Appl. Phys. Lett.*, vol. 6, pp. 171–173, April 15, 1965.

[6] D. I. Mash, V. S. Starunov, and I. L. Fabelinskii, "Investigation of attenuation of hypersound in liquids by an optical method," *Zh. Eksperim. i Teor. Fiz.*, vol. 47, p. 783, 1964. (English transl.: *Soviet Phys.—JETP*, vol. 20, p. 523, 1964).

[7] E. Garmire and C. H. Townes, "Stimulated Brillouin scattering in liquids," *Appl. Phys. Lett.*, vol. 5, pp. 84–86, August 15, 1964.

[8] R. G. Brewer and K. Rieckhoff, "Stimulated Brillouin scattering in liquids," *Phys. Rev. Lett.*, vol. 13, pp. 334a–336a, September 14, 1964.

[9] R. G. Brewer, "The ruby laser as a Brillouin light amplifier," *Appl. Phys. Lett.*, vol. 5, pp. 127–128, October 1, 1964.

[10] R. Y. Chiao, C. H. Townes, and B. P. Stoicheff, "Stimulated Brillouin scattering and coherent generation of intense hypersonic waves," *Phys. Rev. Lett.*, vol. 12, pp. 592–595, May 25, 1964.

[11] H. Takuma and D. A. Jennings, "Stimulated Brillouin scattering in the off-axis resonator," *Appl. Phys. Lett.*, vol. 5, pp. 239–241, December 15, 1964.

[12] D. A. Jennings and H. Takuma, "Optical heterodyne detection of the forward scattered Brillouin scattering," *Appl. Phys. Lett.*, vol. 5, pp. 241–242, December 15, 1964.

[13] L. Brillouin, "Diffusion de la lumiere et des rayon x par un corps transparent homogene," *Ann. Phys. (Paris)*, vol. 17, pp. 88–122, 1922.

[14] W. Gerlach, "Uber die breite der spectrallinien der Ramanstreustrahlung von benzol," *Ann. de Physik*, vol. 1, pp. 301–308, January 1929.

[15] D. H. Rank, "Modified Rayleigh scattering in a liquid," vol. 36, pp. 299–301, May 1946.

[16] D. Birus, "Die Struktur der Rayleighstrahlung von Flüssigkeiten," *Physik Z.*, vol. 39, pp. 80–90, 1938.

[17] J. Brandmüller, "Rayleigh-streuung und rotations-Ramaneffekt von Flüssigkeiten," *Z. Phys.*, vol. 140, pp. 75–91, 1955.

[18] I. L. Fabelinskii, *Bull Acad. Sci. U.S.S.R.*, phys. ser. vol. 17, p. 538, 1953.

[19] R. Y. Chiao and P. A. Fleury, presented at the 1965 Physics of Quantum Electronics Conf., San Juan, Puerto Rico.

[20] I. L. Fabelinskii, "Relative intensities of fine structure components in Rayleigh scattering," *Soviet Phys.—Doklady*, vol. 1, pp. 115–118, 1956.

[21] G. Placzek and E. Teller, "Die rotationsstruktur der Ramanbanden mehratomiger molekule," *Z. Phys.*, vol. 81, pp. 209–257, 1933.

[22] M. A. Leontovich, "Relaxation in liquids and scattering of light," *J. Phys.* (U.S.S.R.), vol. 4, pp. 499–514, 1941.

[23] P. J. Debye, "Der rotationszustand von mulekulen in flüssigkeiten," *Phys. Z.*, vol. 36, pp. 100–101, February 1, 1935.

[24] K. F. Herzfeld and T. A. Litovitz, *Absorption and dispersion of Ultrasonic Waves*. New York: Academic Press, 1959.

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