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$b \approx 0.80$ must be used to adequately approximate Eq. (1) using the same value of α . The trend in the value of b is that which was predicted by the discussion given above. It is clear that b must be a function of the concentration and not a constant as assumed in the derivations in this paper. However, a value of $\alpha = 6.0$ seems to be a good choice for the transfer constant for the self-transfer case. This value of α corresponds to $R_t \approx 13 \text{ \AA}$.

IV. CONCLUSIONS

It has been shown that the concentration depolarization of the $\Delta m = \pm 1$ EPR spectra of naphthalene dissolved in ethanol at 77°K can be semiquantitatively predicted from the same type of analysis used in analyzing

triplet-state energy transfer between unlike molecules. The only modification necessary was to account for the probability of back transfer in the case of the triplet migration between similar molecules. Results are completely consistent with an exchange mechanism being responsible for the depolarization, since Eq. (1) with an appropriate moderating b function can be used to describe concentration depolarization. The magnitude of the transfer radius was found to be essentially the same in the case of self-transfer as that found in triplet energy transfer between unlike molecules. The results are also consistent with the postulate that the rate of triplet energy migration between molecules separated by R_t is considerably slower than the rate of relaxation of the electron spin magnetization in the ethanol glass.

Rayleigh and Brillouin Scattering in Liquids: The Landau-Placzek Ratio*

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The classical theory of light scattering in liquids leading to the Landau-Placzek ratio for the intensities of the Rayleigh and Brillouin components is reviewed. A simple modification is proposed in which the effect of dispersion is included by defining a hypersonic compressibility $\beta_{hs} = 1/(\rho v_{hs}^2)$, where v_{hs} is found from the experimentally measured Brillouin shifts. Further modification is presented to account for dispersion in the electrostriction. A modification of the Landau-Placzek equation due to Fabelinskii is discussed and shown to be essentially equivalent to our equation.

The predictions of the ratios are evaluated for 11 common liquids and compared with new experimental values reported in this paper and with other values taken from the literature. It is found that in most cases the dispersion modification leads to ratios in considerably better agreement with the experimental values than does the simple Landau-Placzek equation.

We present our measurements of the ratio of the Rayleigh and Brillouin intensities obtained with an He-Ne laser light source and photoelectric detection. We discuss the experimental technique and the data-reduction procedure. The detection time constant was sufficiently short that contributions to the Rayleigh component from dust were distinguishable from true molecular scattering. The anomalously large central component for water which has been frequently reported in the literature was thus traced to residual dust contamination and was found to be less than 2% of the Brillouin-component intensity when dust was absent.

I. INTRODUCTION

IN 1922 Brillouin predicted that light which is Rayleigh scattered by homogeneous liquids should consist of a doublet whose components are shifted symmetrically from the frequency ν_0 of the incident light by¹

$$\Delta\nu = \pm 2\nu_0(v/c) \sin\frac{1}{2}\theta, \quad (\text{I.1})$$

where v and c are the velocities of sound and light in

the medium and θ is the angle between k_s and k_0 , the wave vectors of the scattered and incident light. Experimental observations by Gross² in 1930, and subsequently by many others, confirmed Brillouin's prediction, but also revealed the presence of a central unshifted component in the spectrum of the scattered light. Although the central component was initially believed to be an experimental artifact due to instrumental scattering and dust contamination of the sample it was found that even with the most carefully controlled experimental conditions it was never possible to suppress it completely.

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¹ L. Brillouin, *Ann. Phys.* **17**, 88 (1922).

² E. Gross, *Nature* **126**, 201, 400, 603 (1930).

In 1934 Landau and Placzek³ explained the triplet structure and predicted that the ratio of the intensity of the central component to that of the combined doublet should be

$$\frac{I_C}{2I_B} = \frac{C_P - C_V}{C_V} = \frac{\beta_T - \beta_s}{\beta_s}, \quad (I.2)$$

where C_P and C_V are the specific heats at constant pressure and constant volume, and β_T and β_s are the isothermal and adiabatic compressibilities.

Subsequent experiments sometimes confirmed and sometimes contradicted the Landau-Placzek equation (I.2). Venkateswaran⁴ reviewed the situation in 1942 and noted that the central component was frequently observed to be more intense than the Landau-Placzek equation predicts.

One weakness of the LP equation is the neglect of dispersion in the thermodynamic properties of liquids. Since the Brillouin components are generated by high-frequency fluctuations ($\sim 10^9$ cps) while the central component is due to relatively slow disturbances, the neglect of dispersion may lead to significant errors in the predicted intensity ratio—particularly for liquids like carbon disulfide which show a large dispersion in the velocity of sound between the ultrasonic and hypersonic values.

Fabelinskii^{5,6} first pointed out the importance of dispersion and proposed that this difficulty could be eliminated by employing an alternative equation for the intensity ratio—an equation which is still derived from the Landau-Placzek theory, but which results from terminating the reduction short of the assumptions he considered questionable. His tabulated theoretical values of $I_C/2I_B$ for five liquids are in all cases considerably larger than those of Eq. (I.2). His experimental data was also analyzed with more care than much of the earlier work, and he found good agreement between the experimental results and predictions based on his equation, within the rather large error limits of the data then available.

Since the recent advent of lasers, the observation of Brillouin spectra has been greatly simplified due to the combination of high intensity and narrow linewidths not previously available. Several groups have applied continuous-wave lasers to the measurement of Brillouin shifts,^{7,8} and have been able to measure both shifts and

linewidths with greatly increased precision.^{9,10} This work has indicated a re-examination of the intensity-ratio problem and Rank and co-workers have recently published the first intensity ratios obtained with an He-Ne laser.¹¹

In this paper, we present the results of our measurements of the intensity ratios for 11 common liquids, and compare our experimental results and those of others with the various theoretical predictions. We begin, in Sec. II, with a review of the classical theory and rederive the Landau-Placzek formula. This formula (as well as the others) is evaluated for our 11 liquids using physical and thermodynamic constants listed in Table I. These have been selected from the various tables and compilations available at 20°C whenever possible to avoid errors due to the often-neglected temperature dependence of these quantities. We next derive a simple modification of the LP equation which includes the effects of dispersion. The dispersion-corrected LP equation is evaluated for six of our liquids for which all the necessary quantities are available, and estimated for the remaining five. Next, we discuss the equation proposed by Fabelinskii and evaluate it for six of our liquids. These values, along with those published by Fabelinskii, are collected in the $I_C/2I_B$ comparison, Table IV. We also discuss the specific assumptions involved in the LP theory which can contribute to differences in the various theoretical values.

In Sec. III, we discuss the experimental procedure and the data-reduction method. In addition to the intensity ratios, we also give the Brillouin shifts measured in the experiment, and compare the hypersonic velocities derived from our data with other published values in Table V. From our hypersonic-velocity determinations we derive values for the hypersonic adiabatic compressibility which are required in evaluating some of the theoretical expressions.

II. THEORY

A. Classical Scattering Theory

In the classical theory of light scattering in dense media developed by Einstein and Smoluchowski the sample is divided into small volume elements v large enough to contain many molecules, but of linear dimension small compared to the wavelength of the light.¹² The incident light wave induces a dipole moment in each volume element which becomes the source of

³ L. Landau and G. Placzek, *Z. Phys. Sowjetunion* **5**, 172 (1934).

⁴ C. S. Venkateswaran, *Proc. Indian Acad. Sci.* **15**, 322 (1942).

⁵ I. L. Fabelinskii, *Dokl. Akad. Nauk SSSR* **17**, 538 (1953).

⁶ I. L. Fabelinskii, *Soviet Phys.—Doklady* **1**, 115 (1956) [*Dokl. Akad. Nauk SSSR* **106**, 822 (1956)].

⁷ R. Y. Chiao and B. P. Stoicheff, *J. Opt. Soc. Am.* **54**, 1286 (1964).

⁸ G. B. Benedek, J. B. Lastovka, K. Fritsch, and T. Greytak, *J. Opt. Soc. Am.* **54**, 1284 (1964).

⁹ D. I. Mash, V. S. Starunov, and I. L. Fabelinskii, *Soviet Phys.—JETP* **20**, 523 (1965) [*Zh. Eksperim. i Teor. Fiz.* **47**, 783 (1964)].

¹⁰ R. Y. Chiao and P. A. Fleury, *Proc. Conf. Phys. Quantum Electronics*, San Juan, Puerto Rico, 1965 (to be published).

¹¹ D. H. Rank, E. M. Kiess, U. Fink, and T. A. Wiggins, *J. Opt. Soc. Am.* **55**, 925 (1965).

¹² A. Einstein, *Ann. Physik* **33**, 1275 (1910).

TABLE I. Physical properties.

| | Density ρ (T) | Refractive index n (λ) _{μ} (T) | Isothermal compressibility $\beta_T^\circ \times 10^{12}$ (T) | Adiabatic compressibility $\beta_s^\circ \times 10^{12}$ (T) | Hypersonic adiabatic compressibility $\beta_s^{hs} \times 10^{12}$ ($T = 20^\circ\text{C}$) ^h |
|--|-----------------------------|--|--|---|---|
| Acetic acid CH ₃ CO ₂ H | 1.0491 ^a (20) | 1.372 ^d (0.589) (20) | 91 ^b (20) | 75 ^b (20) | 70.6 |
| Acetone CH ₃ COCH ₃ | 0.791 ^b (20) | 1.3573 ^c (0.656) (20) | 125.6 ^b (20) | 90.6 ^b (20) | 89.8 |
| Benzene C ₆ H ₆ | 0.8790 ^a (20) | 1.4965 ^c (0.656) (20) | 95.7 ^a (20) | 67 ^a (20) | 50.6 |
| Carbon disulfide CS ₂ | 1.2632 ^a (20) | 1.6182 ^c (0.656) (20) | 92.7 ^b (20) | 59.8 ^b (20) | 50.7 |
| Carbon tetrachloride CCl ₄ | 1.5940 ^a (20) | 1.4579 ^c (0.656) (20) | 104 ^a (20) | 71.8 ^a (20) | 62.2 |
| Ethyl alcohol C ₂ H ₅ OH | 0.7894 ^a (20) | 1.3605 ^c (0.656) (20) | 111.3 ^b (20) | 94.1 ^b (20) | 93.4 |
| Ethyl ether (C ₂ H ₅) ₂ O | 0.7135 ^a (20) | 1.3515 ^c (0.656) (20) | 186 ^a (20) | 136 ^a (20) | 140 |
| <i>n</i> -Hexane <i>n</i> -C ₆ H ₁₄ | 0.6595 ^a (20) | 1.3734 ^c (0.656) (20) | 157 ^f (23) | 123 ^g (?) | 122 |
| Methyl alcohol CH ₃ OH | 0.7915 ^a (20) | 1.3277 ^c (0.656) (20) | 123.4 ^b (20) | 101.9 ^b (20) | 102 |
| Toluene C ₆ H ₅ -CH ₃ | 0.8669 ^a (20) | 1.4911 ^c (0.656) (20) | 90.6 ^b (20) | 66.4 ^b (20) | 63.3 |
| Water H ₂ O | 0.9982 ^c (20) | 1.3312 ^c (0.656) (20) | 45.80 ^b (20) | 45.5 ^g (?) | 45.7 |

^a J. Timmermans, *Physico-Chemical Constants* (Elsevier Publishing Company, Inc., New York, 1950).

^b *American Institute of Physics Handbook*, edited by D. E. Gray *et al.* (McGraw-Hill Book Company, Inc., New York, 1957).

^c *Smithsonian Physical Tables* (The Smithsonian Institution, Washington, D. C., 1954), 9th ed.

^d *Handbook of Chemistry and Physics*, edited by C. D. Hodgman *et al.* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1958), 40th ed.

^e J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths Scientific Publications Ltd., London, 1959).

^f *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. 3, p. 36.

^g Computed from ultrasonic velocity (Table V) via $\beta_s = (v^2\rho)^{-1}$.

^h Computed from hypersonic velocity (Table V).

scattered radiation. If the induced polarization is constant through the medium the net scattered radiation in all directions but the forward will be zero due to destructive interference. In real media, however, there will be small random fluctuations in the local dielectric constant and the induced polarization will not be constant throughout the medium. If we assume these fluctuations to be uncorrelated from one volume element to the next, we may simply add up the intensities of the dipole radiation from the fluctuating component of the polarization in each volume element.

If the incident light is plane polarized with E perpendicular to the scattering plane (the plane containing the incident wave vector k_0 and the scattered wave vector k_s) the intensity of light scattered by each volume element divided by the intensity of the incident beam is¹³

$$i/I_0 = (\pi^2/r^2\lambda_0^4)v^2 \langle (\Delta\epsilon)^2 \rangle, \quad (\text{II.1})$$

¹³ See, for example, O. K. Rice, in *Thermodynamics and Physics of Matter*, edited by F. Rossini (Princeton University Press, Princeton, New Jersey, 1955), Sec. E9.

where λ_0 is the wavelength of the incident light, r is the distance from the scattering sample to the point of observation, and $\langle (\Delta\epsilon)^2 \rangle$ is the mean-square fluctuation of the dielectric constant ϵ about its mean value in the volume element v .

Evaluation of (II.1) in terms of physical parameters of the medium requires that $\langle (\Delta\epsilon)^2 \rangle$ be related to fluctuations in thermodynamic quantities.

Einstein's Evaluation of $\langle (\Delta\epsilon)^2 \rangle$ ¹⁴

Following Einstein, we can deduce an expression for the scattering intensity by considering ϵ as a function of the density ρ and the temperature T .

Let $\epsilon = \epsilon(\rho, T)$; then

$$\Delta\epsilon = (\partial\epsilon/\partial\rho)_T \Delta\rho + (\partial\epsilon/\partial T)_\rho \Delta T.$$

¹⁴ Thermodynamic arguments of this and the following section follow L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958), Secs. 20 and 111; and *Electrodynamics of Continuous Media* (Pergamon Press, Inc., New York, 1960), Sec. 94.

Since ρ and T are statistically independent,

$$\langle(\Delta\epsilon)^2\rangle = (\partial\epsilon/\partial\rho)_T^2 \langle(\Delta\rho)^2\rangle + (\partial\epsilon/\partial T)_\rho^2 \langle(\Delta T)^2\rangle.$$

If we assume

$$(\partial\epsilon/\partial T)_\rho \ll (\partial\epsilon/\partial\rho)_T$$

and use the result from thermodynamic-fluctuation theory for the mean-square fluctuation in density in the volume element v ,

$$\langle(\Delta\rho)^2\rangle/\rho^2 = kT\beta_T/v,$$

where k is Boltzmann's constant and β_T is the isothermal compressibility, then we have

$$\langle(\Delta\epsilon)^2\rangle = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T^2 \langle(\Delta\rho)^2\rangle = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T^2 \frac{kT\beta_T}{v}.$$

Substituting into (II.1), we find,

$$\frac{i}{I_0} = \frac{\pi^2}{r^2\lambda_0^4} kT\beta_T v \left(\frac{\partial\epsilon}{\partial\rho}\right)_T^2. \quad (II.2)$$

If we take

$$(\rho\partial\epsilon/\partial\rho)_T^2 = (\epsilon-1)^2,^{15}$$

then Eq. (II.1) for the scattered intensity becomes

$$i/I_0 = (\pi^2/r^2\lambda_0^4) (\epsilon-1)^2 kT\beta_T v, \quad (II.3)$$

which differs from Einstein's result only in the absence of a factor $[(\epsilon+2)/3]^2$ arising from his use of the Clausius-Mosotti equation.

B. Landau-Placzek

Suppose we choose entropy and pressure as the independent variables rather than density and temperature

$$\epsilon = \epsilon(S, P),$$

then

$$\Delta\epsilon = (\partial\epsilon/\partial S)_P \Delta S + (\partial\epsilon/\partial P)_S \Delta P,$$

and thus

$$\langle(\Delta\epsilon)^2\rangle = (\partial\epsilon/\partial S)_P^2 \langle(\Delta S)^2\rangle + (\partial\epsilon/\partial P)_S^2 \langle(\Delta P)^2\rangle, \quad (II.4)$$

where the cross term again vanishes since fluctuations in S and P are independent.

According to Landau and Placzek, the first term represents local entropy fluctuations which do not propagate in normal liquids and are the source of the central (unshifted) component of the scattered light, while the second term represents the isentropic pressure fluctuations (i.e., sound waves) which are the source of the Brillouin doublet.

¹⁵ The use of this relation in place of the Clausius-Mosotti equation is discussed in Sec. 7 of A. B. Bhatia and K. S. Krishnan, Proc. Roy. Soc. (London) **A192**, 181 (1948).

Since $\langle(\Delta P)^2\rangle = kT/v\beta_s$, where β_s is the adiabatic compressibility, while

$$\left(\frac{\partial\epsilon}{\partial P}\right)_S = \left(\frac{\partial\epsilon}{\partial\rho}\right)_S \left(\frac{\partial\rho}{\partial P}\right)_S = \left(\frac{\partial\epsilon}{\partial\rho}\right)_S \rho\beta_s,$$

the second (Brillouin) term in (II.4) becomes

$$\left(\frac{\partial\epsilon}{\partial P}\right)_S^2 \langle(\Delta P)^2\rangle = \left(\frac{\partial\epsilon}{\partial\rho}\right)_S^2 \rho^2 \beta_s^2 \left(\frac{kT}{v\beta_s}\right) = \left(\frac{\partial\epsilon}{\partial\rho}\right)_S^2 \frac{kT\beta_s}{v}.$$

The first (Rayleigh) term in (II.4) may be simplified. Again, from thermodynamic-fluctuation theory, $\langle(\Delta S)^2\rangle = kC_P\rho v$ where C_P is the specific heat per unit mass of the medium, while

$$\left(\frac{\partial\epsilon}{\partial S}\right)_P = \left(\frac{\partial\epsilon}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial\epsilon}{\partial T}\right)_P \frac{T}{C_P\rho v},$$

whence

$$\left(\frac{\partial\epsilon}{\partial S}\right)_P^2 \langle(\Delta S)^2\rangle = \left(\frac{\partial\epsilon}{\partial T}\right)_P^2 \frac{T^2}{C_P^2 \rho^2 v^2} kC_P\rho v = \left(\frac{\partial\epsilon}{\partial T}\right)_P^2 \frac{kT^2}{C_P\rho v}.$$

Thus, (II.4) becomes

$$\langle(\Delta\epsilon)^2\rangle = \left(\frac{\partial\epsilon}{\partial T}\right)_P^2 \frac{kT^2}{C_P\rho v} + \left(\frac{\partial\epsilon}{\partial\rho}\right)_S^2 \frac{kT\beta_s}{v}. \quad (II.5)$$

Substituting (II.5) into Eq. (II.1), we have

$$\frac{i}{I_0} = \frac{\pi^2 v}{r^2\lambda_0^4} \left[\left(\frac{\partial\epsilon}{\partial T}\right)_P^2 \frac{kT^2}{\rho C_P} + \left(\frac{\partial\epsilon}{\partial\rho}\right)_S^2 kT\beta_s \right]. \quad (II.6)$$

(Rayleigh) (Brillouin)

Further simplification of (II.6) occurs if we note that¹⁴

$$\left(\frac{\partial\epsilon}{\partial\rho}\right)_S = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T + \frac{T}{C_V\rho^2} \left(\frac{\partial P}{\partial T}\right)_\rho \left(\frac{\partial\epsilon}{\partial T}\right)_\rho$$

and assume that the second term is negligible. Then

$$\frac{i}{I_0} = \frac{\pi^2 v}{r^2\lambda_0^4} \left[\left(\frac{\partial\epsilon}{\partial T}\right)_P^2 \frac{kT^2}{\rho C_P} + \left(\frac{\partial\epsilon}{\partial\rho}\right)_T^2 kT\beta_s \right]. \quad (II.7)$$

Since the second term in (II.7) gives the intensity of the Brillouin doublet ($2I_B$), whereas (II.2) gives the intensity of the entire triplet ($I_C + 2I_B$), we find

$$\frac{I_C + 2I_B}{2I_B} = \frac{(\pi^2/r^2\lambda_0^4) v (\partial\epsilon/\partial\rho)_T^2 kT\beta_T \rho^2}{(\pi^2/r^2\lambda_0^4) v (\partial\epsilon/\partial\rho)_T^2 kT\beta_s \rho^2} = \frac{\beta_T}{\beta_s} = \frac{C_P}{C_V}$$

which is the formula given in 1934 by Landau and Placzek.³ It is usually rewritten as

$$\frac{I_C}{2I_B} = \frac{\beta_T - \beta_s}{\beta_s} = \frac{C_P - C_V}{C_V} = \gamma - 1. \quad (II.8)$$

Equation (II.8), which is frequently called the Landau-

TABLE II. Evaluation of dispersion-corrected Landau-Placzek equation (II.9).

| | (A) $[(\partial\epsilon/\partial\rho)_T^\circ/(\partial\epsilon/\partial\rho)_T^{hs}]^2$ | (B) $(\beta_T - \beta_s)^\circ/\beta_s^{hs}$ | $A \times B = I_C/2I_B$ |
|----------------------|---|---|-------------------------|
| Acetic acid | (1.21) ^a | 0.23 ^c | (0.28) |
| Acetone | (1.21) ^a | 0.39 | (0.47) |
| Benzene | 1.15 ^b | 0.57 | 0.66 |
| Carbon disulfide | (1.21) ^a | 0.65 | (0.79) |
| Carbon tetrachloride | (1.21) ^a | 0.51 | (0.62) |
| Ethyl alcohol | 1.35 ^b | 0.18 | 0.25 |
| Ethyl ether | 1.21 ^b | 0.36 | 0.43 |
| n-Hexane | (1.21) ^a | 0.28 | (0.34) |
| Methyl alcohol | 1.28 ^b | 0.21 | 0.27 |
| Toluene | 1.08 ^b | 0.38 | 0.41 |
| Water | 1.17 ^b | 0.007 | 0.008 |

^a "Estimated" value is average of six from b.

^b See Ref. 16. Values used for $(\partial\epsilon/\partial\rho)_T^{hs}$ are 10⁷ cps, measurements which are probably more reliable than those from light scattering.

^c From Table I.

Placzek equation, is evaluated for the 11 liquids studied in our experiment in Table IV, Column 1.

C. Dispersion Correction

In deriving the Landau-Placzek equation (II.8), the effects of dispersion have been ignored. Equation (II.7) can be modified to include dispersion since the first (Rayleigh) term represents slowly damped fluctuations and the quantities in it may be quite accurately represented by their static values, while the second (Brillouin) term represents fluctuations of frequency equal to the Brillouin-shift frequency and the quantities in it may thus be represented by their appropriate hypersonic (hs) values. This was first recognized by Fabelinskii and Ginzburg.⁶

Equation (II.7) then becomes

$$\frac{i}{I_0} = \frac{\pi^2 v}{r^2 \lambda_0^4} \left\{ \left[\left(\frac{\partial\epsilon}{\partial T} \right)_P \frac{kT^2}{\rho C_P} \right]_{\text{static}} + \left[\left(\frac{\partial\epsilon}{\partial\rho} \right)_T kT\beta_s \right]_{\text{hs}} \right\}. \quad (\text{II.7}')$$

This dispersion modification is possible because the choice $\epsilon = \epsilon(S, P)$ separates the fluctuations into low- and high-frequency terms.

Equation (II.2) for the total scattering cannot be corrected in this way because the Rayleigh and Brillouin terms are lumped together, and the thermodynamic quantities would have to be replaced by weighted averages which requires previous knowledge of the relative intensities. We note, however, that if we evaluate (II.2) using static values of the quantities involved, the result will be in error only in the contribution from the Brillouin components. If we then subtract from (II.2) the second (Brillouin) term of (II.7) evaluated in the static limit, we should be left with a correct expression for the intensity of the central component. Combining this with the second term in (II.7')

for the corrected Brillouin doublet intensity, we have

$$\frac{I_C}{2I_B} = \frac{[(\rho\partial\epsilon/\partial\rho)_T^2(\beta_T - \beta_s)]_{\text{static}}}{[(\rho\partial\epsilon/\partial\rho)_T^2\beta_s]_{\text{hs}}}. \quad (\text{II.9})$$

The hypersonic adiabatic compressibility β_s^{hs} is defined as $\beta_s^{hs} = 1/(\rho v_{hs}^2)$ in order to correspond to dynamical calculations of the intensity of scattering from phonons. Since the hypersonic velocity v_{hs} can be determined from the Brillouin shift $\Delta\nu$ by Eq. (I.1) (see Table V) β_s^{hs} can be calculated.

The ratio

$$\frac{[(\rho\partial\epsilon/\partial\rho)_T^2]_{\text{static}}}{[(\rho\partial\epsilon/\partial\rho)_T^2]_{\text{hs}}}$$

is more difficult to determine. Motulevich and Fabelinskii¹⁶ have given both quantities for six of our liquids. The ratios are listed in Table II and range from 1.08 to 1.35. For the remaining five we use an estimate of 1.21 from the average value of the known six.

Dispersion-corrected predictions for $I_C/2I_B$ derived from (II.9) are evaluated in Table II and tabulated in Table IV, Column 2.

D. Fabelinskii's Theory

Fabelinskii⁶ has argued that one can avoid most of the questionable assumptions of the Landau-Placzek theory in computing the intensity ratio by employing Eq. (II.6) directly with no further reduction. This gives

$$\frac{I_C}{2I_B} = \frac{[(\partial\epsilon/\partial T)_P^2(T/\rho C_P)]_{\text{static}}}{[(\rho\partial\epsilon/\partial\rho)_T^2\beta_s]_{\text{hs}}} \quad (\text{II.10})$$

which is equivalent to Fabelinskii's equation (4).⁶

¹⁶ G. P. Motulevich and I. L. Fabelinskii, Soviet Phys.—Doklady 1, 81 (1956) [Dokl. Akad. Nauk SSSR 106, 637 (1956)].

TABLE III. Evaluation of Fabelinskii's equation (II.10).

| | $[\rho(\partial\epsilon/\partial\rho)]_S^{hs}$ | β_s^{hs} | ρ | C_P | n | $(dn/dt)_P$ | $\frac{[(T/\rho C_P)(\partial\epsilon/\partial T)_P^2]_{static}^*}{\{[\rho(\partial\epsilon/\partial\rho)]_S^2 \beta_s\}^{hs}}$ |
|----------------|--|-------------------------------------|--------------------|---------------------------------|--------------------|------------------------------------|---|
| Benzene | 1.46 ^a | 50.6×10^{-12} ^b | 0.879 ^c | 1.72×10^7 ^d | 1.496 ^e | 6.38×10^{-4} ^f | 0.66 |
| Ethyl alcohol | 0.87 ^a | 93.8×10^{-12} | 0.789 | 2.39×10^7 ^d | 1.360 | 3.9×10^{-4} ^d | 0.25 |
| Ethyl ether | 0.88 ^a | 140×10^{-12} | 0.714 | 2.31×10^7 ^d | 1.352 | 5.6×10^{-4} ^d | 0.38 |
| Methyl alcohol | 0.79 ^a | 104×10^{-12} | 0.792 | 2.53×10^7 ^d | 1.328 | 4.0×10^{-4} ^d | 0.25 |
| Toluene | 1.52 ^a | 63.4×10^{-12} | 0.867 | 1.70×10^7 ^d | 1.491 | 5.62×10^{-4} ^f | 0.38 |
| Water | 0.79 ^a | 45.7×10^{-12} | 0.998 | 4.18×10^7 ^e | 1.331 | 9×10^{-5} ^e | 0.014 |

^a See Ref. 16. (Values used are at 10^7 cps.)

^b From this work (see Table I, Column 5 and Footnote h).

^c From Table I.

^d J. Timmermans, Footnote a, Table I.

^e Footnote d, Table I.

^f See Ref. 17.

* $T=293^\circ\text{K}$.

Although this procedure does circumvent several assumptions of the Landau-Placzek theory, it requires accurate knowledge of $(\partial\epsilon/\partial T)_P^{static}$ and $(\rho\partial\epsilon/\partial\rho)_S^{hs}$. [Although our dispersion-corrected Landau-Placzek equation, (II.9), involved the factor $(\partial\epsilon/\partial\rho)_T$, it depends only on the ratio of the static to hypersonic values and is, therefore, less sensitive than (II.9) to errors in the experimental determination.]

Values of $(\partial\epsilon/\partial\rho)_S$ at 10^7 cps are given for six of our liquids by Motulevich and Fabelinskii¹⁶ along with values of $(\partial\epsilon/\partial\rho)_T$ which we have used in the evaluation of (II.9). $(\partial\epsilon/\partial T)_P$ is found from the temperature dependence of the refractive index n through

$$(\partial\epsilon/\partial T)_P = 2n(dn/dt)_P.$$

In Table III we evaluate Eq. (II.10) for the six liquids for which $(\rho\partial\epsilon/\partial\rho)_S$ is given in Ref. 16. The results are tabulated in Table IV, Column 4, while Fabelinskii's values are given in Column 3. Unfortunately, Fabelinskii has not derived intensity ratios for four of the six liquids for which he and Motulevich give $(\rho\partial\epsilon/\partial\rho)_S$ values. Furthermore, theoretical intensity ratios for three additional liquids (acetone, carbon disulfide, and carbon tetrachloride) are given without tabulating or giving reference to the additional thermodynamic values involved. Thus Fabelinskii's evaluation of his equation (II.10) and our evaluation overlap in only two cases, benzene and water, for which we agree rather well. It is also seen that of our six values, all but the one for water also agree closely with the dispersion-corrected LP equation (II.9), a result which should be expected as we show below. The rather large values given by Fabelinskii (relative to the dispersion-corrected LP equation) therefore appear questionable, perhaps as a result of using imprecise thermodynamic data. This conclusion is supported by the fact that his predictions (0.98 for CS_2 , 0.84 for CCl_4 , and 0.57 for acetone) are clearly larger than the experimental values.

Next we examine the specific assumptions of the LP theory in an effort to determine whether or not there should in fact be a discrepancy between Eqs. (II.9) (dispersion-corrected LP) and (II.10) (Fabelinskii). Apart from the neglect of dispersion in the original LP theory which has been corrected in (II.9), there is one additional assumption which could produce a difference between (II.9) and (II.10). This assumption occurs in the derivation preceding Eq. (II.2), and again following (II.6). In both cases, terms involving $(\partial\epsilon/\partial T)_P$ are dropped. Physically the assumption is that the temperature dependence of the dielectric constant is caused by thermal expansion (and resultant density changes) and not by the intrinsic temperature dependence at constant density. Formally,

$$\left(\frac{\partial\epsilon}{\partial T}\right)_P = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T \left(\frac{\partial\rho}{\partial T}\right)_P + \left(\frac{\partial\epsilon}{\partial T}\right)_\rho.$$

If we assume that the second term is small compared to the first, then

$$\left(\frac{\partial\epsilon}{\partial T}\right)_P = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T \left(\rho^{-1} \frac{\partial\rho}{\partial T}\right)_P = \left(\rho \frac{\partial\epsilon}{\partial\rho}\right)_T \alpha, \quad (\text{II.11})$$

where α is the thermal expansion coefficient. If we approximate $(\rho\partial\epsilon/\partial\rho)_S$ by $(\rho\partial\epsilon/\partial\rho)_T$ and substitute (II.11) into Fabelinskii's (II.10) we get

$$\frac{I_C}{2I_B} = \frac{[(\rho\partial\epsilon/\partial\rho)_T^2 (\alpha^2 T / \rho C_P)]_{static}}{[(\rho\partial\epsilon/\partial\rho)_T^2 \beta_s]^{hs}}$$

which is the same as our (II.10) since $(\beta_T - \beta_s) = \alpha^2 T / \rho C_P$. Thus (II.10) and (II.9) should not differ if the assumption that the intrinsic temperature dependence of the dielectric constant $(\partial\epsilon/\partial T)_\rho$ can be ignored is correct.

Coumou, Mackor, and Hijmans¹⁷ have recently in-

¹⁷ D. J. Coumou, E. L. Mackor, and J. Hijmans, *Trans. Faraday Soc.* **60**, 1539 (1964).

TABLE IV. The intensity ratio $I_C/2I_B$.

| | Theory | | | |
|----------------------|---------------------------|-----------------------------------|------------------|------------------------|
| | Landau-Placzek | | Fabelinskii | |
| | Without dispersion (II.8) | With dispersion (II.9) (Table II) | His ^a | Ours (II.10) Table III |
| Acetic acid | 0.21 | (0.28) | | |
| Acetone | 0.39 | (0.47) | 0.57 | |
| Benzene | 0.43 | 0.66 | 0.70 | 0.66 |
| Carbon disulfide | 0.55 | (0.79) | 0.98 | |
| Carbon tetrachloride | 0.45 | (0.62) | 0.84 | |
| Ethyl alcohol | 0.18 | 0.24 | | 0.25 |
| Ethyl ether | 0.37 | 0.43 | | 0.38 |
| <i>n</i> -Hexane | 0.28 | (0.34) | | |
| Methyl alcohol | 0.21 | (0.27) | | 0.25 |
| Toluene | 0.36 | 0.41 | | 0.38 |
| Water | 0.007 | 0.008 | 0.012 | 0.014 |

| | Experiment | | | |
|----------------------|---------------------|--------------------|------------------|--|
| | Present | | | Other |
| | Directly from trace | Overlap correction | Corrected result | |
| Acetic acid | 0.41±2% | 1.00±1% | 0.41±0.01 | |
| Acetone | 0.45±2% | 1.01±1% | 0.44±0.01 | 0.44 ^b 0.59±0.12 ^c 0.42 ^d 0.79 ^e |
| Benzene | 0.85±5% | 1.04±1% | 0.84±0.05 | 0.98±0.25 ^a 0.97 ^e |
| Carbon disulfide | 0.70±5% | 1.02±1% | 0.71±0.04 | 0.77 ^b 0.93±0.18 ^a |
| Carbon tetrachloride | 0.64±1% | 1.13±3% | 0.72±0.03 | 0.75 ^b 0.84 ^e 1.10±0.30 ^a |
| Ethyl alcohol | 0.25±1% | 0.93±1% | 0.23±0.01 | 0.26 ^b 0.39 ^d 0.15 ^d 0.38 ^f |
| Ethyl ether | 0.39±1% | 0.90±1% | 0.35±0.01 | 0.45 ^e |
| <i>n</i> -Hexane | 0.37±2% | 0.95±3% | 0.35±0.02 | |
| Methyl alcohol | 0.28±2% | 0.93±1% | 0.26±0.01 | 0.28 ^f |
| Toluene | 0.41±5% | 1.02±1% | 0.42±0.03 | 0.41 ^b |
| Water | | | <0.02 | 0.14 ^b ~0 ^e 0.14 ^d 0.36 ^f 0.05 ^e |

^a See Ref. 6.^b See Ref. 11.^c See Ref. 6.^d D. H. Rank, J. S. McCartney, and G. J. Szasz, *J. Opt. Soc. Am.* **38**, 287 (1948).^e See Ref. 4.^f K. Sunanda Bai, *Proc. Indian Acad. Sci.* **15**, 349 (1942).^g L. V. Lanshina and M. I. Shakhparonov, *Soviet Phys.—Doklady* **6**, 320 (1961) [*Dokl. Akad. Nauk SSSR* **137**, 830 (1961)].

investigated this assumption for a number of organic liquids by measuring both $(\partial n/\partial T)_P$ and $(\partial n/\partial p)_T$, and find that Eq. (II.11) holds to well within 1%. An exception will occur, however, with water where $(\partial \rho/\partial T)_P$ is so small that the neglect of $(\partial \epsilon/\partial T)_P$ is probably not justified. In this case there *should* be a discrepancy between Fabelinskii's prediction and that of the Landau-Placzek equation (dispersion corrected) and the first should be a better approximation. Thus, both our equation (II.9) and Fabelinskii's (II.10) include the frequency dependence of the thermodynamic properties and should be better than the simple LP equation (II.8). Differences between the two should occur only for liquids like water which show excep-

tionally small thermal expansion coefficients. A crucial test of this point would be to measure the scattering from water at 4°C where α goes through zero. In this case, only the $(\partial \epsilon/\partial T)_P$ term can contribute to the Rayleigh scattering.¹⁸

Finally, we point out that the inclusion of dispersion in this discussion has been limited to a consideration of the frequency dependence of relevant properties, but ignored the effects of the associated hypersonic absorption. In the thermodynamic-fluctuation theory em-

¹⁸ This experiment has been attempted, but the resolution was too low to resolve the triplet. L. V. Lanshina and M. I. Shakhparonov, *Soviet Phys.—Doklady* **6**, 320 (1961) [*Dokl. Akad. Nauk SSSR* **131**, 830 (1961)].

ployed in the LP derivation, the probability of a fluctuation is taken to be $A \exp(-R_m/kT)$, where R_m is the minimum work required to bring about the fluctuation. R_m is evaluated under the assumption of reversibility.¹⁴

If the hypersonic attenuation is very large, the pressure fluctuations are not truly reversible, and the simple thermodynamic-fluctuation theory is not valid. Qualitatively, one might expect the inclusion of the damping terms to reduce the magnitude of the pressure fluctuations thereby increasing the $I_C/2I_B$ ratio. It may also be possible to circumvent the problem by evaluating the pressure fluctuations without invoking the thermodynamic theory as Komarov has recently shown.¹⁹

These considerations may eventually account for some of the remaining discrepancies evident in Table IV. A thorough test must await the availability of more precise thermodynamic data, particularly of the dispersion of $(\rho\partial\epsilon/\partial\rho)$.

III. EXPERIMENT

Previous efforts to test the Landau-Placzek prediction have been marked by wide divergence in experimental results. It seems that no past attempts have been without large uncertainties, if not large errors.

With the continuous laser we now can produce an ideal incident beam for light-scattering experiments. Adding photoelectric detection to the system we are equipped to do meaningful intensity measurements.

An adequate test of the theory requires that several experimental conditions be met. In addition to well-resolved components in spectral traces with good signal to noise, the data must be taken at a controlled temperature on pure, dust-free liquids in carefully cleaned, highly polished sample cells. Every effort must be made to test for and eliminate stray light since on the trace this will appear as a contribution to the central unshifted component thereby increasing the apparent $I_C/2I_B$. Failure to meet this last condition (along with inadequate resolution) seems to have been the weakness of previous experiments.

Preliminary measurements indicated to us that there were real deviations from the Landau-Placzek prediction [Eq. (I.2)] and so we decided to add the measurement of the Brillouin shift, $\Delta\nu$, in order to determine from it the adiabatic compressibility β_s at the frequency of the sound waves giving rise to the Brillouin components. This made an additional experimental requirement of having an accurately known scattering angle. We would like to emphasize that, contrary to the usual situation in spectroscopy, the frequency shift of the Brillouin components depends on the angle of observation. Hence a precise measurement of the shift is meaningful only insofar as the scattering angle is known.

Ignoring this fact has caused the disagreement in published values of the hypersonic velocities where the stated precision has been much better than the accuracy. Differentiating Eq. (I.1), one finds

$$d\nu/\Delta\nu = \frac{1}{2} (\cot \frac{1}{2}\theta) d\theta.$$

This shows that in order to determine $\Delta\nu$ to within $\pm 1\%$ at $\theta = 90^\circ$ one must set θ to within $\pm 1^\circ$.

The general requirement of having a fixed temperature for all measurements is important. Not only is the sound velocity temperature dependent, but also we wished to make use of tabulated values of thermodynamic and optical properties of the liquids studied. These properties are generally temperature dependent so a constant evaluation of the various theoretical predictions required knowing values of the properties at a single temperature. We choose to do our work at a temperature of 20°C because most of the thermodynamic properties had been measured at this temperature. The temperature inside the sample compartment was maintained at $(20.0 \pm 0.3)^\circ\text{C}$ by the room air-conditioning system. The essentially constant temperatures while taking the traces for each liquid all fell in the indicated range.

A diagram of our apparatus is shown in Fig. 1. It is basically that used by Chiao and Stoicheff⁷ and the present authors²⁰ in previous work on Brillouin scattering, modified in that chopping the beam and ac detection were found to be unnecessary. The EMI 9558B photomultiplier was cooled by a dry-ice-methanol mixture, but a nonstatistical component of the noise current makes it less than an ideal detector. The Spectra Physics Model-115 He-Ne laser provided nominally 7 mW of $6328\text{-}\text{\AA}$ -wavelength light in the incident-beam, running multimode. The signal current from the photomultiplier was typically about 5×10^{-9} A. Two Invar pin spacers were used, 1.002 and 1.502 cm

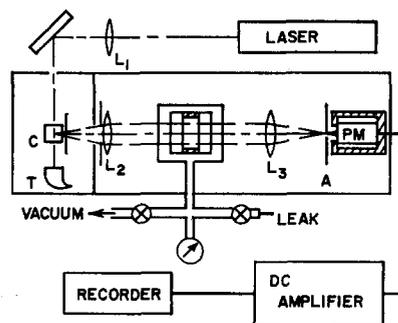


Fig. 1. Diagram of apparatus. L_1 , 48-cm FL lens; L_2 , 25-cm FL lens; L_3 , 36-cm FL lens; A, 1.0-mm aperture; C, 1.00-cm, square sample cell; T, light trap; PM, EMI 9558B photomultiplier, dry ice cooled.

¹⁹ L. I. Komarov, Soviet Phys.—JETP **21**, 99 (1965) [Zh. Eksperim. i Teor. Fiz. **48**, 145 (1965)].

²⁰ H. Z. Cummins and R. W. Gammon, Appl. Phys. Letters **6**, 171 (1965).

long, giving free spectral ranges of 0.4990 cm^{-1} and 0.3329 cm^{-1} , respectively. The interferometer was pressure scanned by evacuating the box enclosing the etalon and allowing air to slowly lead back to it. The time to sweep over one order was about 4 min. (Acetic acid, acetone, carbon tetrachloride, ethyl alcohol, ethyl ether, *n*-hexane, and methyl alcohol data were taken with the longer spacer. Data for the other liquids were taken with the shorter spacer.) The over-all instrumental linewidths (including laser linewidth, Fabry-Perot finesse, and effect of the finite hole size) were approximately 0.050 and 0.042 cm^{-1} , respectively, varying slightly for different alignments and laser running conditions.

Great care was taken to set the scattering angle accurately at 90° . We based our setting of the scattering angle on a right-angle prism. One face was set perpendicular to the axis of the collecting system by autocollimation. The laser and the mirror bringing the beam into the box were set with the prism in the sample position by requiring that the beam transmitted by the prism continue down the axis of the collecting system and that the reflections from the prism faces perpendicular to the beam send light back along the beam to the laser. Precision, square sample cells assured that the scattering angle remained 90° when the sample was placed in position for measurements. We believe that during the measurements, the angle was within $\pm 0.5^\circ$ of 90.0° giving an uncertainty in $\Delta\nu$ of $\pm 0.5\%$.

The ample size of our apparatus allowed us to make good use of a telescope in aligning the collecting optics and checking for extraneous scattering. For example, placing a telescope between the collecting lens (L_2) and the interferometer allowed us to look into the scattering volume. We were able to check the effectiveness of the baffles in this way and, more crucially, we checked each sample for dust which was easily seen in the volume crossed by the beam.

The cells used to hold liquids during measurement were precision, square, 1.00-cm-light-path cells made by Hellma GmbH and Company. They were carefully cleaned, including as a final and important step being scrubbed with a calcium carbonate and water paste, directly followed by dipping in concentrated nitric acid and rinsing in distilled water. They were dried in a stream of purified nitrogen and placed in the dust-free²¹ box where they were to be loaded. We found that an empty cell freshly cleaned in this way would give no detectable Rayleigh scattering on a trace made with the sensitivity used in taking the spectra of liquids. Since the surfaces of an empty cell scatter more light than those of a loaded cell we are sure that this source of extraneous scattering did not affect our results.

The liquids used in this experiment with the exception

²¹ This box was supplied with a flow of mechanically filtered air sufficient to keep it above the ambient atmospheric pressure and thus swept clear of dust.

of water were taken from sealed, pint bottles of reagent chemicals opened inside the dust-free box just prior to loading the cells. The liquids acetic acid, carbon disulfide, ethyl ether (anhydrous), methyl alcohol, and toluene were Baker-analyzed reagents. Benzene (thiophen free) and *n*-hexane (Spectranalyzed) were Fisher-Certified Reagents. The carbon tetrachloride was Merck reagent. The acetone was Matheson, Coleman & Bell (Spectroquality). The ethyl alcohol was U.S.P. (reagent quality) produced by U.S. Industrial Chemicals Company. The water sample was obtained by redistilling Tripure distilled water.

The liquids were loaded into freshly cleaned cells in the dust-free box. The bottled liquids were poured directly from the bottle through a clean thistle tube into the cell, the thistle tube having been first flushed with some of the liquid being loaded.

Two liquids could not be used directly and required distillation in order to get a dust-free sample. Distillation of water was essential since it is never available dust free. (It apparently disintegrates its storage containers.) Distillation of ethyl alcohol was necessary because the bottled liquid was quite dusty, in contrast to the other reagent liquids. A sample of distilled benzene was also prepared because benzene appears to be anomalous in its light-scattering properties. It was found that the distilled benzene sample gave a lower ($I_C/2I_B$) ratio so the data for this sample is given in the tables of our experimental results.

The distillation was done inside the dust-free box. A Yoe-type still, with two trap bulbs to prevent direct transfer of liquid between the evaporating flask and the condenser, was found to be very satisfactory for preparing dust-free samples. After running the still long enough to flush the condenser spiral of dust, the distilled liquids were loaded directly into the cells.

Good samples of ethyl alcohol and benzene were easily obtained. On the other hand water is notorious in its ability to pick up and hold dust and it did not come out of the still dust free. Nevertheless the dust that remained was not charged so that most of it settled out.

The fact that we were electronically detecting the scattered light allowed us to discriminate against the light scattered from dust in the samples. A particle of dust moving through the scattering volume while the interferometer is scanning over the Rayleigh component of the spectrum gives a spike superimposed on the trace of the Rayleigh peak. The dust, however, does not affect the trace of the Brillouin components. If the concentration of dust particles is small enough then these spikes are infrequent and so are easily distinguished from the smooth trace of the spectrum. Thus we have a direct way to test liquids for residual dust and in the present measurements to separate the molecular Rayleigh scattering from extraneous scattering due to dust.

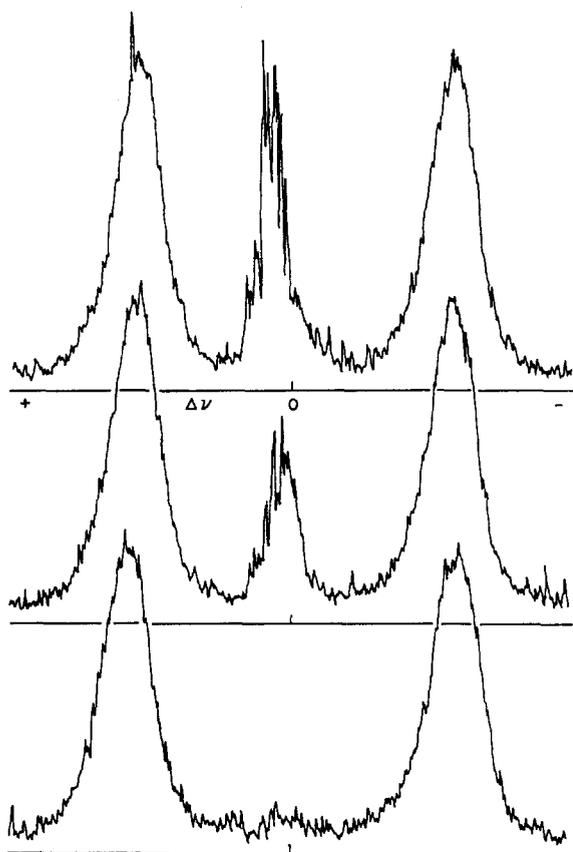


FIG. 2. Spectrum of light scattered from water. Traces from three consecutive orders of a single scan (top to bottom) showing the extraneous, unshifted scattering due to dust passing through the scattering volume.

For the case of water the spikes due to dust are not all temporally resolved, but in scanning over several orders the change in the average height of the Rayleigh component on the trace shows that dust is still present. We can then at least set an upper bound on the possible amount of molecular Rayleigh scattering.

Traces of the spectrum from our best water sample are given in Fig. 2 to illustrate the effect of dust and to show how small the upper limit of the molecular Rayleigh scattering intensity appeared in our work. These spectra are from consecutive orders of a single pressure scan of the interferometer. It is unfortunate that water is so difficult to free from dust because it presents a case where the effects of $(\partial\epsilon/\partial T)_\rho$ might appear.

In analyzing the spectral traces it was important to consider two instrumental problems. First, pressure scanning of the interferometer with a fixed leak results in a nonuniform (exponential) scan rate. This requires that an averaging technique be applied in computing the Brillouin shift from the distances between peaks on the chart. Our method was to measure the distance between Rayleigh components of the m and $m+2$ orders

and divide this into the distance between the Stokes and anti-Stokes components of the $m+1$ order. The quotient gives the Brillouin shift as a fraction of the free spectral range, correct to first order in $\Delta P/(P_0 - P)$. (ΔP is the pressure difference corresponding to one order, P is the pressure in the interferometer box at the $m+1$ order, P_0 is the ambient pressure outside of the box.) For exponential dependence of pressure with time the second-order error, expressed as a fraction, is

$$-\frac{1}{3}[\Delta P/(P_0 - P)]^2.$$

We ran spectra with $(P_0 - P)$ between 1 and $\frac{1}{2}$ atm. For the 1-cm spacer, ΔP is $\frac{1}{3}$ atm. This gives an error between -0.4% and 1.7% . The error in the mean of the sequence of measurements from one scan is expected to be -0.8% for a 1-cm spacer and -0.4% for a 1.5-cm spacer.

We tested this technique by making a scan with a 3-cm spacer in the interferometer. We divided the set of Rayleigh peaks on the trace into sets of three adjacent peaks. Considering these as model triplets, we calculated a Brillouin shift. Theoretically the result should have been one-third of an order. The mean of measurements for a single sequence of orders was $\frac{1}{3}(1 - 0.005)$ with a precision of $\pm 0.3\%$.

In treating the data presented in this paper, we did not apply a correction for this second-order error.

The second problem to be considered is that of limited finesse. We computed the ratio of peak heights, $H_C/(2H_B)$, and the ratio of widths, W_C/W_B , of the Rayleigh (R) and Brillouin (B) components from measurements on the trace. Assuming the integrated intensity to be proportional to the product of the height and the width, the ratio of intensities, $I_C/(2I_B)$, is calculated as the product of these ratios. But, on the traces the lines overlap and so a correction must be applied to the $I_C/(2I_B)$ ratios from correction factors for the heights and widths. Moreover, for the liquids benzene, toluene, carbon disulfide, and acetic acid there exists a background of inelastically scattered light on the traces, due to the so-called wings of the Rayleigh line. These wings are depolarized, but in contrast to the statement by Fabelinskii⁶ we do not find the depolarization to correspond to $\rho_u = \frac{6}{7}$. Instead of setting the background level using an assumed depolarization, we chose to use a numerical technique. This technique required knowing the true linewidths, i.e., not broadened by overlapping lines on the trace. These were taken from measured over-all finesse and the interorder spacing on the trace. The finesse for each spectrum was not known with great accuracy but since the corrections to be computed are not large, this caused only a small uncertainty in the final, corrected result.

The liquids not listed above did not show significant background intensity on the traces. This was checked by looking for depolarized scattering intensity and

finding it negligible compared to the intensity of the (polarized) Rayleigh and Brillouin components. For these liquids the base line of the components was taken at the zero level and overlap corrections were computed using a Lorentzian model of the line shapes and considering the overlap of only the adjacent peaks. In calculating the corrections the width of the Rayleigh peak was taken as the instrumental width increased by a factor of the ratio of the widths on the trace. Significant broadening of the Brillouin peak occurred only for acetic acid, carbon tetrachloride, hexane, and toluene. This agrees with the high-resolution observations of Chiao.¹⁰ For the rest of the liquids the width of the Brillouin peak was taken as equal to the instrumental width. In Fig. 3 we show a spectrum for carbon tetrachloride, a liquid showing broadened Brillouin com-

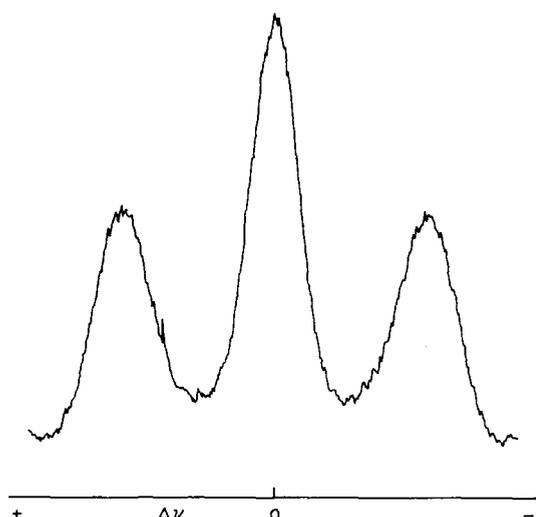


FIG. 3. Spectrum of light scattered from carbon tetrachloride.

ponents and in Fig. 4 we show a spectrum for ethyl alcohol, a liquid for which we could not detect broadening of these components.

For the liquids showing a background the calculation was begun by computing the expected height of the Rayleigh peak above the level of the minimum between the Brillouin components of adjacent orders, again using a Lorentzian model of the line shapes. The difference between the expected height and the measured height gives the distance between the level of the minimum between the Brillouin components and the true background level. With the level set in this way, the ratios and corrections are computed in the same way as before. As an example of a triplet superimposed on a background, the spectrum for benzene is shown in Fig. 5. On this spectrum we indicate the zero (dc dark current) level and the calculated background level.

The results obtained from the traces are given in

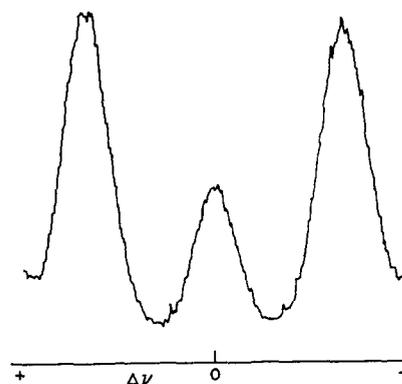


FIG. 4. Spectrum of light scattered from ethyl alcohol.

Tables IV and V, along with the correction factors applied to get the final ratios. The uncertainties indicated in the tabulations of the results were calculated from the statistics of the data plus, in the case of $I_C/2I_B$, the calculated uncertainty in the correction factors. We have not taken into account the possibility of a non-Lorentzian line shape. Such line shapes would cause us to have overestimated the overlap of the components. The most important deviation this could cause would be that the calculated position of the background level would be set too low in the cases where this calculation was necessary. In all cases the maximum change in the $I_C/2I_B$ ratio which this could produce, falls within the uncertainty already attached to the ratio.

IV. CONCLUSIONS

From the information collected in Table IV, it seems that the tendency of experimental $I_C/2I_B$ values to

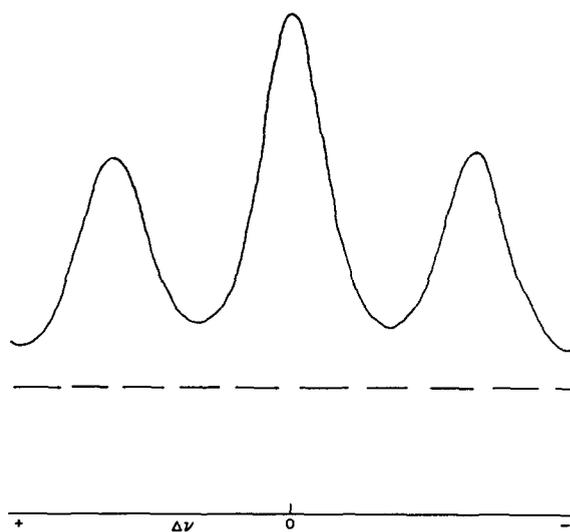


FIG. 5. Spectrum of light scattered from benzene. (The dashed line is the calculated level of the background.)

TABLE V. Brillouin shifts and acoustic velocities (20°C).

| | Observed shift | | Hypersonic velocity v^{hs} (10 ⁶ cm/sec) | | | v^{us} Ultrasonic velocity |
|----------------------|---------------------|----------|---|--|--|--|
| | (cm ⁻¹) | (Gc/sec) | Present | Other | | |
| Acetic acid | 0.119 | 3.57 | 1.16 ^a | 1.180 ^b 1.212 ^c | 1.140 ^f 1.139 ^g | 1.144 ^h |
| Acetone | 0.120 | 3.60 | 1.19 | 1.190 ^b 1.144 ^d 1.174 ^e | 1.190 ^f 1.139 ^g | 1.190 ^h |
| Benzene | 0.167 | 5.01 | 1.50 | 1.501 ^b 1.464 ^d | 1.470 ^f 1.290 ^g | 1.324 ^h |
| Carbon disulfide | 0.151 | 4.53 | 1.25 | 1.250 ^b 1.253 ^c 1.242 ^e | 1.265 ^f | 1.158 ^h |
| Carbon tetrachloride | 0.109 | 3.27 | 1.00 | 1.046 ^b 0.998 ^d 1.007 ^e | 1.040 ^f 0.932 ^g | 0.920 ^h |
| Ethyl alcohol | 0.118 | 3.54 | 1.16 | 1.162 ^b 1.169 ^g | | 1.150 ^h |
| Ethyl ether | 0.101 | 3.03 | 1.00 | 0.999 ^b 1.003 ^c 0.943 ^g | | 0.985 ⁱ |
| <i>n</i> -Hexane | 0.114 | 3.42 | 1.11 | | | 1.113 ⁱ |
| Methyl alcohol | 0.110 | 3.30 | 1.11 | 1.118 ^b 1.102 ^d 1.100 ^e | | 1.105 ⁱ |
| Toluene | 0.150 | 4.50 | 1.35 | 1.376 ^b 1.380 ^c 1.317 ^d | 1.314 ^f | 1.324 ^h |
| Water | 0.147 | 4.41 | 1.48 | 1.488 ^b 1.470 ^c 1.457 ^d | 1.471 ^e 1.480 ^f 1.518 ^g | 1.492 ^h 1.489 ^h |

^a From Eq. (1.1), $v = (\Delta\nu/n) [\lambda_0/2 \sin(\frac{1}{2}\theta)]$ with $\theta=90^\circ$ and $\lambda_0=6328 \text{ \AA}$.

^b See Ref. 10. Values for $\theta=180^\circ$ ($\nu\sim 6$ (kMc/sec)).

^c See Ref. 7.

^d See Ref. 8. ($\theta=90^\circ$.)

^e E. Garmire and C. H. Townes, *Appl. Phys. Letters* 5, 84 (1964). (Stimulated scattering $\theta=180^\circ$.)

^f L. L. Fabelinskii, *Soviet Phys.—Usp.* 5, 667 (1963) [*Usp. Fiz. Nauk* 77, 649 (1963)]. ($T=20^\circ\text{C}$.)

^g See Ref. 4.

^h K. K. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves*, (Academic Press Inc., New York, 1959), p. 362.

ⁱ See Footnote b, Table I.

exceed the values predicted by the Landau-Placzek theory is remedied in many cases by the inclusion of dispersion in the theory.

This is particularly evident for carbon disulfide since as Rank¹¹ points out, the simple LP prediction is clearly in disagreement with experiment, whereas the inclusion of dispersion leads to agreement between theory and experiment.

Our data for water indicate that the previous high values of $I_C/2I_B$ were probably due to parasitic scattering or sample contamination. Unfortunately, signal-to-noise limitations prevent us from accurately measuring the small water ratio and conclusively choosing between Fabelinskii's equation and the dispersion-corrected LP equation.

We have attempted to use thermodynamic constants

measured at 20°C, whenever possible, to avoid inaccuracies resulting from the common neglect of the temperature dependence of density, specific heats, compressibilities, refractive index, etc. The largest remaining uncertainty is in $(\rho\partial\epsilon/\partial\rho)_T$, and further measurements of this quantity (and particularly of its dispersion) would be useful.

Finally, we note that for two of the materials studied, benzene and acetic acid, there still remains an apparent disagreement which seems too large to attribute to uncertainties in the thermodynamic properties alone.²²

²² For additional discussion of many of these points, see the review article, I. L. Fabelinskii, *Usp. Fiz. Nauk.* 63, 355 (1957) [English transl.: *Advan. Phys. Sci.* 63, 474 (1957), AEC Translation 3973, Part 1 (1960)]. Also see R. D. Mountain, "On the Interpretation of Brillouin Spectra" (to be published).