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Intermolecular Light Scattering in Liquids

J. P. McTague
Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360

and

P. A. Fleury
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

D. B. DuPré*
Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360

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The inelastic scattering of light arising from the time-dependent polarizability induced by intermolecular interactions has been observed in the simple classical liquid, argon. The spectrum at 90 °K and 1.5 atm is centered at zero frequency shift, and is exponential in shape, with a characteristic width of 21 cm^{-1}. The depolarization ratio for the scattered light is 0.72 ± 0.02, implying that the anisotropy of the polarizability dominates the scattering. The liquid spectra are compared with previously obtained spectra in gaseous argon and with the low-temperature gas data obtained in the present work. Both the linewidth and intensity for the liquid spectra suggest the inadequacy of the simple collision-induced view of the scattering process when clustering occurs. Calculations of the liquid spectrum, based on a model which is a generalization of the second-order Raman effect, yield for the liquid the correct line shape and a linewidth much closer to that observed than does the binary collision model. The lack of structure in the spectrum is taken as direct evidence against the existence of well-defined collective modes of short wavelength in liquid argon.

I. INTRODUCTION

Traditionally, monatomic fluids have been expected to exhibit no Raman effect since they possess no vibrational or rotational degrees of freedom to modulate the polarizability. Recently, however, Raman spectra have been predicted and observed in (a) the classical monatomic gases[1,2] argon and krypton and (b) the quantum liquid superfluid helium.[3,4] The former results (a) were explained in terms of a polarizability modulation associated with changes in translational states of pairs, triplets, etc., of atoms during collision encounters; while the latter results (b) were attributed to a second-order Raman effect in which pairs of excitations on the phonon-roton branch combine to scatter the light.

It is naturally of some interest to explore systems which are similar to, yet different from, the classical gas and the quantum liquid, namely, a classical liquid. Original motivation for these experiments arose from several recent theoretical speculations on collective excitations in simple classical liquids. Several authors[5,6] have suggested that well-defined collective modes might exist in monatomic liquids out to quite large wave vectors. The calculated dispersion relations are often qualitatively quite similar to that known for superfluid helium. Thus, a second-order Raman scattering from such excitations should exhibit structure associated with extrema in such a dispersion curve. Other authors[7,8] have argued that under certain general assumptions, all generalized transport coefficients become purely imaginary in the limit of very high frequency and very long wavelength. Frisch[7] has, therefore, suggested that at very high frequencies (10^{12}–10^{13} Hz) there should exist certain long-wavelength excitations which propagate without damping. One might hope to observe these excitations in a first-order Raman experiment.

In this paper, we report the results of intermolecular light scattering experiments in liquid argon and the extension of previous experiments in the gas phase to low temperatures. The linewidth, line shape, intensity, and polarization properties of the liquid spectra are compared with the gas spectra to elucidate some of the differences in short-time intermolecular motions between the liquid and gas phases. Comparison of the spectrum of liquid argon with that of liquid helium provides direct evidence for the absence of well-defined collective modes at short wavelength in the classical liquid argon. Some calculations of the spectrum for liquid argon are presented, which treat the scattering as a second-order

Raman process from pairs of overdamped phonons. The relation between the spectrum and the pair correlation function, $S(\vec{k}, \omega)$, measured by x-ray or neutron scattering is assumed to be that derived by Stephen[9] for his theory of Raman scattering in helium. A semiquantitative measure of the effects of higher-order density correlations on the Raman spectrum of a classical fluid is obtained from a comparison of experimental and theoretical spectral shapes and intensities.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The Raman spectra reported here were excited with ~300 mW of linearly polarized, 5145 Å light from an argon-ion laser. The light scattered through 90° was frequency analyzed by a double spectrometer, photoelectrically detected, amplified, and displayed. The sample fluid was condensed directly into an optical cell whose temperature could be controlled to ±0.02 °K. Details of the cell construction and operation are published elsewhere.[10]

The experimental geometry permitted any of the elements of the Raman tensor R_{ij} to be studied independently. Considerable care was taken to ensure that impurity concentration in the sample fluid was below 20 ppm.

A typical spectrum R_{xz} obtained at 90 °K ($P = 1.5$ atm) in liquid argon appears in Fig. 1. The "elastic" peak is due to stray light scattered by cell windows and indicates the instrumental profile. For the diagonal scattering R_{zz}, this central peak is some three times larger, the increase being due to Rayleigh and Brillouin scattering which is unresolved by the spectrometer. These very low-frequency spectra have been previously studied in detail.[10] The integrated intensity of the liquid-argon spectrum is ~100 times less than that of the Rayleigh-Brillouin spectrum and more than twice that of the 459 cm^{-1} Raman lines in liquid CCl_4. As shown in Fig. 2, the scattered intensity on the Stokes sides is well approximated by $I(\nu) = I_0 e^{-\nu/\Delta}$, where $\Delta = 21 \pm 1$ cm^{-1}. On the anti-Stokes side the spectrum is also exponential, but exhibits an additional factor $e^{-h\nu/kT}$ arising from detailed-balance conditions.

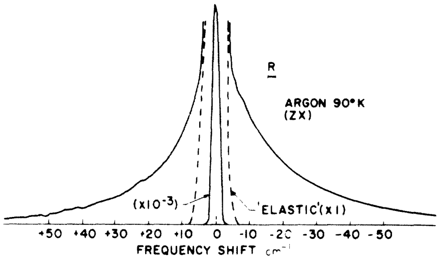

FIG. 1. Depolarized Raman spectrum of liquid Ar at 90 °K. Instrumental profile on same gain scale as the spectrum is indicated by dashed lines; on a 10^3 less sensitive scale by the sharp peak centered at zero frequency shift.

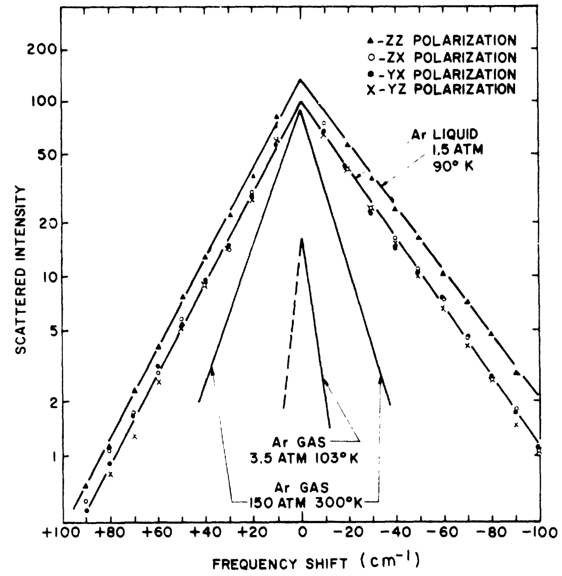

FIG. 2. Line-shape and polarization analysis of the Raman scattering in liquid Ar. The polarization notation refers to the laboratory direction of incident and scattered electric field vectors. The low-temperature gas-phase spectra are not drawn to the same intensity scale as are the others.

Note that the off-diagonal (depolarized) scattering was measured in three different ways, all of which are in excellent agreement, demonstrating the absence of spurious instrumental effects. The observed depolarization ratio I_{zx}/I_{zz} is 0.72 ±0.02.

Attempts were also made to observe changes in the liquid spectrum with P and T over a limited range. However, in changing the liquid conditions from 84 °K (0.7 atm) to 103 °K (3.6 atm), no change in Δ could be detected outside experimental error (i.e., $\Delta = 21 \pm 1$ cm^{-1}).

McTague and Birnbaum[2] have previously observed an exponentially shaped Raman spectrum in gaseous Ar at 300 °K and at densities ranging from ~0.8 to 8 moles/liter. The characteristic $1/e$ width Δ of these spectra was taken to be the inverse duration of a two-particle collision $\tau_D^{-1} = v_{\text{th}}/r_0$, where r_0 is the range within which two atoms affect each other's polarizability, v_{th} is their relative thermal velocity. This view of Raman scattering as collision-induced[1] predicts that at low densities (a) the scattered intensity should vary as ρ^2, (b) the characteristic spectral width, $\Delta = 1/\tau_D$ should be independent of ρ, and

(c) Δ should vary as $(kT)^{1/2}$. Predictions (a) and (b) have been previously demonstrated by observing the pressure dependence of the gas spectra at room temperature.[2] By observing collision-induced scattering in Ar gas at 103 °K, $\rho = 0.57$ moles/liter, we have verified (c) for the vapor.

The Ar-gas spectra at 300 °K, 150 atm^2 and at 103 °K, 3.6 atm are shown in Fig. 2. In the former case the $1/e$ width Δ is 10 cm^{-1}; in the latter it is 6.5 cm^{-1}. These results are in agreement with the hypothesis that the two-body collision duration τ_D proportional to $(kT)^{-1/2}$, controls the linewidth in the gas.

When compared to the gas results, the spectra we observe in liquid argon are surprising in three ways: (i) the linewidth in the liquid is nearly 4 times greater than that in the gas at the same temperature (103 °K) and pressure; (ii) the line shape in the liquid is still exponential, as it is in the gas; and (iii) the integrated intensity in the liquid is an order of magnitude smaller than expected on the basis of a density-squared dependence. These differences indicate clearly the breakdown in the liquid of the simple binary collision-induced scattering model which is adequate for the gas up to densities $\frac{1}{4}$ that of the liquid.

Point (i) indicates that in the liquid shorter time processes are involved than in the gas, while (ii) suggests that there is little qualitative difference in the short-time dynamics between the liquid and gas phases. Although part of the large difference in the integrated intensities between liquid and gas [(iii)] is partially attributable to the difference in radial distribution functions, the major cause of the relative decrease in intensity in the liquid is probably the contribution of three-, four-, etc., particle correlations, which tend to make the local liquid environment more symmetrical, leading to a lower anisotropy of the polarizability.

Before discussing the interpretation of these argon results, it seems appropriate to point out that intermolecular light scattering should be a universal phenomenon, common to all fluids. The recent experiments of McTague and Birnbaum[11] in high-pressure gaseous Xe, CH_4, and CF_4 demonstrate this for the gas phase. As far as liquids are concerned, intermolecular light scattering may have been inadvertently observed earlier in the more complex liquids CS_2 and CCl_4. Replots on semilog scale of data for liquid CS_2 and CCl_4, obtained by Shapiro and Broida[12] and by Gabelnick and Strauss,[13] respectively, are shown in Fig. 3. In the case of CS_2 there is a Lorentzian line centered at zero frequency which is caused by rotational relaxation of the anisotropic CS_2 molecule (the so-called "Rayleigh wing"). In both liquids the major contribution to the integrated intensity comes from an exponentially shaped wing. The appropriate Δ's are 22 and 20 cm^{-1} for CS_2 and CCl_4, respectively. The departure from a Lorentzian shape in the far wings of the CS_2 spectrum was noted but not explained in Ref. 12. It now seems clear that intermolecular light scattering accounts well for this departure.

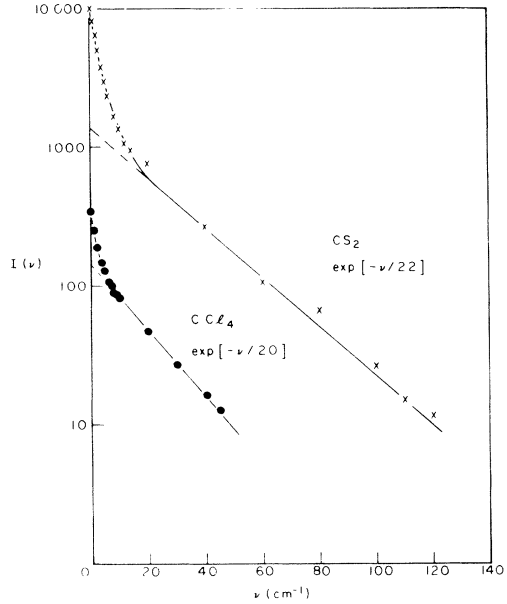

FIG. 3. Low-frequency Raman spectra of liquid CS_2 and CCl_4, replotted on semilogarithmic scale, from the original data of Shapiro and Broida (Ref. 12) and of Gabelnick and Strauss (Ref. 13). In both cases, most of the integrated intensity is describable in terms of an exponential line shape.

III. DISCUSSION AND INTERPRETATION

The time dependence of the polarizability necessary to scatter light inelastically can generally be attributed to fluctuations in the local field at the scattering particle. The local field is a sum of the electric field of the incident light wave and the fields due to the point dipoles induced on neighboring molecules. Consider a representative molecule (i). Its induced dipole moment $\vec{\mu}^{(i)}$ may be written

$$\vec{\mu}^{(i)} = \alpha^{(i)} \vec{E}_{\text{loc}}^{(i)} = \tilde{\alpha}_{\text{eff}}^{(i)} \cdot \vec{E}^0 , \tag{1}$$

where $\alpha^{(i)}$ is the molecular polarizability, $\vec{E}_{\text{loc}}$ and $\vec{E}^0$ are the local and external electric fields, respectively. The effective polarizability tensor $\tilde{\alpha}_{\text{eff}}^{(i)}$ is then a function of the instantaneous coordinates of all the particles in the medium, and is in general anisotropic. The observed depolarization ratios imply that in both the liquid and the gas phases the intermolecular light scattering is caused almost entirely by fluctuations in the anisotropy, or the traceless part $\tilde{\beta}$ of $\tilde{\alpha}_{\text{eff}}$. The experiments indicate that the calculation of $\tilde{\alpha}_{\text{eff}}$ based on the binary collision model is adequate for the gas, but inadequate for the liquid. We shall discuss below a recent calculation by Stephen[9] in which $\tilde{\alpha}_{\text{eff}}$ is related to the four-particle correlation function, and upon further assumption, to the two-particle correlation function whose Fourier transform is the familiar $S(\vec{k},\omega)$. This represents an improved theory for the liquid case.

Regardless of how one calculates $\tilde{\alpha}_{\text{eff}}$, the integrated scattered intensities may be written

$$I_{zx}=(\omega^4/c^4)I_0(\langle\beta^2\rangle/15),$$

and $$I_{zz}=(\omega^4/c^4)I_0(45\langle\alpha^2\rangle+4\langle\beta^2\rangle)/45, \tag{2}$$

where $\langle\alpha^2\rangle\equiv\langle(\alpha-N\alpha_0)^2\rangle$ is the mean-square deviation of the polarizability of the scattering volume (small compared with the wavelength of liquid but large compared with molecular dimensions) from $N\alpha_0$, the average polarizability of the N molecules in the volume. $\langle\beta^2\rangle$ is the mean-square anisotropy of the polarizability of this volume. The form of Eq. (2) and the fact that the observed depolarization ratio I_{zx}/I_{zz} is very nearly $\frac{3}{4}$ implies that $\langle\alpha^2\rangle\ll\langle\beta^2\rangle$ for both gaseous and liquid argon.

For a dilute gas where only terms involving the interaction of two particles need be considered, this anisotropy of the polarizability is described by the scalar

$$\beta(\vec{r})=\alpha_{\parallel}(\vec{r})-\alpha_{\perp}(\vec{r}), \tag{3}$$

where $2\alpha_{\parallel}(\vec{r})$ is the component of the polarizability tensor along the intermolecular axis of a pair of molecules or atoms separated by a distance r, and $2\alpha_{\perp}(\vec{r})$ is the corresponding component perpendicular to the internuclear axis. At long range $\beta(\vec{r})$ has the value

$$\beta(r)=3\alpha_0^2r^{-3}\,. \tag{4}$$

The mean-square anisotropy of the polarizability may be written

$$\langle\beta^2\rangle=2\pi\int_0^\infty\beta^2(r)g(r)r^2\,dr, \tag{5}$$

where $g(r)$ is the radial distribution function. Thus, the depolarized integrated intensity can in general be related to the second-virial Kerr constant, for which absolute values are available.[14] Using the induced dipole model and the measured Kerr coefficient one predicts an intensity only 25% greater than that observed for gaseous argon. For the liquid, however, the corresponding calculated intensity[15,16] exceeds the observed intensity by more than a factor of 4.

As mentioned above the linewidth Δ in the gas is well described by the relation $\Delta=v_{\text{th}}/r_0\doteq(kT/m)^{1/2}\times r_0^{-1}$. The exponential line shape for the gas was predicted theoretically by Levine and Birnbaum.[1] They assumed that only binary collisions are important and that the particle paths are straight lines. The predicted line shape emerges upon integration over relative particle velocities and impact parameters. The assumed form for $\beta(\vec{r})$ in Ref. 1 differs from that shown in Eq. (4); but the results are rather insensitive to the detailed shape of $\beta(\vec{r})$.

Turning our attention now to the liquid, we recall that the most striking difference from the gas spectrum lies in the linewidth Δ. For $T\approx100$ °K the liquid Δ is nearly 4 times that predicted by the binary collision model and observed in the gas at the same temperature. For the liquid a more appropriate characteristic time than τ_D, the collision duration, would appear to be the diffusion time $\tau_d=kT/MD$ (where M is the molecular mass and D the diffusion coefficient). τ_d classically describes the temporal decay of the velocity autocorrelation function $\Phi(t)=\langle\vec{v}(0)\circ\vec{v}(t)\rangle$.[17] Experimentally, Δ in liquid argon has nearly the same value as $\tau_d^{-1}(8\times10^{12}\ \text{sec}^{-1})$, although τ_d^{-1} has too strong a temperature variation[18] (~25% in 10 °K) to be identified directly with Δ (which changes by no more than 10% in 19 °K). Φ itself has been associated with the frequency spectrum of short-time highly damped intermolecular vibrations in the liquid,[19] and while the correlation function $\int dt\,e^{-i\omega t}\langle\text{Trace}\ \tilde{\beta}(0)\text{:}\ \tilde{\beta}(t)\rangle$ which describes the Raman spectrum is not identical with $\Phi(\omega)$, the two are related for harmonic motion. In fact the second and fourth frequency moments of $\Phi(\omega)$ and of the observed Raman spectrum are remarkably close. Rahman's computer experiments[17] on liquid argon yield the following values for the moments of Φ at 85.5 °K: $\langle\omega^2\rangle=50\times10^{-24}\ \text{sec}^{-2}$ and $\langle\omega^4\rangle/4!=277\times10^{48}\ \text{sec}^{-4}$. The moments of the measured argon Raman spectrum are $\langle\omega^2\rangle=(34\pm4)\times10^{24}\ \text{sec}^{-2}$ and $\langle\omega^4\rangle/4!=(295\pm65)\times10^{48}\ \text{sec}^{-4}$ over the temperature range 84 °K $\lesssim T\lesssim$ 103 °K.

These similarities suggest that the description of liquid argon in terms of highly damped intermolecular vibrations is appropriate. This has led us to consider the liquid spectra in terms of a generalized two-phonon or second-order Raman scattering process.[20] The details of the mechanism are as follows.

A density fluctuation of wave vector $\vec{k}$ is polarized by the electric field of the incident light. This polarization then generates a dipolar field which interacts with another density fluctuation having wave vector $-\vec{k}$, inducing in it an additional time varying polarization, which in turn scatters the incident light. The over-all process thus has $\vec{k}+(-\vec{k})=0$ as is required by momentum conservation. In analogy with second-order Raman effect in solids it is expected that the magnitude of k's contributing to the process will range from zero to order $2\pi/a$, where a is the intermolecular spacing in the liquid.

Stephen[9] has considered this type of scattering process and has shown that, subject to two assumptions the second-order light-scattering spectrum is proportional to

$$I_2(\Omega) \propto \int d\vec{K}' d\omega' \; G^2(K') S(-\vec{K}', \Omega-\omega') S(\vec{K}', \omega'), \tag{6}$$

where $G(K)$ is a weighting factor arising because an atom does not polarize itself. $S(\vec{K}, \omega)$ is the Fourier transform in space and time of the usual density-density correlation function. The assumptions leading to Eq. (6) are (a) the polarizability change in the liquid is due solely to the long-range induced dipole contribution, (b) the fourth-order density-correlation-function factors so that

$$\langle \delta n(1) \delta n(2) \delta n(3) \delta n(4) \rangle = S(1-2)S(3-4)$$
$$+ S(1-3)S(2-4) + S(2-3)S(1-4).$$

Thus, we may calculate the line shape once we know $S(\vec{k}, \omega)$, which is obtainable from neutron scattering. The data of Skold and Larson[21] indicate that, for the important values of $k, S(k, \omega)$ is approximately exponential in ω

$$S(k, \omega) \approx c(k) \exp[-b(k)|\omega|]. \tag{7}$$

The values of $c(k)$ and $b(k)$ can be determined by use of the known moments of $S(k, \omega)$[22]:

$$\int d\omega \, S(k, \omega) = S(k),$$
$$\text{and} \quad \int d\omega \, \omega^2 S(k, \omega) = k^2 k_B T/M, \tag{8}$$

where $S(k)$ is the scattering factor measured by x-ray scattering, k_B is the Boltzmann constant, and M is the molecular mass.

Using $S(k)$ determined for liquid Ar by Mikolaj and Pings[23] and by Gingrich and Tompson[24] we have calculated the second-order scattering spectrum (Fig. 4) for liquid argon at two temperatures.

These calculations, near the triple point (84.25 °K) and the critical point (143 °K), are approximately exponential in the wings, but give $\Delta \simeq 15$ cm^{-1} in contrast to the observed value, $\Delta \simeq 21$ cm^{-1}. In addition, the predicted intensity is still slightly larger than observed. Thus, the second-order Raman scattering model represents a considerable improvement over the pair-collision model in describing the liquid. The lack of better quantitative agreement with experiment is probably due to the simplifications made in obtaining the form of Eq. (6). Of course, the additional approximation we have made [Eq. (7)] in evaluating the integral of Eq. (6) also contributes. The latter is perhaps less important because of the comparative insensitivity of Eq. (6) to the precise shape of $S(\vec{k}, \omega)$ when $S(\vec{k}, \omega)$ is rather structureless. Despite the absence of quantitative agreement with experiment, we believe that the basic description of intermolecular light scattering in liquids in terms of a generalized second-order Raman process is essentially correct. We note that the correctness is more obvious in cases where $S(\vec{k}, \omega)$ exhibits the sharp structure associated with well-defined excitations, such as occur in superfluid liquid helium.

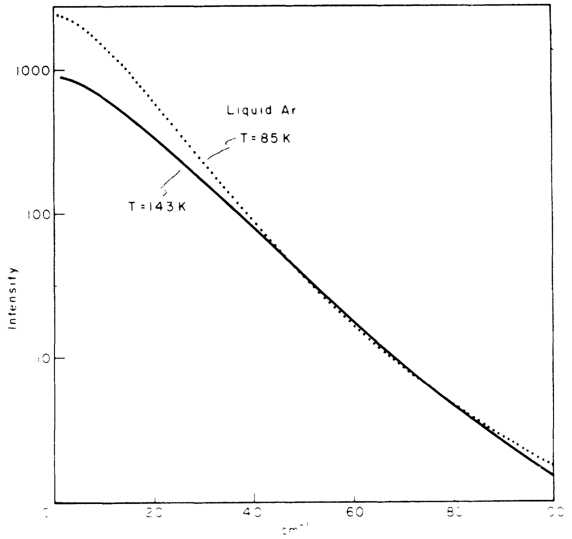

FIG. 4. Theoretical calculation of the Raman line shape for liquid Ar at 85 ° and at 143 °K. The calculated line shape has a $1/e$ half-width of ~15 cm^{-1}; while that observed is ~21 cm^{-1} at 90 °K.

Greytak and Yan[4] have observed the spectrum of light scattered by liquid helium. Its shape contrasts sharply with that for liquid argon. The helium spectrum (at 1.16 °K) exhibits peaks at ~ 13 and ~ 25 cm^{-1} with a tail extending beyond 50 cm^{-1}. The positions and shapes of the peaks can be understood in terms of scattering from paired excitations on the phonon-roton branch. Peaks occur where the joint density of states is large for pair excitations having zero total wave vector, K. For example, the 13 cm^{-1} peak is due to pairs of excitations which individually reside near $K = 2A^{-1}$, the "roton minimum." The existence of sharp peaks in the helium spectrum implies that the individual excitations forming the pairs are long lived. In fact one expects that more refined Raman experiments should permit accurate measurement of roton lifetimes.

Were similar long-lived excitations of large K to exist in classical liquids, a topic of some recent theoretical interest[5,6] their presence should cause peaks in the spectrum of scattered light like those observed in superfluid helium. Thus, the absence of such structure in Fig. 1 provides direct evidence against such long-lived large-K excitations in simple classical liquids such as argon.

In addition, the spectrum in Fig. 1 exhibits no structure which could be interpreted as due to first-order scattering from the high-frequency long-wavelength excitations expected by Frisch[7] and others. These excitations, alluded to in the Introduction, are expected to propagate undamped when the linear response of the fluid becomes wholly dissipationless. We may conclude from our experiments that either these excitations do not exist, or their coupling to light is sufficiently weak that they cannot be observed in a scattering experiment.

A remark about the possible contribution of argon "molecules" $(\mathrm{Ar})_n$ to the spectrum seems appropriate here. Were the argon atoms to form semipermanent clusters of two, three, etc., one would expect to observe an inelastic depolarized light scattering due to orientation fluctuations. Such Rayleigh wing scattering has been studied in detail for polyatomic molecules by a number of authors. The resulting line shape is Lorentzian with a characteristic frequency width $\sim k_B T/N_S V$. Here N_S is the shear viscosity and V the volume of a single molecule. The expected width for a diatomic argon molecule is $\sim 2\ \mathrm{cm}^{-1}$, and decreases as the number of atoms in such a molecule increases. Therefore, it seems clear that the spectra of Fig. 2 are not due to quasimolecules of argon. The above simple picture holds only if the "molecules" are strongly enough bound to live several orientation times. However, since the binding energy of an isolated pair is only about $k_B T$, the concept of well-defined dimers, etc., seems unrealistic for argon. If the lifetime of such a dimer is much shorter than $N_S V/k_B T$, the spectral width would reflect the lifetime, not the reorientation time. Indeed, a two-particle collision may be viewed as the formation and destruction of a very short-lived dimer. Contributions of quasimolecules to the Raman spectrum of liquid Xe[2] are now believed to be negligible.[25] Experiments now in progress should clarify the question of quasimolecules in argon. We are investigating the intermolecular light scattering near the critical point. If the number of dimers, etc., increases near T_c, their presence should give rise to a noticeable line-shape change to the spectrum. The second-order Raman effect in solid argon is also under investigation, in hopes of correlating these results with the data on liquid argon.

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*Present address: Department of Chemistry, University of Louisville, Louisville, Ky.

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