function with a single zero at $X=X_0$. Physically, the coupling decreases for increasing $\eta$ when $\eta>1$ because of the increasing width of the region of attenuation (for the extraordinary wave) between the cutoff at $\omega_p^2 = \omega(\omega-\omega_c)$ and the hybrid resonance region.

For $\eta \rightarrow 0$, (29) and (30) give a step discontinuity in $q$ (and therefore in $\omega_p^2$) so the result that $T_p \rightarrow 0$ should be valid for any rapidly varying transition region within the limit defined by $\beta^2 < O[(c^2/\langle v_x^2\rangle_{\mathrm{av}})^{1/2}]$. In this case the coupling to plasma wave is small because the width of the coupling region decreases as $\eta$ decreases.

## ACKNOWLEDGMENTS

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# Light Scattering from Fluctuations in Orientations of $CS_2$ in Liquids*

S. L. SHAPIRO AND H. P. BROIDA
*Department of Physics, University of California, Santa Barbara, California*

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Frequency broadening caused by fluctuations in orientations of anisotropically polarizable molecules in liquid carbon disulfide and in liquid mixtures of carbon disulfide and carbon tetrachloride has been investigated by observing scattered light from an $Ar^+$ laser at 4880 Å. This scattering has been found to be a broad line with a maximum intensity at zero frequency shift. Intensities and half-widths of the scattered radiation were measured in carbon disulfide from 161 to 313°K; half-widths range from about 0.1 $cm^{-1}$ near the triple-point to 6 $cm^{-1}$ near the boiling point. Addition of $CCl_4$ to $CS_2$ at room temperature causes the line to narrow. These measurements show that the half-widths of the scattered radiation are approximately proportional to the temperature divided by the viscosity of the liquid, in agreement with Debye's simple picture for orientation scattering in an electromagnetic field. The line shape close to 4880 Å in $CS_2$ is found to be nearly Lorentzian, but details in the structure of the scattered-light spectrum show that there are other scattering processes. Line-shape measurements and polarization measurements are in agreement with theoretical predictions. The total scattering intensity in $CS_2$ is constant over the range of temperatures investigated. Measurement of the half-widths of the scattered radiation from anisotropic molecules appears to provide a way to obtain viscosities of liquids and the volume of interaction of molecular scatterers.

## I. INTRODUCTION

MOLECULES scatter light because of their polarizability. Optically anisotropic molecules scatter light with a change in frequency when their orientations are changing with time. For brevity we shall call this depolarized-light orientation scattering. The motion of the individual molecules in a fluid is influenced by thermal collisions with other molecules and by the viscous damping of the medium, so that details of the rotational diffusion of molecules in liquids may be examined by studying the scattered light. Although scattering from anisotropic molecules was observed as early as 1928 by Raman and Krishnan,[1] there have been very few detailed investigations of this effect. Part of the difficulty of early investigators was due to the use of Hg light sources with the consequent difficulty of isolating the orientation scattering from instrumental scattering. Recently, several authors have reported observing stimulated Rayleigh scattering in liquids using pulsed ruby lasers,[2,3] but there have been no reported accurate measurements of linewidths or shapes of the scattered radiation using a ruby-laser source. Some measurements of orientation scattering using an $Ar^+$ laser were recently reported.[4]

A study of scattered radiation from liquid samples has been undertaken using an $Ar^+$ laser to obtain precise measurements of half-widths, line shapes, depolarization ratios, and intensities and their correlation with theory. It is found that the study of light scattering from anisotropic molecules provides a method of studying rotational diffusion and possibly also a way of measuring viscosities of liquids and the interaction size of molecules. In addition, a study of the scattering as the liquid approaches the triple point may provide information on the ordering in the liquid and solid.

## II. THEORY

Scattering of light is due to induced dipole moments produced by the oscillating electric field of the light wave. Fluctuations in the orientation of anisotropic molecules lead to scattering of light with a small fre-

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[*] Supported in part by the Advanced Research Projects Agency and the Office of Naval Research.

[1] C. V. Raman and K. S. Krishnan, Nature **122**, 278 (1928); **122**, 882 (1928).

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

[3] D. I. Mash, V. V. Morozov, V. S. Starunov, and I. L. Fabelinskii, JETP Pis'ma v Redaktsiya **2**, 41 (1965) [English transl.: JETP Letters **2**, 25 (1965)].

[4] S. L. Shapiro, M. McClintock, D. A. Jennings, and R. L. Barger, Proc. IEEE, J. Quantum Electron. **2**, 89 (1966).

quency shift and depolarization. The energy of the induced dipole moment interacting with the field is too small to produce reorientation of the molecules except under extremely intense electric fields such as provided by a *Q*-switched ruby laser. The relaxation time is given by $\tau=1/\omega_{1/2}$, where $\omega_{1/2}$ is the frequency [$\frac{1}{2}$ the full width at half-maximum (FWHM) intensity] shift at which orientation scattering reaches half-maximum intensity. The relaxation time is the time needed for the distribution of molecular orientations to approach a random distribution from fluctuations from equilibrium. Because of the thermal motion of the surrounding molecules in the liquid, collisions tend to randomize the orientational distribution. The intensity of the scattered light is proportional to the optical anisotropy. Thus molecules which have large differences in their polarizabilities in different directions are excellent scatterers of this radiation, while molecules which are isotropic in their polarizabilities are poor scatterers.

Debye has developed an approximate relation for the relaxation time for the molecular distribution to return to a random distribution in a polar liquid subject to a dc electric field which is given as follows[5]:

$$\tau_D=4\pi\eta a^3/kT, \tag{1}$$

where $\tau_D$ is the time for the nonrandom part of the distribution to go to $1/e$ of its value at time $t=0$, $\eta$ is the macroscopic viscosity of the medium surrounding the molecule, $a$ is the average radius of the molecule when the molecule is approximated as a sphere, $T$ is the temperature of the medium, and $k$ is the Boltzmann constant. For nonpolar molecules in an ac electric field this relation must be modified and the relaxation time is given by

$$\tau=\tau_D/3=4\pi\eta a^3/3kT. \tag{2}$$

This relaxation time is given also by Leontovich, who has developed a theory for the scattering of light by anisotropic molecules in liquids.[6] He has obtained equations for determining the change of the anisotropy tensor with time, assuming that small disturbances from equilibrium are linear, and that the equations are of the first order with respect to the time derivative of a tensor which measures the deviation from isotropy. His kinetic equations for the anisotropy tensor can be obtained from Debye's conceptions of rotations of molecules in a liquid.

Leontovich also has obtained equations for the intensity of the polarized components of the light scattered by the liquid and these can be easily checked in this experiment. If the $x$ axis is denoted as the direction of the incident laser beam, the $y$ axis as the direction of observation of the scattered light, and the $z$ axis is chosen as perpendicular to the $xy$ plane of scattering and in the direction of polarization of the incident beam, then the intensity of the light scattered from anisotropic molecules when the analyzer is positioned so that it will pass light polarized perpendicular to the plane of scattering is given by

$$I_\perp=(2A^2/3\eta)[\tau^2/(1+\omega^2\tau^2)], \tag{3}$$

where $\tau$ is the relaxation time, $\omega$ is the frequency shift due to orientation scattering, $\eta$ is the viscosity of the liquid, and $A$ is the proportionality constant between the optical anisotropy tensor and the change in the dielectric tensor produced by the optical anisotropy. The intensity with the analyzer positioned parallel to the plane of scattering is given by

$$I_{\shortparallel}=(A^2/2\eta)[\tau^2/(1+\omega^2\tau^2)]. \tag{4}$$

Thus $I_{\shortparallel}/I_\perp=\frac{3}{4}$, and the line shape should be Lorentzian with a half-width equal to $2\omega_{1/2}$.

Rytov[7] has extended Leontovich's theory by using correlation theory to describe the wings of the Rayleigh line. He considers fluctuations of anisotropy associated with changes in the deformation tensor. Shear deformations give rise to anisotropic fluctuations which cause light scattering. Ginzburg[8] has pointed out, however, that even in the absence of stress deformations, shear deformations, and temperature fluctuations, a medium consisting of anisotropic molecules can scatter light as a result of fluctuations in the orientations of the axes of the molecules.

Starunov[9] has extended the theories of Leontovich and Rytov by considering fluctuations of orientation resulting from rotational Brownian motion and fluctuations of anisotropy due to elastic oscillations. His expressions for intensity of the scattered light under the same experimental conditions as Eqs. (3) and (4) can be put in the form

$$I_\perp=\tfrac{4}{3}I_{\shortparallel}=(\alpha_1-\alpha_2)^2\left[\frac{\beta}{((1-I'\omega^2/4kT)^2+\omega^2\tau^2)}+\frac{\gamma}{((1-\omega^2/\omega_c{}^2)^2+(\zeta/\mu)^2\omega^2)}\right], \tag{5}$$

where $\alpha_1$, $\alpha_2=\alpha_3$ are the principal polarizabilities of the molecule, $I'$ is the molecular moment of inertia, $\zeta=8\pi a^3\eta$ is the Stokes coefficient for a sphere of radius $a$ rotating in a medium of viscosity $\eta$, $\tau$ is the Debye relaxation time given by Eq. (2), $\mu$ is an elastic force constant, and $\omega_c=\sqrt{\mu/I'}$ is the oscillation frequency. In Eq. (5) $\beta$ and $\gamma$ depend on the temperature $T$, the fourth power of frequency of the incident radiation $\omega_0{}^4$,

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[5] P. Debye, *Polar Molecules* (Dover Publications, Inc., New York, 1929), Chap. V.

[6] M. Leontovich, J. Phys. USSR **4**, 449 (1941).

[7] S. M. Rytov, Zh. Eksperim. i Teor. Fiz. **33**, 514 (1957) [English transl.: Soviet Phys.—JETP **6**, 401 (1958)].

[8] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **34**, 246 (1958) [English transl.: Soviet Phys.—JETP **7**, 170 (1958)].

[9] V. S. Starunov, Doklady Akad. Nauk SSSR **153**, 1055 (1963) [English transl.: Soviet Phys.—Doklady **8**, 1206 (1964)].

the distance $R$ of observation from the sample and also upon $\mu$, $\zeta$, and $\tau$. According to Starunov, if it is assumed that at low frequencies the molecular motion has the nature of self-diffusion, then the first term describes the motion of the molecules at low frequencies, and the last term describes the motion of the molecules at high frequencies.

Recently, Steele[10] has given relationships between the angle-dependent properties of a fluid made up optically anisotropic molecules and the intensity of the scattered light. He has shown that light-scattering experiments may yield information on angular correlation functions of molecules. Steele obtains relations which give information concerning the time dependence of certain functions of the molecular orientation, as well as giving a measure of the static angular correlations in the liquid. He relates the integrated intensity of depolarized orientation scattering to the static angular correlations. The theories of Leontovich, Rytov, Starunov, and Steele all predict Lorentzian line shapes for the orientation scattering for molecules which have two principal polarizabilities which are the same and when inertial effects are neglected. All the theories predict that the ratio of the light polarized perpendicular to that polarized parallel to the plane of scattering is $\frac{4}{3}$ for the orientation scattering. However, recent experimental results[4,11,12] suggest that the depolarization of the orientation scattering differs from $\frac{4}{3}$ in some liquids.

## III. EXPERIMENTAL TECHNIQUE

$CS_2$ was chosen as a sample scatterer because it is a highly polarizable molecule with much different polarizabilities along the internuclear axis and perpendicular to the internuclear axis. $CCl_4$, on the other hand, is a poor scatterer because it is an isotropic molecule. Thus, if $CS_2$ is mixed with $CCl_4$, the $CS_2$ molecules should cause most of the scattering, and the rotational diffusion of $CS_2$ molecules can be studied in a new environment.

Scattered light from samples of $CS_2$, $CCl_4$, and mixtures of $CS_2$ and $CCl_4$ were observed at 90° with respect to the incident light beam from an $Ar^+$ laser. The laser output, which was monitored by a phototube, was about 3 mW at 4880 Å and could be maintained constant to $\pm 1\%$. The scattered light was focused with a lens on to a 0.8-m $f/10$ Fastie-Ebert scanning monochromator with a photoelectric recording attachment. With a monochromator slit width of 17 $\mu$, the instrumental resolution was 0.17 Å (0.7 $cm^{-1}$) at 4880 Å. For scans of carbon disulfide at 161°K, a double-pass $f/10$ Fastie-Ebert monochromator with a slit width of 10 $\mu$ and a resolution of 0.09 Å (0.38 $cm^{-1}$) was used. Experimentally it was found by observing the scattered light with slits of different widths that no instrumental width correction needed to be made to the measured linewidth when the instrumental width was less than 1/7 the width of the line to be measured. As the instrumental width approached the width of the line, the corrections become large. Instrumental width corrections obtained experimentally agreed closely with the theoretical corrections. In this experiment the slit-width function on the monochromator was found to be Gaussian, whereas the light scattered from anisotropic molecules is Lorentzian. The folding of a Gaussian instrumental profile and a Lorentzian line function is a Voight function, values of which have been tabulated recently in convenient form by Davies and Vaughn.[13] A knowledge of the half-width of the experimentally measured line (a Voight function) and of the instrumental function (Gaussian) is sufficient to determine the half-width of the actual distribution of the scattered light (Lorentzian) and can be found from the tables. The correction turned out to be extremely important for narrow half-widths such as are obtained at low temperatures in liquid $CS_2$. When the measured linewidth is seven times the instrumental width, the correction amounts to only 2%, whereas if the linewidth is three times the instrumental width, the correction becomes 12%, and at one and one-half times the slit width, it becomes 45%. Over most of the temperature range studied in this experiment and for most mixtures, this correction was small since the instrumental linewidth was small compared to the natural line, but for mixtures containing 10% $CS_2$ in $CCl_4$ the correction amounted to 9%, and for $CS_2$ just above the triple point this correction amounted to 65%.

A polarizer was used to polarize the laser beam perpendicular to the plane of scattering while an analyzer was positioned successively both perpendicular and parallel to the plane of scattering. With the analyzer positioned in either way, the orientation-scattered light close to the incident laser frequency has the same shape and half-width. However, for the measurements of half-widths of the orientation scattering, it was more convenient to analyze light which is polarized parallel to the plane of scattering. This is because the light which is polarized perpendicular to the plane of scattering is composed not only of a broad line due to orientation scattering, but also a triplet, two lines of which are Brillouin components arising from the scattering of light by phonons in the liquid, and the third of which is the Rayleigh line arising from entropy fluctuations at constant pressure.[14] Thus slight errors in half-width

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[10] W. A. Steele, in *Proceedings of the IUPAP Conference on Statistical Mechanics and Thermodynamics, Copenhagen, 1966*, edited by Dr. Thor Bak (W. A. Benjamin, Inc., New York, to be published). See also R. Pecora and W. A. Steele, J. Chem. Phys. **42**, 1872 (1965).

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

[12] D. H. Rank, Amos Hollinger, and D. P. Eastman, J. Opt. Soc. Am. **56**, 1057 (1966).

[13] J. Tudor Davies and J. M. Vaughn, Astrophys. J. **137**, 1302 (1963).

[14] See, for example, R. D. Mountain, Rev. Mod. Phys. **38**, 205 (1966).

measurements introduced by subtracting the Rayleigh line and the Brillouin lines are eliminated by viewing light with the polarization vector parallel to the plane of scattering. The Rayleigh and Brillouin components can be eliminated because they are polarized perpendicular to the plane of scattering, whereas the orientation scattering is highly depolarized.

All liquids used in this experiment were carefully vacuum-distilled from spectroscopic-grade liquids. The liquids were distilled into a graduated cylinder and then redistilled into scattering cells which had been previously rinsed under vacuum with a vacuum-distilled solution. No Tyndall scattering due to dust particles was visible when the laser beam passed through the liquids. Liquids of spectroscopic purity which have not been vacuum-distilled can have strong scattering due to dust at the incident laser frequency. With high resolution the dust contribution can be differentiated from the line since light scattered from dust has a very small frequency shift, but a problem still arises in deciding the position of peak intensity for the orientation scattering. Two linear polarizers could reduce the laser beam to less than 0.01% when crossed, and could be aligned so that the light transmitted is only the light polarized parallel to the plane of scattering. This is important since the intensity of the Rayleigh component and Brillouin components is much greater at zero frequency shift than the anisotropic scattered component in $CS_2$ or $CCl_4$. A small transmission in the perpendicular component by a polaroid positioned parallel to the plane of scattering could therefore significantly alter the results.

For observing scattered radiation from $CS_2$ as a function of temperature, a cell which was 25 mm long and 28 mm in diameter was mounted in a Dewar and then viewed at right angles with respect to the incident laser beam. For observing scattering from mixtures of $CS_2$ and $CCl_4$, identical cells 50 mm long and 28 mm in diameter were used.

## IV. EXPERIMENTAL RESULTS

### A. Temperature Dependence of Scattered Radiation in $CS_2$

The half-widths of the depolarized light scattered by orientation fluctuations were measured in $CS_2$ from 161 to 313°K. A copper-Constantan thermocouple was immersed in the liquid to measure temperature. By pumping on liquid ethylene as a refrigerant, temperatures as low as 161°K were reached. A methyl alcohol–dry ice bath was used to obtain temperatures between 203 and 293°K, while water was heated with a resistor to obtain temperatures between 293 and 313°K. Figure 1 shows scans of the scattered light with the analyzer positioned perpendicular and parallel to the plane of scattering.

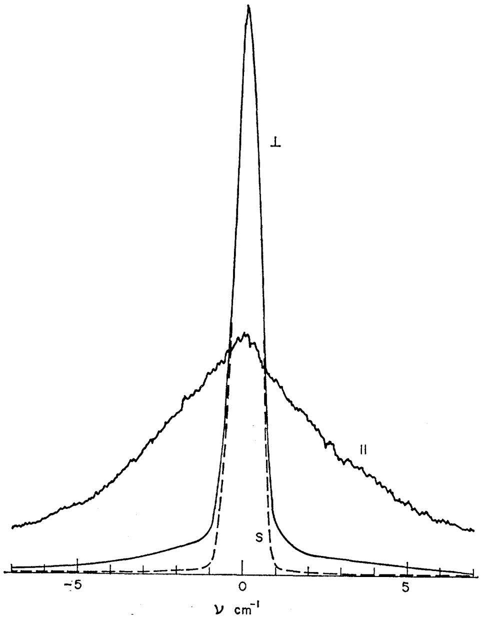

FIG. 1. Frequency scans of light scattered from liquid $CS_2$ near room temperature. Light polarized perpendicular to the plane of scattering, ⊥, consists of the unresolved Rayleigh and Brillouin lines and the wing due to fluctuations of the molecular orientations. Light polarized parallel to the plane of scattering, ||, is due to orientation scattering only. Also shown is the instrumental line-shape function $S$ with the same peak height as the ⊥ scattering. If the polarization scans are at the same scale, the intensity ratio of the parallel to perpendicular components in wings of the line is $\frac{3}{4}$.

Measured values $\nu_{1/2}$ of half-widths at one-half the intensity maxima of the scattered radiation plotted as a function of temperature are shown in Fig. 2. Since viscosity measurements in $CS_2$ have been reported[15] from 260 to 313°K, the results can be compared with an assumption of proportionality of the half-width to $T/\eta$. It can be seen in Fig. 2 that $\nu_{1/2}$ follows a $T/\eta$ dependence between 260 and 313°K. Also, it can be

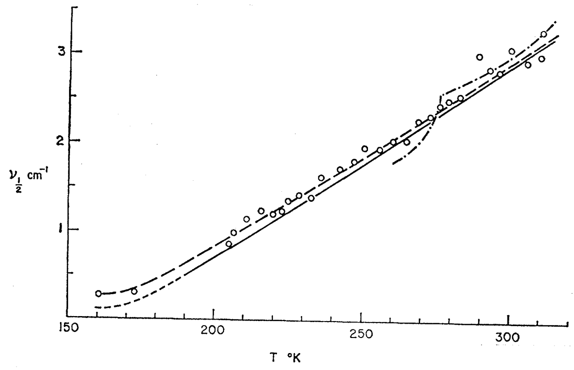

FIG. 2. Temperature dependence of frequency shift at half-maximum intensity due to orientation scattering by $CS_2$; dashed line represents experimental measurements; solid line represents experimental measurements corrected for instrumental broadening; dashed-dot line represents plot of $T/\eta$ versus $T$.

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[15] *Handbook of Chemistry and Physics* (The Chemical Rubber Company, Cleveland, Ohio, 1965), p. F-34.

seen that the half-width of the orientation scattering becomes very small as the liquid approaches the triple point of $CS_2$ at 161°K. The value of $\nu_{1/2}$ near the triple point of $CS_2$ is about 0.1 to 0.15 $cm^{-1}$ after correcting for instrumental broadening. However, the width of the multimode laser beam is approximately 0.12 $cm^{-1}$, so that this value of 0.1 $cm^{-1}$ for $\nu_{1/2}$ is an upper limit. From Fig. 2 the half-width is also approximately proportional to the temperature minus the triple-point temperature. This is not inconsistent with $\nu_{1/2}$ being approximately proportional to $T/\eta$ because of the way the viscosity varies. Uncorrected frequency scans of the light scattered from $CS_2$ at different temperatures are shown in Fig. 3.

The relative intensities as measured by the area under the intensity profile of orientation scattering in $CS_2$ at 215 and at 284°K were found to be the same within 3%. The half-width as measured at half-maximum intensity at 215°K is about $\frac{1}{3}$ of the half-width as measured at 284°K, but the amplitude at zero frequency shift is about 3 times as great at the lower temperature.

Several lines appeared in the room-temperature spectrum of light polarized perpendicular to the plane of scattering which could not be attributed to grating ghosts, to the emission lines of the $Ar^+$ discharge, or to known Raman lines. These observed lines occur at 306, 457, and 529 $cm^{-1}$. No explanation has as yet been found for these lines. One additional note of interest is that another line begins to appear in liquid $CS_2$ near the triple point of the liquid at 52 $cm^{-1}$.

### B. Orientation Scattering from Liquid Mixtures of $CS_2$ and $CCl_4$

In mixtures of $CS_2$ and $CCl_4$, orientation scattering is mainly due to the $CS_2$ because the polarizability of $CS_2$ is highly anisotropic, whereas $CCl_4$ is isotropic. The intensity at zero frequency shift for the orientation-scattered light for various mixtures of $CS_2$ and $CCl_4$ is shown in Fig. 4. It is evident from the results that the scattered intensity at zero frequency shift is strictly proportional to the $CS_2$ concentration except at very low concentrations. The total scattered radiation at room temperature was found experimentally to be about 60 times weaker in $CCl_4$ than in $CS_2$. The relative intensities of scattering for the two liquids were measured by taking very large slits on the monochromator, 200 $\mu$, and integrating the area under the curves of the scattered light.

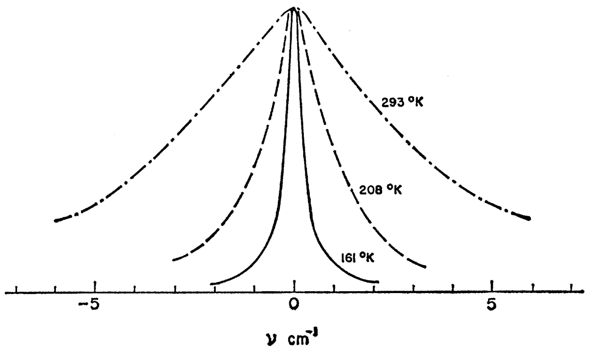

FIG. 3. Orientation scattering from $CS_2$ at different temperatures. The frequency scans show the scattered light polarized parallel to the plane of scattering between the incident laser beam at 4880 Å and the detection instrument at an angle of 90° with respect to the incident beam. The curves are not to scale as the total integrated intensity remains approximately constant as a function of temperature.

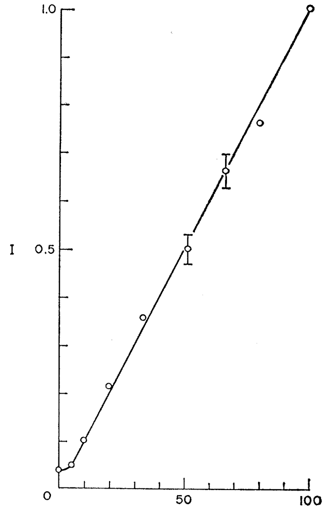

FIG. 4. Peak intensity of scattering at zero frequency shift in mixtures of $CS_2$ and $CCl_4$ at 20°C. The intensities relative to the intensity of pure $CS_2$ are shown along the vertical axis while the percent $CS_2$ by volume is indicated along the horizontal axis.

The viscosity of the mixture was increased from 0.362 to 0.963 cp by taking mixtures ranging from pure $CS_2$ to mixtures of 5% $CS_2$ by volume. The resulting measured half-widths are plotted versus percent concentration by volume of $CS_2$ in Fig. 5. A plot of the

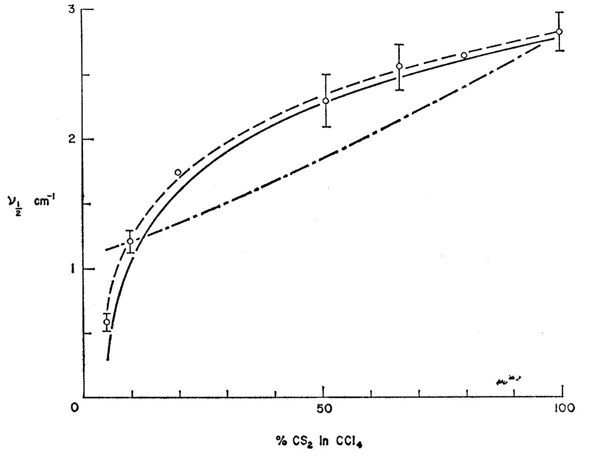

FIG. 5. Frequency broadening at half-maximum intensity due to fluctuations of orientation of $CS_2$-$CCl_4$ mixtures at 20°C. The percent $CS_2$ by volume is indicated along the horizontal axis: Dashed line represents experimental measurements; solid line represents experimental measurements corrected for instrumental effects; dash-dot line represents theoretical results based on proportionality of the frequency broadening to the inverse of the viscosity.

inverse viscosity versus percent concentration of $CS_2$ is also shown in Fig. 5. Since viscosity data on mixtures of $CS_2$ and $CCl_4$ were not available, viscosity values were approximated in a simple manner by taking linear combinations of the viscosity of the separate constituents weighted in proportion to the number of molecules of each constituent in the sample. This approach is too simple since $CS_2$ and $CCl_4$ molecules have much different shapes; $CS_2$ is nearly an ellipsoid of revolution, whereas $CCl_4$ is a sphere. Thus if a coordinate system is fixed in the molecule with the $z$ axis along the internuclear axis and the $x$ and $y$ axes perpendicular to the internuclear axis, two of the friction constants for rotation, $\xi_x=\xi_y$, are the same, and differ from the third friction constant $\xi_z$. This means that the molecule can orient more easily in certain directions. Our approximation for the viscosity in the mixture also neglects the possibility of short-range order in the liquid. It is a difficult theoretical problem to predict the angular correlations between different molecules. However, according to Steele,[10] information on the angular correlation functions can be found by measuring the depolarization of the scattered light. Using the data in Table I from which depolarization ratios can be found, Steele's formulas predict that the arrangement of $CS_2$ molecules about a central $CS_2$ molecule favors orientations where the angle between the internuclear axes is such that the molecules are perpendicular rather than parallel.[16]

For $CS_2$ mixed with $CCl_4$ the total intensity changes substantially for different mixtures even though account is taken of the fact that the total number of $CS_2$ scatterers in mixtures of $CS_2$ and $CCl_4$ is less at lower concentrations.

Since the scattered radiation is approximately Lorentzian, the total intensity is proportional to the product of the intensity at zero frequency shift and the full width at half-maximum intensity. But since the intensity at zero frequency shift is directly proportional to the concentration of $CS_2$ as was shown in Fig. 4, the intensity at zero frequency shift is a constant for all $CS_2$ mixtures if the data is corrected to consider an equal number of scattering centers. Thus the FWHM intensity becomes a measure of the relative total intensities scattered by a $CS_2$ molecule in different mixtures, and hence the results in Fig. 5 show that the total orientation scattering is significantly altered by the surrounding molecules in liquid mixtures. It appears that some of this deviation occurs because the local field in the liquid acting at the individual molecules is different from the applied macroscopic field.[17] The deviation associated with this effect is large in liquid mixtures when the indices of refraction $n$ of the liquids are very different. Since the intensity is approximately proportional to $(n^2+2)^4$ and the indices of refraction of liquid $CS_2$ and $CCl_4$ at room temperature and at 4880 Å are 1.65 and 1.45, respectively, the correction due to the local field in the mixture may become considerable. Thus in mixture which contains 50% $CS_2$ by volume, a $CS_2$ molecule should scatter approximately 75% as much light as a $CS_2$ molecule in the pure liquid, and in a mixture containing 10% $CS_2$ by volume a $CS_2$ molecule should scatter about 60% as much light as it does in pure $CS_2$. In addition, since viscosity is a measure of hindrance to translation and not to rotation, a molecule in an environment which approaches spherical symmetry may experience little hindrance to rotation even though the viscosity of the system is large. Hence part of the deviation at low concentrations from the simple viscosity approximation shown in Fig. 5 may be due to the fact that $CS_2$ molecules find themselves in an environment approaching spherical symmetry and there may be less hindrance to rotation.[16]

TABLE I. Polarization ratios and intensity ratios for orientation scattering $I_A$. Rayleigh radiation due to entropy fluctuations $I_C$ and Brillouin components $2I_B$.

| Sample | $T$(°K) | $I_{A\parallel}/I_{A\perp}$ | $(I_C+2I_B)/I_A$ | $I_C/I_A$[a] |
|---|---|---|---|---|
| $CS_2$ | 215 | 0.74±0.05 | 0.17 | [b] |
| $CS_2$ | 283 | 0.76±0.05 | 0.39 | [b] |
| $CS_2$ | 294 | 0.75±0.03 | 0.47 | 0.20 |
| $CS_2$ 10%+$CCl_4$ 90% | 293 | 0.70±0.10 | ~12.5 | [b] |
| $CS_2$ 53%+$CCl_4$ 47% | 293 | 0.76±0.02 | 1.11 | [b] |
| $CS_2$ 67%+$CCl_4$ 33% | 293 | 0.77±0.06 |  | [b] |
| $CCl_4$ | 293 | [c] | ~33[d] | 13.8 |

[a] The results of this column were calculated using values of $I_C/2I_B$ taken from H. Z. Cummins and R. W. Gammon, J. Chem. Phys. **44**, 2785 (1966).
[b] $I_C/2I_B$ data not available.
[c] $I_{A\perp}$ measurement was not possible because $I_B$ and $I_C$ dwarf $I_A$.
[d] Calculated on the assumption that $I_{A\parallel}/I_{A\perp}=0.75$.

### C. Polarization Measurements

From Eqs. (3) and (4) or (5) for linearly polarized light perpendicular to the plane of scattering, the theoretical ratio of the intensity of the orientation-scattered light polarized parallel to the plane of scattering to that polarized perpendicular to the plane of scattering is three fourths. Experimentally this ratio can be found by positioning the analyzer successively so that it passes light polarized perpendicular or parallel to the plane of scattering. The results are shown in Table I for various mixtures and temperatures. It is apparent that the results are in excellent agreement with the theory. Experimentally a correction factor was introduced because of the polarization effects of the monochromator. This correction factor was found by taking totally depolarized Hg light at 4916 Å and finding the intensity of the light passing perpendicular and parallel to the plane of scattering by the polarizer as recorded by the instrument. It was found that the monochromator discriminated against light polarized perpendicular to the plane of scattering due to the fact that the grating causes polarization effects. This correction increased the measured perpendicular com-

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[16] W. A. Steele (private communication).

[17] G. Eckhardt and W. Wagner, J. Mol. Spectry. **19**, 407 (1966).

ponent by 1.55, as compared to the measured parallel component. The results in Table I have taken this correction factor into account. Shown in columns four and five of Table I are the experimentally obtained ratios of the intensities of the Rayleigh scattering plus the Brillouin scattering as compared to the orientation scattering in $CS_2$, and the ratio of the Rayleigh scattering to the orientation scattering. The intensities were obtained by integrating the area under the curves.

### D. Line Shape of the Orientation Scattering

The intensity of the scattered radiation was studied at various frequency shifts from the incident laser frequency. The relative intensities at various frequency shifts for light polarized parallel to the plane of scattering is given in Table II for $CS_2$ at room temperature. The calculated results for a Lorentzian line and a Gaussian line of the same half-width also are given. The Lorentzian curve gives a much better fit than a Gaussian curve to the experimental shape. Whereas a Gaussian curve would reach "zero" ($10^{-6}$) intensity three half-widths away from the center of the line, the actual experimental line is easily detectable 200 $\text{cm}^{-1}$ away from the central peak. Since the instrumental function of the monochromator is very nearly Gaussian, and much less than the linewidth of the scattered light, there is little doubt that the radiation is indeed the non-Gaussian orientation-scattered radiation.

The intensity distribution may be studied by plotting the inverse of the intensity at different frequency shifts versus the square of the frequency shift. A Lorentzian intensity distribution yields a straight line on such a plot. At room temperature (293°K) the plot is a straight line over the first 10 $\text{cm}^{-1}$. At frequency shifts greater than 10 $\text{cm}^{-1}$, the line shape differs from the Lorentzian shape because of increased intensity over the pure Lorentzian shape. At 233°K, the line shape is Lorentzian for the first three to four $\text{cm}^{-1}$, while at 161°K the shape is Lorentzian for only the first two $\text{cm}^{-1}$. The line shape appears to be Lorentzian for the first two half-widths except for intensity deviations very near $\nu=0$. At $\nu=0$ an increase of intensity is found for scattered light polarized parallel to the plane of scattering. The spectrum of the scattered light at two temperatures is shown in Fig. 6. The plot is logarithmic, so that a large range of frequency shifts and intensities can be

TABLE II. Line shape of orientation light scattering from anisotropic $CS_2$ molecules. Light polarized parallel to plane of scattering.

| Frequency shift $\nu$ ($\text{cm}^{-1}$) | Experimental ratio of intensity to peak intensity (anti-Stokes side) | Lorentzian with same half-width | Gaussian with same half-width |
|---|---|---|---|
| 0 | 1.00 | 1.00 | 1.00 |
| 0.5 | 0.95 | 0.97 | 0.98 |
| 1 | 0.81 | 0.90 | 0.93 |
| 2 | 0.64 | 0.70 | 0.73 |
| 3 | 0.49 | 0.50 | 0.50 |
| 4 | 0.37 | 0.36 | 0.29 |
| 5 | 0.29 | 0.26 | 0.15 |
| 6 | 0.23 | 0.20 | 0.06 |
| 7 | 0.19 | 0.15 | 0.02 |
| 8 | 0.16 | 0.12 | 0.007 |
| 10 | 0.13 | 0.08 | 0.0004 |
| 12 | 0.10 | 0.06 | $\sim 10^{-6}$ |
| 14 | 0.09 | 0.04 | |
| 20 | 0.07 | 0.02 | $\sim 10^{-11}$ |
| 40 | 0.022 | 0.0055 | |
| 60 | 0.008 | 0.0025 | $\sim 10^{-120}$ |
| 80 | 0.0046 | 0.0014 | |
| 100 | 0.00160 | 0.00088 | |
| 110 | 0.00090 | 0.00073 | |
| 120 | 0.00065 | 0.00061 | $\sim 10^{-500}$ |
| 140 | 0.00052 | 0.00045 | |
| 160 | $\sim$0.0003 | 0.00035 | |

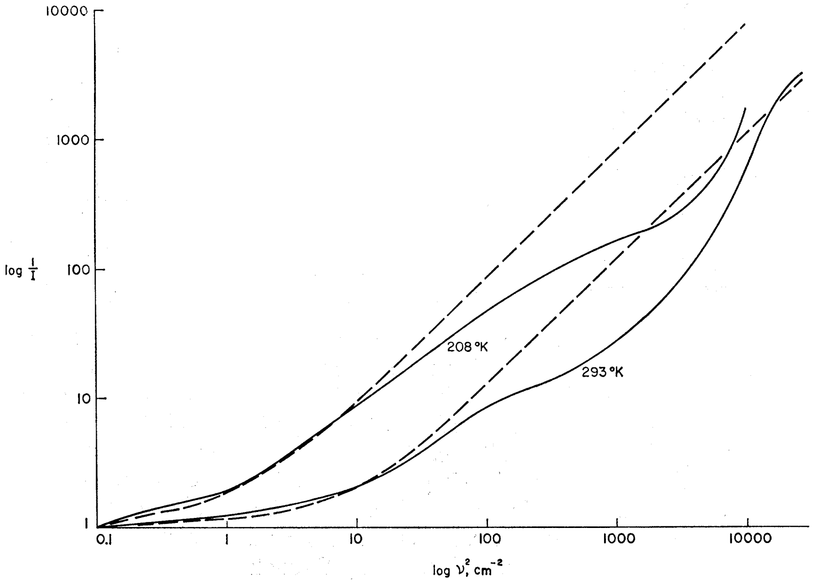

FIG. 6. Behavior of broadening in liquid $CS_2$ at large frequency shifts. Plot of logarithm of inverse intensity relative to inverse intensity at zero frequency shift as a function of the logarithm of the square of the frequency shift: Solid line represents experiment; dashed line represents Lorentzian shape of same width at half-intensity.

TABLE III. Comparison of anti-Stokes intensity $I_{AS}$ to Stokes intensity $I_S$ at different frequency shifts from peak intensity. Column 2 shows the experimental values obtained with the analyzer parallel to the plane of scattering, while column 3 shows the values with the analyzer perpendicular to the plane of scattering. Column 4 shows theoretical results expected on the basis of Maxwell-Boltzann statistics.

| $\nu$ (cm$^{-1}$) | $(I_{AS}/I_S)_{\parallel}$ | $(I_{AS}/I_S)_{\perp}$ | $(I_{AS}/I_S)_{\text{theory}}$ |
|---|---|---|---|
| 1 | 1.0 | ~0.95 | 0.995 |
| 5 | 1.0 | 1.0 | 0.98 |
| 10 | 0.93 | 0.87 | 0.95 |
| 20 | 0.83 | | 0.91 |
| 40 | 0.81 | | 0.82 |
| 50 | 0.81 | 0.73 | 0.78 |
| 60 | 0.76 | 0.68 | 0.74 |
| 75 | 0.75 | 0.63 | 0.69 |
| 85 | 0.65 | 0.69 | 0.66 |
| 100 | 0.64 | 0.55 | 0.61 |
| 120 | 0.59 | 0.62 | 0.55 |
| 150 | 0.48 | 0.65 | 0.48 |
| 170 | 0.4 | [a] | 0.43 |
| 200 | ~0.4 | [a] | 0.37 |
| 250 | ~0.3 | ~0.2 | 0.29 |
| 300 | ~0.2 | | 0.23 |

[a] Grating ghosts near this position.

accommodated. The orientation scattering follows the Lorentzian shape for small frequency shifts, but the intensity increases over a Lorentzian shape at higher frequencies. The results of the line shapes for liquid mixtures are more complicated. The line shape deviates from the Lorentzian shape over the whole spectrum. The intensity near $\nu=0$ is very large. When the inverse of the intensity is plotted versus the square of the frequency shift, it is found that the inverse intensity increases rapidly at first, but then increases less rapidly up to the first 10 cm$^{-1}$.

The ratios of the anti-Stokes intensity to the Stokes intensity at different frequency shifts from the main peak in liquid $CS_2$ are given in Table III for the scattered radiation polarized both parallel and perpendicular to the plane of scattering. A comparison of Maxwell-Boltzmann statistics to the measured values also is given. The ratio of the intensity of the anti-Stokes radiation to the Stokes radiation for a small energy shift $\hbar\omega$ should be given by $e^{-\hbar\omega/kT}$, where $\omega$ is the frequency shift of the scattered radiation, $T$ is the temperature of the medium, and $\hbar$ and $k$ are the Planck and Boltzmann constants, respectively.

## V. COMPARISON OF EXPERIMENTAL MEASUREMENTS WITH THEORY

According to Eq. (2) given by Debye, the theoretical half-widths of the scattered radiation should be proportional to $T/\eta$. In $CS_2$ this relation has been found in the temperature region from 260 to 313°K, the range in which viscosity data were available. The agreement (Fig. 2) with the Debye equation is good considering the crudeness of the theoretical approximation which assumes that the molecule can be considered as a sphere ($CS_2$ is a linear triatomic molecule) interacting through the friction provided by the average macroscopic viscosity, not the microscopic molecular interactions at the individual molecular sites.

In the plot of $T/\eta$ versus $T$, shown in Fig. 2, there is an abrupt change in viscosity at 278°K. The scatter of the experimental measurements was too large to detect such a change.

The results for the experimental half-widths in mixtures of $CS_2$ and $CCl_4$ are more difficult to interpret. As shown in Fig. 5, the experimental data approximately follow the simple predictions. As the viscosity of the mixture is increased by adding more $CCl_4$, the half-width does indeed decrease as predicted by Eq. (2). The half-width at 10% concentration of $CS_2$ is about 38% of the half-width of pure $CS_2$, which agrees closely with the theoretical predictions. The deviation of the experimental curve of half-width versus the inverse viscosity at 5% concentration of $CS_2$ might be explained by the fact that $CCl_4$ scattering or Tyndall scattering causes the line to appear narrower. Since the total integrated intensity of scattering of $CCl_4$ is 1/60 that of the $CS_2$ scattering and since the scattered radiation from $CCl_4$ should give rise to a much narrower scattered-light spectrum as the Debye relaxation time is longer because $CCl_4$ is a larger molecule and the liquid has a larger viscosity than $CS_2$, the deviation at very low concentrations of $CS_2$ is not surprising. On the other hand, most of the deviation in curvature of the plot in Fig. 5 can be explained by the different shapes of the molecules and of the Lorentz local-field corrections.

The line shape of the scattered light polarized perpendicular and parallel to the plane of scattering appears to be the same from room-temperature measurements. The line shape of the scattered radiation in liquid $CS_2$ has been shown experimentally to deviate from the Lorentzian shape near zero frequency shift and at frequency shifts greater than 10 cm$^{-1}$. Thus the equations of Leontovich [Eqs. (3) and (4)] are only partially adequate in explaining the shape. The equations of Starunov predict deviations from the Lorentzian shape because of an inertial term and oscillation frequencies [Eq. (5)]. The deviations in intensity caused by the inertial term do not cause the increased intensity over a Lorentzian shape occurring at higher frequencies because the inertial term tends to decrease the intensity at higher frequencies. The increased intensity could be caused by molecular oscillations. At large frequency shifts of from 30 to 100 cm$^{-1}$ the oscillation term is found to describe the curve adequately and Eq. (5) has been used to calculate an oscillation frequency. From the intensity of the scattered light at frequency shifts of 30 to 100 cm$^{-1}$ an oscillation frequency of 63 cm$^{-1}$ has been calculated at 198°K, while an oscillation frequency of 55 cm$^{-1}$ has been found at 293°K. These values compare with the oscillation frequency of 71 cm$^{-1}$ which Starunov[9] found at room temperature. It was not established whether a line which appeared near the

TABLE IV. Experimental values of the relaxation time $\tau$ for $CS_2$ as compared with the theoretical values calculated from Debye's equation.[a]

| Temperature (°K) | $\tau=1/\omega_{1/2}$ from half-widths | $\tau=4\pi a^3\eta/3kT$ | $\tau$ from inverse intensity graphs |
|---|---|---|---|
| 313 | $1.67\times10^{-12}$ sec | $1.58\times10^{-12}$ sec | |
| 293 | 1.96 | 1.86 | $1.5\times10^{-12}$ sec |
| 273 | 2.34 | 2.39 | 2.55 |
| 260 | 2.68 | 2.96 | 3.03 |
| 233 | 3.76 | [b] | 3.36 |
| 208 | 6.10 | [b] | 4.9 |
| 161 | >30 | [b] | [c] |

[a] The volume of the molecules, $4\pi a^3/3$, is taken to be $20.7\times10^{-24}$ cm³ and the viscosity values $\eta$ are taken from the *Handbook of Chemistry and Physics*, 46th edition (Chemical Rubber Company, Cleveland, Ohio, 1966), p. F-34.

[b] No viscosity data available.

[c] Measurement not possible because the shape changes very rapidly near the peak intensity.

triple point of the liquid at 52 $cm^{-1}$ was related to the oscillation phenomena. A study of the appearance of such lines would lend useful information on the structure of the liquid as it nears the phase-transition line.

The increased intensity which appears at very small frequency shifts may be due to the interaction of phonons with the fluctuations in the orientations of the molecules. Such an interaction may result in adding anisotropic scattering spectra to the Brillouin lines in much the same way as rotational spectra are added to vibrational lines in vibration-rotation spectra.

The total intensity in $CS_2$ was found to be approximately equal at 215 and 284°K. This is in agreement with the first term of Eq. (5) of Starunov, which when integrated over all frequencies yields an integrated intensity which is independent of temperature. Mixtures of $CS_2$ and $CCl_4$ produce complicated intensity distributions. The deviations from the Lorentzian line shape are manifested throughout the spectrum. It is difficult to treat intensities in mixtures theoretically because the local fields depend on the different molecular shapes and upon angular correlations. The ratio of the anti-Stokes to the Stokes radiation for light scattered parallel and perpendicular to the plane of scattering follows Maxwell-Boltzmann statistics in $CS_2$, as was shown in Table III.

## VI. DISCUSSION

It has been shown that the experimentally measured half-widths of the scattered radiation from liquid $CS_2$ are proportional to the temperature of the liquid divided by the viscosity of the liquid. The lifetime measurements as calculated from $\tau=1/\omega_{1/2}$ are tabulated in Table IV and compared to those calculated according to Eq. (2). If the size of a $CS_2$ molecule is chosen to be $20.7\times10^{-24}$ cm³, then the theoretical relaxation time calculated from Eq. (2) agrees well with the experimentally measured relaxation times. Alternatively, the interaction volume of the molecule may be calculated from the knowledge of the half-width and the viscosity of the liquid, and thus half-width measurements of the scattered radiation might provide a method of determining sizes of molecules in certain liquids.

Furthermore, half-width measurements may provide a convenient way of measuring the viscosity of a liquid. For according to Eq. (2), if one knows the size of the molecule, the temperature of the liquid, and the half-width of the scattered radiation, then one can calculate the viscosity of the liquid. If the size of the $CS_2$ molecule is taken to be $20.7\times10^{-24}$ cm³, the viscosity of liquid $CS_2$ is calculated to be 0.79 cp at 210°K, 0.60 cp at 230°K, and 0.50 cp at 250°K (measured half-widths were taken from Fig. 2).

Several authors[18–20] have reported that the "Rayleigh wing" goes to zero intensity at zero frequency shift and that the maxima of intensity are spaced 10 to 20 $cm^{-1}$ from the unshifted exciting line; the present results do not support such a conclusion. The rotational Raman-effect distributions for gaseous $CS_2$ would be expected to have "zero" intensity at the center and maxima at about 100 $cm^{-1}$ from the center. If a similar distribution of intensity is seen in the liquid, then one might postulate that the rotational Raman effect in $CS_2$ liquid is similar to that of the gas. Such abnormalities as the peak of the distribution being shifted closer to the center of the line or of a lack of rotational levels could be explained by postulating hindered rotation. In fact, the distribution has been found in the present experiment to have maximum intensity at the zero frequency shift in $CS_2$ and to be "symmetric." This is the case whether the analyzer is positioned perpendicular or parallel to the plane of scattering. This is not to deny that the orientation scattering can be looked upon as damped rotational Raman scattering, but only that the distribution in liquid $CS_2$ is not similar to a gaseous rotational Raman effect. All authors who have found doublets or that the anisotropic scattering goes to zero intensity at zero frequency shift have used mercury sources, photographic detection, and relatively poor spectroscopic resolution. The present measurements have had the advantage of a monochromatic light source, photoelectric detection, and good polarization. Our results disagree with the photographic results of Sirkar and Mookerjee[18] on $CS_2$ because they have obtained a greater half-width for the scattered radiation and also an inflection point in the intensity distribution of the scattered light. Sirkar and Maiti[19] have looked at benzene at room temperature and at 210°C and have found a broadening with increasing temperature but report a doublet distribution. Our line-shape results agree qualitatively with Bhagavantam,[21] who obtained a maximum for benzene at the center of the line and a

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rapid decrease in intensity until about a distance of 20 $\text{cm}^{-1}$ is reached, and also agree qualitatively with Ranganadham,[22] who obtained a maximum at the Rayleigh line of benzene and a gradual falling off of intensity from a maximum at or very near the Rayleigh line itself.

Fabelinskii[23] has obtained the orientation relaxation time in several liquids. His photographic results on $CS_2$ yield a relaxation time of $2.4\times10^{-12}$ sec. Our result for the relaxation time at room temperature is $1.96\times10^{-12}$ sec from measurement of the half-widths of the scattered light and $1.5\times10^{-12}$ sec when measured by plotting the inverse of the intensity at different frequency shifts versus the frequency shift squared. Recent results[4] obtained with an $Ar^+$ laser for orientation scattering in $CS_2$ at room temperature differ from these results because the weak exciting source used in their experiment prevented as accurate measurements. Starunov and Zaitsev[24] have examined orientation scattering by observing the wings of the Raman and Rayleigh lines in liquids and conclude that at large frequency shifts faster processes take place such as oscillation of the molecule as a whole.

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# Mobility of Electrons in Low-Temperature Helium Gas*

JAMES L. LEVINE† AND T. M. SANDERS, JR.‡
*School of Physics, University of Minnesota, Minneapolis, Minnesota*

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Experimental measurement of the mobility of photoelectrons in low-temperature helium gas is described. At the highest gas densities (near the normal boiling point) the mobility is lower than the value predicted by kinetic theory by four orders of magnitude. At intermediate density a transition region occurs, and at the lowest densities studied, the mobility approaches the kinetic-theory limit. A theoretical discussion of the interaction of a slow electron with a collection of helium atoms is given, and it is shown that at high density and low temperature a correlated ("bubble") state becomes thermodynamically stable. The theory predicts correctly the mobility at high density, the critical density at which the transition occurs, and the approach to the kinetic-theory value at low density. It does not, however, account for the details of the transition region. The observations, and their interpretation, provide strong support for the "bubble" model for electrons in liquid helium.

## I. INTRODUCTION

THE present work, a study of electron mobilities in dense, low-temperature helium gas, was motivated by the idea that it might shed some light on the interpretation of electron and ion mobilities in liquid helium.[1]

The observation that in liquid helium the negative carrier (whether produced by ionizing radiation or by injection of photoelectrons) has a mobility somewhat below that of the positive carrier suggested that the negative carrier was not a free electron. Various possible structures appeared in the literature but were not subjected, it seemed, to very critical experimental tests. At the time when the present experiments were begun we were inclined to believe that an electron injected into helium gas would form a dense complex, bound together by electrostatic polarization. Such a structure had been suggested by Atkins[2] in connection with charged particles in liquid helium. Such a complex might also be expected to be stable in sufficiently cold and dense helium gas. At any rate, in the gaseous phase, the helium density could be varied over a wide range and the possibility of complex formation could be studied in a manner not possible in the liquid.

First measurements[3] showed that at high gas density

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† Present address: I.B.M. Watson Laboratory, New York, New York.

‡ Present address: Harrison M. Randall Laboratory, University of Michigan, Ann Arbor, Michigan.

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