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Collision-induced light scattering: Integrated intensity of argon

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The collision-induced light scattering of argon has been measured as a function of density in the gas phase up to 530 amagat at room temperature and in the liquid phase near the triple point. The present measurement of the integrated intensity near the triple point is in strong disagreement with the previous result of Fleury and McTague and is much closer (within a factor of 1.5) to the molecular-dynamics calculations of Alder, Weiss, and Strauss. When the interaction function for collision-induced anisotropy, which accounts well for the results of the dilute-gas experiment, was used in the molecular-dynamics calculations the agreement between the calculated and measured integrated intensity at the triple point was found to be within the experimental error. It is concluded that the effect on the intensity of higher-order terms (i.e., other than the double-double scattering) cannot account for more than $\simeq 10\%$ of the total integrated intensity of argon.

I. INTRODUCTION

Collision-induced light scattering (CILS) in simple fluids composed of atoms or spherically symmetric molecules has been extensively studied for many years, both experimentally and theoretically.[1]

The first[2(a)] experiment showed an almost square-law dependence of the integrated intensity on density, indicating the collisional nature of the depolarized intensity from compressed argon. Further experiments[2b-2e] measured the depolarized spectrum from noble gases and interpreted it in terms of the duration of collisions. Moreover, the dipole-induced dipole (DID) model for collision-induced anisotropy used in the molecular-dynamics (MD) computer simulations of atomic gases[3] gave a fair description of the spectra.

In a successive series of experiments,[4] the measurement of the absolute intensity of argon at low density was attempted; the results were 30–35% lower than the values determined with the DID model. At liquid densities, a comparison between the experimentally determined intensity of argon[5] and the MD calculation showed the discrepancy to be approximately an order of magnitude.[6]

The existence of discrepancies in both the gas and liquid phase suggested that some correction to the DID model was needed. The major discrepancy at liquid densities was at first interpreted as a breakdown of the DID model, leading many researchers[7] to attempt to calculate corrections to the simple DID model, such as taking into account the overlapping of the electronic wave functions. In further theoretical work,[8] the contribution to the integrated intensity from higher-order terms than the double-double scattering in the collision induced polarizability was taken into account.

Recently, three independent experiments[9] in the low-density gas phase of argon showed a better agreement between the experimental CILS integrated intensity and the one obtained from theoretical calculation by means of the DID model for the pair anisotropy, if one considers[10] the dispersion of isolated atomic polarizability and an interaction potential more realistic than the simple Lennard-Jones (L-J). In spite of the fair agreement between the calculated and measured scattered integrated intensities, a careful analysis of the two-body spectrum still showed the inadequateness of the DID model for describing the wing of the CILS spectrum, even in the dilute gas phase. In fact, a comparison of the higher-order spectral moments (derived from the experimental results) with the theoretical calculations, showed that the DID model alone could not account properly for the whole spectrum.[9(a)] A similar conclusion has been drawn by comparing the experimental spectrum with the MD calculations at low density.[11] Recent MD calculations[12] performed with modified pair anisotropies where the electronic overlap effect was included, could not reproduce the experimental value[5] of the integrated intensity of argon near the triple point. Since the improved polarizability models were insufficient to explain the major discrepancy between the experimental results and MD calculations for the CILS intensity in liquid argon, we were therefore led to investigate more closely the reliability of the old experimental data and then to perform a new experiment to measure the CILS integrated intensity of argon as a function of density in the range from zero to the triple point.

In addition, MD calculations have also been carried out with the double aim of checking the reliability of MD calculations[13] and of investigating the dependence of the results for the integrated intensity upon the form of the polarizability model. In Sec. II the theoretical formulation is outlined with the purpose of establishing the notations of the present work and linking them with previous papers. In Secs. III and IV we describe the experiments in both the gas and the liquid phase respectively. In Sec. V, we give an account of the MD calculations and in Secs. VI and VII, the dependence of the integrated intensity upon the form of the polarizability model is analyzed. A discussion along with the conclusion is the argument of Sec. VIII.

II. THEORETICAL OUTLINE

A. Expression for measuring cross section of argon for CILS

One of the aims of this work is to obtain a measurement of the cross section of CILS for argon, $G_A(0)$, over a wide-density range. This can be determined if the constant C_A of the experiment that relates the measured CILS integrated intensity I_A to $G_A(0)$ is known. Because C_A depends on the refractive index of the sample and on other experimental parameters, we need a calibration procedure which allows us to obtain $G_A(0)$ without actually calculating C_A. So we use the rotational Raman lines of a dilute solution of molecular hydrogen in argon as an internal intensity reference standard since their cross sections can be theoretically calculated using standard quantum mechanics.

We define the laboratory coordinate system with the $\hat{z}$ axis perpendicular to the scattering plane, the $\hat{y}$ axis parallel to the incident laser beam wave vector, $\vec{k}_0$, and the $\hat{x}$ axis oriented along the scattered field wave vector, $\vec{k}_s$.

Both the CILS spectrum of argon and the rotational Raman lines of hydrogen are totally depolarized, and so the following relation for the intensities holds:

$$I_{HH}=I_{HV}=I_{VH}=\tfrac{3}{4}I_{VV}\,, \tag{2.1}$$

where the first subscript designates the direction of the incident light polarization and the second the scattered light polarization. In this picture, H lies in the scattering plane whereas V is normal to it. The incident beam is polarized in the scattering plane and both the vertical and horizontal components of the scattered light are collected.

$$I=I_{HV}+I_{HH}=2I_{HH}\,. \tag{2.2}$$

Since we are concerned only with the ratios of the measured intensities of argon and hydrogen, we will outline the theory for a single scattering component I_{HH}.

The CILS steradiance of argon can be written by generalizing Eq. (5) of Ref. 14 as

$$S_A=I_0Vk_s^4G_A(0)\,, \tag{2.3}$$

where I_0 is the time averaged Poynting vector which is related to the electric field in the solution of hydrogen in argon, and $G_A(0)$ is given by

$$G_A(0)=\frac{1}{V}\left\langle\sum_{P,Q}[\hat{y}\cdot\underline{\alpha}(P,0)\cdot\hat{x}][\hat{y}\cdot\underline{\alpha}(Q,0)\cdot\hat{x}]\right\rangle\,, \tag{2.4}$$

where $\underline{\alpha}(P,0)$ is the total polarizability of the local configuration P which produces the scattering process. The summations are extended over all the possible configurations within the scattering volume V.

In our experiment, we measure $\tilde{I}_A$, the number of photons collected per unit time in a solid angle, $\Delta\Omega$. Thus,

$$\tilde{I}_A=\frac{\Delta\Omega S_A}{h\nu_s}\,,$$

and this is related to $G_A(0)$ by

$$\tilde{I}_A=C_AG_A(0)(k_s/k_0)^3\,, \tag{2.5}$$

where C_A is a constant given by

$$C_A=\frac{2\pi I_0V\Delta\Omega k_0^3}{hc}\,. \tag{2.6}$$

The steradiance, $\langle S\rangle$ of the light scattered by N molecules of hydrogen has also been derived in Ref. 14, which for a rotational transition $j\rightarrow j'$ may be expressed as

$$\langle S\rangle_{j\rightarrow j'}=I_0k_0^4N\sum_{m=-j}^{j}\sum_{m'=-j'}^{j'}\left(\frac{\nu_s(j,j')}{\nu_0}\right)^4\left(\frac{n_j\exp[-w(j)/kT]}{Z_0}\right)|\langle jm|\beta_{\mathrm{H}_2}l_zl_x|j'm'\rangle|^2\,, \tag{2.7}$$

where ν_s and ν_0 are the scattered and incident photon frequencies, n_j is the nuclear degeneracy, $w(j)=j(j+1)B$ is the energy of the rotational level j and B is the rotational constant of hydrogen whose experimental value is 58.7 cm^{-1}, and β_{H_2} is the molecular anisotropy of H_2, whose theoretically calculated value[15] is in very good agreement with the value measured by Bridge and Buckingham.[14] In our work, the measured[14] value of β_{H_2} (0.134 Å) at 6328 Å has been extrapolated to 0.318 Å^3 at the laser frequency, 5145 Å, by using the theoretical results.[15] Equation (2.7) may be rewritten in the form

$$\langle S\rangle_{j\to j'}=I_0\,\rho_{H_2}Vk_0^4\left(\frac{\nu_s(j,j')}{\nu_0}\right)^4 P_j\, b_{j\to j'}\,\tfrac{1}{15}\,\beta_{H_2}{}^2\,, \tag{2.8}$$

where ρ_{H_2} is the number density of hydrogen, $b_{j\to j'}$ is the probability of transition which for $\Delta j=0,\pm 2$ is given by

$$b_{j\to j}=\frac{j(j+1)}{(2J-1)(2j+3)}\,, \tag{2.9a}$$

$$b_{j\to j+2}=\frac{3(j+1)(j+2)}{2(2j+1)(2j+3)}\,, \tag{2.9b}$$

$$b_{j\to j-2}=\frac{3j(j-1)}{2(2j+1)(2j-1)}\,, \tag{2.9c}$$

and the probability of occupation of the level j is given by

$$P_j=\frac{(2j+1)n_j(s)\exp[-j(j+1)B/kT]}{Z_0(s)}\,X(s)\,, \tag{2.10}$$

where $Z_0(s)$ is the partition function for the species s (ortho or para), $n_j(s)$ is its nuclear degeneracy, and $X(s)$ is the fraction of s type molecules. In the calculations, the fraction $X(s)$ has been assumed to be equal to that at room temperature because its value does not change with temperature for a nonequilibrium mixture of ortho and para H_2 in the absence of a catalyst.[16] This was verified by measuring the ratio of the intensities of the S_0 and S_1 lines at room temperature.

From Eq. (2.8), one can write an expression for $\tilde{I}_{H_2}[S_0]$, the number of photons collected per unit time in the solid angle $\Delta\Omega$, related to the S_0 rotational Raman line of hydrogen

$$\tilde{I}_{H_2}[S_0]=C_{H_2}\sigma[S_0]\,, \tag{2.11}$$

where the cross section of the S_0 transition is given by

$$\sigma[S_0]=\rho_{H_2}\,\frac{\beta_{H_2}{}^2}{15}\left(\frac{\nu_s(0\to 2)}{\nu_0}\right)^3 P(j=0)b_{0\to 2}\,, \tag{2.12}$$

and where C_{H_2} has been set equal to C_A. In equating C_{H_2} and C_A, it is assumed that the local configurations of argon atoms which give rise to the scattered intensity and hydrogen molecules see the same electric field. Thus, one can express $G_A(0)$ in terms of the S_0 transition as

$$G_A(0)=\rho_{H_2}\,\frac{\tilde{I}_A}{\tilde{I}_{H_2}[S_0]}\;\frac{\beta_{H_2}{}^2}{15}\left(\frac{\nu_s(0\to 2)}{\nu_0}\right)^3 P(j=0)b_{0\to 2}\,. \tag{2.13}$$

A similar expression holds for the S_1 rotational Raman line. One should note that Eq. (2.13) ignores the cross correlations of argon atoms with hydrogen molecules since we have presumed that this collisional contribution is much smaller, compared to the single molecule rotational cross section.

B. Low-density limit of $G_A(0)$

In order to relate the present experiment with the ones performed in the low-density gas phase, one must obtain the limiting value of $G_A(0)$ appropriate for low densities. This can be done if one expands $G_A(0)$ into its constituent terms as

$$G_A(0)=G_2(0)+G_3(0)+\cdots\,, \tag{2.14}$$

where $G_2(0)$ and $G_3(0)$ are the pair and triplet terms of the cross section respectively. In the zero-density limit, $G_A(0)$ approaches $G_2(0)$, whose value can be obtained by taking the binary limit of Eq. (2.4), which is given by

$$G_2(0)=\frac{\rho_A^2}{30}\,V\langle\beta^2\rangle_0\,, \tag{2.15}$$

where β is the anisotropy of a pair of atoms and $\langle\cdots\rangle_0$ implies averaging over the radial pair distribution function at the zero density limit.

In Refs. 9(a) and 9(b), a quantity $\phi_2^{(0)}$ was measured which is defined as

$$\phi_2^{(0)}=V\langle\beta^2\rangle_0\,. \tag{2.16}$$

By comparing Eqs. (2.15) and (2.16), we find

$$G_2(0)=\frac{\rho^2}{30}\,\phi_2^{(0)}\,. \tag{2.17}$$

An advantage of working at low densities is that one can calculate theoretically $\phi_2^{(0)}$ and can make a good estimate of $\phi_3^{(0)}$ (Ref. 17) using a model for polarizability and the interaction potential. At higher densities, the evaluation of Eq. (2.14) from first principles is almost impossible. Consequently, one has to rely on computer simulations to obtain a value for the cross section.

C. Relation between $G_A(0)$ and S^{zz}

MD calculations usually assume a pair-wise additive polarizability and microscopic configurations containing pairs of atoms. In this approximation the correlation function (2.4) is composed of only pairs of atoms, which reduces to

$$G_A(0)=\frac{1}{V}\left\langle\left(\sum_i\sum_{j>i}\hat{y}\cdot\underline{\alpha}(ij,0)\cdot\hat{x}\right)^2\right\rangle. \tag{2.18}$$

Assuming the DID model of polarizability, we have for the pair (i,j),

$$\underline{\alpha}(ij) = 2\alpha_0^2 \underline{T}(ij)\,, \tag{2.19}$$

where α_0 is the polarizability of an isolated atom and $\underline{T}(ij)$ is the electric dipole field propagator defined as

$$\underline{T}(ij) = \frac{1}{r_{ij}^3}\left(\underline{I} - 3\frac{\vec{r}_{ij}\vec{r}_{ij}}{r_{ij}^2}\right), \tag{2.20}$$

where $\vec{r}_{ij}$ is the vector from the ith to jth particle, I is the unit second-rank tensor and $\vec{r}\vec{r}$ is a second-order dyadic. If we define, following Alder,[6]

$$S^{\alpha\beta} = \frac{\sigma^6}{N}\left\langle\left(\sum_i \sum_{j\neq i} T^{\alpha\beta}(ij)\right)^2\right\rangle \tag{2.21}$$

we can obtain a relation connecting $G_A(0)$ and S^{zz} and we find

$$G_A(0) = \frac{3}{4}\frac{\alpha_0^4}{\sigma^6}\rho_A S^{zz}\,. \tag{2.22}$$

S^{zz} is the usual output of MD calculations and $G_A(0)$ is derived from experiment. Equation (2.22) will be used to compare MD calculations with the experimental results.

III. THE EXPERIMENT IN THE GAS PHASE[18]

The apparatus for the experiment in the gas phase at room temperature has been extensively described elsewhere[19] and so only a few further remarks will be made here. In order to obtain a depolarized spectrum, the incident laser beam must have its polarization vector lying in the scattering plane inside the scattering cell. This can be done by using a Glan-Thompson prism but because of the fact that the cell windows become optically active under high stresses caused at high densities of the sample (in gas phase at high pressures), they therefore rotate the direction of the polarization vector of the incoming beam slightly out of the scattering plane. Under such circumstances, one must use a Babinet-Soleil compensator to cancel this optical effect. At low pressures, however, there is no optical activity of the windows and so one can still use the Babinet-Soleil compensator, which now merely serves the purpose of a polarization rotator.

Unlike the previous experiment[9a,19] at low density, the intensity calibration was made by using H_2 as an internal reference standard. In fact, in this experiment, large variations in the geometrical parameters of the experiment were expected because of the change in the refractive index of the sample at high pressures. Comparing the present data (Fig. 1) with the previous data[20] in the overlapping density region, it was found that there was no appreciable difference. This confirmed that the presence of a small amount of H_2 mixed with argon did not affect the integrated intensity of argon, especially in the low-density region where this effect is larger. To assure the constancy of the amount of H_2 inside the cell, successive addition of pure argon was made by always keeping a pressure drop of at least 50 atmospheres between the compression vessel and the cell. The pressure of the sample was measured by means of four gauges of different sensitivity in order to maintain an overall accuracy of better than 0.5%. The temperature of the cell was stabilized at 25°C by means of an external thermostatic bath and was monitored by two thermocouples placed in the body of the cell. The PVT data of the gaseous argon were obtained from Ref. 21. The experiment was performed up to 1015 atm, which corresponds to a density of 546 amagat at 25°C. For each density, the depolarized spectrum of argon along with both the S_0 and S_1 rotational Raman lines of hydrogen were recorded. Because of the presence of wall scattering in the cell and the leakage of the polarized light into the depolarized spectrum (finite dimension of the collection solid angle), it was not possible to obtain data between 3 cm^{-1} and

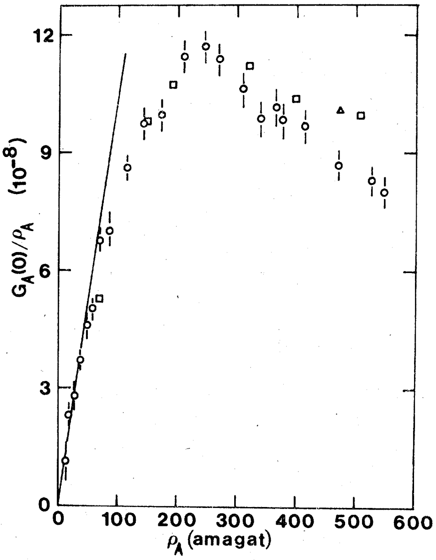

FIG. 1. CILS integrated intensity in the gas phase. The figure shows the behavior of the quantity $G_A(0)/\rho_A$ (Å^3/amagat, see Sec. II for definitions) as a function of density (amagat). The dots are the experimental points along with the relative error (standard deviations). The MD results are taken from Ref. 6 (open triangle) and Ref. 20 (open squares). Both the MD calculations have been performed with a 6-12 Lennard-Jones potential and simple DID polarizability model. The straight line represents the extrapolated two-body contribution from Ref. 9a.

the excitation frequency (ω_0). From this point on we had to extrapolate the spectrum to ω_0. This method of extrapolation of the spectrum is one of the main sources of error in the computation of the integrated intensity. Since on varying the density of argon, the integrated intensity of the rotational lines of hydrogen changed, due to the change in the refractive index of the sample, we normalized the depolarized intensity of argon to that of the Raman lines of hydrogen.

IV. THE EXPERIMENT IN THE LIQUID PHASE[22]

The experimental set up in this case is similar to the one used by An[23] for the measurement of CILS intensity at low temperatures so that only a few specific points will be mentioned briefly.

(a) The scattering cell was a modified version of the preceding one[23] which confined the overwhelming spurious scattering to within 2.5 cm^{-1} from the laser line using 50 μm for the entrance slit. However, the extrapolation procedure was still necessary.

(b) The overall temperature stability was within 1°C over a period of 3-4 days, which does not change the liquid argon density by more than 1%. But it can affect the concentration of H_2 in liquid argon by approximately 6-7%. This has been taken into account in the computation of the total error.

(c) The use of a Babinet-Soleil compensator to cancel the optical activity of the windows was not necessary since the experiment was performed at low pressures in the liquid phase. Instead a Glan-Thompson prism was used to align the direction of the polarization vector in the scattering plane.

(d) Because of the possibility of long-time drift of the photo-multiplier noise, a mechanical shutter was placed near the entrance slit of the spectrometer which allowed us to subtract the electronic noise from the spectrum at small periods of time and thus helped us to measure very accurately the far wing. This device is equivalent to the one we used in the gas phase.

(e) The detection system (spectrometer and photomultiplier) used here is identical to the one used earlier[19] but in order to be sure that the response of the system was the same, a calibration check was performed which was found to be in good agreement with the previous one.[19] This was done by placing an oven stabilized at 1145 °K, having a small aperture, in front of the spectrometer which served as a black-body radiation source.

In a previous experiment performed in liquid argon,[5] the 459-cm^{-1} vibrational Raman line of CCl_4 was used as an intensity reference. Since the refractive index of liquid argon is appreciably different from that of liquid CCl_4, the measured integrated intensity must be strongly corrected (the local-field correction goes as n^8). In order to avoid this complication, we chose to work again with an internal intensity reference standard using a weak solution of H_2 in liquid argon. The low concentration of H_2 (~1%) and its small polarizability does not substantially affect the depolarized spectrum of argon even at liquid densities. This allows us to perform a relative measurement of CILS intensity with respect to the rotational Raman lines S_0 and S_1 of hydrogen, which in turn can be theoretically calculated.

The temperature of the scattering cell was lowered to the desired value keeping a positive pressure of argon inside in order to avoid the possibility of changing the purity of the sample. To assure that the liquid was in equilibrium with its vapor, the cell was not completely filled. After thermodynamic equilibrium was established, a very slow flow of pure hydrogen was bubbled through it. The system was then left at rest for several hours to equilibrate. Both temperature and pressure were recorded during the experiment, which determined the thermodynamic state of the sample. The concentration of hydrogen was calculated according to the data of Ref. 24. The intensities of the rotational lines of hydrogen were measured several times over regular interval of days and no change was observed in their values (within the errors), confirming that the system remained at a fixed thermodynamic state.

The depolarized spectrum of argon has been recorded up to the S_0 Raman line of hydrogen (352 cm^{-1}) together with the S_0 and S_1 lines. Figure 2 shows the low frequency part of the spectrum, which mostly contributes to the integrated intensi-

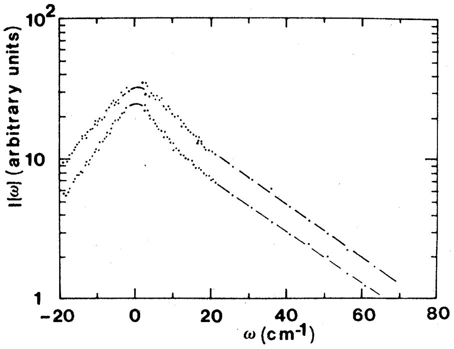

FIG. 2. Depolarized spectra of liquid argon at two different temperatures, 90.8 K (lower curve) and 103.5 K (upper curve). It may be noted that the intensity of the spectra in the low-frequency region is enhanced with respect to the extrapolated exponential behavior of the wings. The visual fitting of the wings and the extrapolated spectra to the excitation line are denoted by full lines.

TABLE I. Integrated intensity at two thermodynamic states. T = temperature, P_0 = argon vapor pressure, $\Delta P = P_{tot} - P_0$ = differential pressure, x_2 = calculated concentration of hydrogen in argon, ρ = density, $G_A(0)$ = measured absolute cross section.

T (K)	P_0 (atm)	ΔP (atm)	x_2 (10^{-2})	ρ_A (mole/liter)	ρ_{H_2} (mole/liter)	$G_A(0)$ (Å^3) (10^{-5})	$G_A(0)/\rho_A$ (Å^3/amagat) (10^{-8})
90.8 ± 1.5	1.43 ± 0.22	6.0 ± 0.4	0.73 ± 0.06	34.35 ± 0.24	0.25 ± 0.02	1.21 ± 0.17	1.57 ± 0.22
103.5 ± 1.0	3.89 ± 0.31	10.7 ± 0.5	1.55 ± 0.09	32.22 ± 0.18	0.50 ± 0.03	1.82 ± 0.19	2.52 ± 0.26

ty. It may be noted from the figure that the behavior of the exponential wing changes as we approach the excitation line. This has also been observed by An (Ref. 23). A careful comparison of this portion of spectrum with the previous one[23] shows a good agreement, confirming that the presence of a small amount of hydrogen in liquid argon does not measurably affect the spectra.

The extrapolation of the depolarized spectrum to the excitation frequency is still a major source of error in computing the total integrated intensity. Since we were able to detect the spectra down to 2.5 cm^{-1}, it was easier for us to make a good estimate of the scattered intensity at the excitation frequency than in the previous experiment,[5] where this value was obtained by extrapolating the exponential behavior of the wings. We made the extrapolation by extending the Lorentzian behavior of the first portion of the spectrum, which gives a more accurate value for the integrated intensity. The error in our method was estimated by comparing the different extrapolation procedures allowed by the scattering of the experimental data. Table I summarizes the thermodynamic states and the results for this part of the experiment.

V. ROLE OF THE CUT-OFF RADIUS AND THE MOLECULAR-DYNAMICS RESULTS

Before making any extensive comparison between our results and the MD calculated values, it was thought necessary to check the reliability of the MD data since a recent paper[13] showed for argon at liquid densities a strong oscillatory dependence of the calculated S^{zz} upon the truncation radius, R_c. We presumed that this dependence was somehow related to the oscillatory behavior of $g(r)$ and therefore if one were to extend the MD calculations to larger truncation radii, a more precise value for the calculated S^{zz} could be obtained. For this purpose, the MD calculation was carried out with a system of 864 atoms near the triple point of argon. The molar volume was set to 28.62 cm^3, corresponding to a density of 780 amagat, and the temperature was fixed at 89 °K. With these parameters the size of the box is 34.5 Å, which allows one to extend the truncation radius up to 5σ, that is, into the range where the $g(r)$ is relatively smooth and approaches the value one.[25] The interactions were calculated by means of a 6–12 Lennard-Jones potential ($\sigma = 3.405$ Å, $\epsilon/k = 120$ °K) truncated at 2.5σ, and Verlet's algorithm, with a time step of 0.02 ps, was used to numerically integrate Newton's equations in 1600 time steps. To improve the statistics, S^{zz} was calculated as an average of the six independent components of S^{ij},

$$S^{zz} = \tfrac{1}{6}[S^{xx} + S^{yy} + S^{zz} + \tfrac{4}{3}(S^{xy} + S^{xz} + S^{yz})], \quad (5.1)$$

and each component was calculated according to the definition (2.21) using the DID model. The dependence on R_c was obtained by putting $T(ij)$ identically equal to zero when $r_{ij} > R_c$ and the resulting S^{zz} was calculated as a function of R_c on a fifty point interval between 0 and 5σ.

The previous[13] oscillatory behavior of S^{zz} was well reproduced. We were, however, able to detect a "damping" in its oscillations which approached a constant value as R_c tended to 5σ. Figure 3 shows this result and confirms what we had anticipated (i.e., the strong correlation between $g(r)$ of argon and the oscillations of the calculated S^{zz} as a function of R_c). The numerical value of S^{zz} at 5σ is 0.26, which should no longer change significantly for values of R_c greater than 5σ since $g(r)$ is practically constant beyond this point. It is interesting to note that if a truncation radius, $R_c = 2.5\sigma$, is used, we get a value of 0.21 for S^{zz} which is identical to the one already published by Alder.[6] Table II summarizes the results of the experiment and MD calculations in the liquid state. The first and third thermodynamic states are very close and the value obtained from the MD calculation is 1.7 times the experimental one. Possible reasons for this difference are (a) argon does not interact with an $L-J$ potential; (b) the MD calculations assume only pair-pair correlations; and (c) the collision-induced pair anisotropy is not described by the DID model alone.

The form of the potential does not seem to play

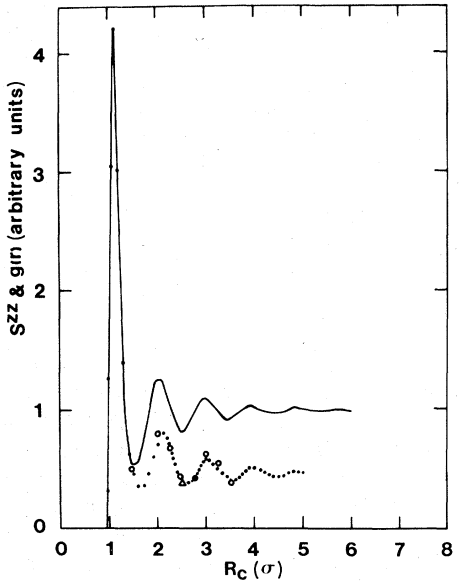

FIG. 3. MD calculations for the integrated intensity. The calculated values of S^{zz} are reported as a function of cut-off radius R_c (arbitrary units). For the sake of comparison, the previously calculated values are also shown. ● = present calculation, ○ = data from Ref. 26, △ = data from Ref. 6. The solid line represents the experimentally determined $g(r)$ as tabulated in Ref. 27.

an important role in the calculation of the integrated intensity. In the low-pressure gas, it was observed[9(a),28] that if one uses the Bobetic-Barker potential instead of the Lennard-Jones (L-J) one, the integrated intensity changes by less than 10%. This is found to be true even at liquid densities where it was observed[27] that the $g(r)$ calculated by using the L-J or the Barker potential does agree well with the experimental one. Thus we consider it highly unlikely that the use of the L-J potential is the cause of the 70% discrepancy between MD and experimental results.

The assumption that S^{zz} involves only the pair-pair correlations (double-double scattering, DD) has been questioned by Keyes, *et al.*,[8] who have proposed that the higher-order terms such as the double-triple (DT) and the triple-triple (TT) are present in CILS. Unfortunately, no quantative results have been published so far. It is difficult to estimate the contribution of the DT term to the intensity even using MD.

Before further effort is put into investigation of these higher-order terms one should consider the possibility that the CILS is based on the DD effect but that the pair interaction polarizability is not simply DID. This possibility is strongly supported by the available data in the low-density gas phase[9(a),29] and is discussed in Sec. VI.

VI. APPLICATION OF THE GAS PHASE POLARIZABILITY MODEL TO THE LIQUID PHASE

Many efforts have been made to modify the DID model of polarizability in order to explain the CILS data. For this purpose, the method of spectral moments, first introduced by Levine and Birnbaum,[28(a)] is extremely useful for the analysis of the CILS spectrum in the low-density limit and allows one to investigate the form of the polarizability if a precise spectrum extending up to very large frequency shifts is known. Recent experiments at low density give a more accurate value for the two-body integrated intensity of argon and which is significantly different from the previously measured ones.[4] In addition, because of the greater accuracy, better estimates of the higher-order moments could be made.[9(a),19] It was found that McTague's model[4b] did not fit the experimental data[30] and a new model of anisotropy had to be proposed.

The model of anisotropy that fit the two-body spectrum by the method of spectral moments has the functional form

$$\beta(x)=\frac{6\alpha_0^2}{b^3}\left[x^{-3}+A^*x^{-6}-B^*\exp\left(\frac{-x}{x_0}\right)\right], \qquad (6.1)$$

where b is the distance parameter of the interaction potential ($b=\sigma$ for L-J), and $x=r/b$ is a reduced variable. It must be emphasized that the above procedure was applied to reduced experi-

TABLE II. A comparison of experimental depolarized CILS integrated intensity, $G_A(0)/\rho_A$, with a result obtained using MD, S^{zz}.

T (K)	ρ_A(amagat)	$G_A(0)/\rho_A(10^{-8})$ (Å^3/amagat)	S^{zz}	
90.8 ± 1.5	770 ± 5	1.57 ± 0.22	0.15 ± 0.02[a]	Present experiment
103.5 ± 1.0	721 ± 4	2.52 ± 0.26	0.25 ± 0.03	Present experiment
89.0	780	2.7[a]	0.26[b]	MD(DID)

[a] Converted value. The conversion constant is 1.031×10^{-7} Å/amagat.
[b] DID only.

TABLE III. Values of the experimental and calculated integrated intensity of argon near the triple point. The parameters used in the calculation are $\alpha_0 = 1.68$ Å^3, $\sigma = 3.405$ Å, $\epsilon/k = 119.8$ K.

Parameter Set	A^*	B^*	x_0	S^{zz}
a	0.325	2.00×10^4	0.091	0.21
b	0.894	7.19×10^2	0.15	0.18
c(DID)	0.0	0.0		0.26
d(expt)				0.15 ± 0.02

mental data where the interactions are *strictly* two body.

The functional form of the anisotropy given in Eq. (6.1) is in qualitative agreement with a recent theoretical calculation of the collision-induced polarizability,[31] where the authors included the higher-order terms in the multipole expansion of the pair polarizability.

Two sets of the parameters A^*, B^*, and x_0, have been calculated[29] for the Bobetic-Barker[32] pair interaction potential but because our MD calculations employ the (L-J) potential, we recalculated A^*, B^*, and x_0 from the low-density gas phase data for the L-J by fitting the spectral moments to the experimental ones. We used this model of polarizability to compute S^{zz} at the triple point of argon. The various other parameters used in this calculations were the same as employed in the DID calculation described in Sec. V. The results along with the parameters are listed in Table III. The value of the computed integrated intensity is now smaller with respect to our DID value with either set of the parameters. The (*b*) set in Table III gives a value for S^{zz} which is very close (within 1.5 standard deviations) to our experimental value.

VII. ANALYSIS OF THE INTEGRATED INTENSITY IN TERMS OF THE EMPERICAL MODEL OF POLARIZABILITY

It has been explained above that the empirical model represented by Eq. (6.11) was derived from the CILS data using the method of moments at room temperature in the binary-collision limit. Inspection of Table IV tells us that the behavior of the resulting empirical anisotropy function, $\beta(r)$, remains quite close to but slightly higher than the corresponding DID function in the region $r > \sigma$ and becomes lower than the DID for smaller values of r. In the low-density gas phase, where the average interatomic distance $\langle r\rangle$ is significantly greater than σ, one obtains a 7% positive correction to S^{zz} on using the empirical model.[29] At liquid densities, however, where $\langle r\rangle$ is of the order of σ, it would appear from Table IV that the use of the empirical model would not bring large changes in the value of S^{zz}. Actually this model, when used in MD at the triple point, reduces the value of S^{zz} by about 30% with respect to the DID one and brings it just outside the standard deviation of the experimental value.

TABLE IV. Deviation of the empirical model of polarizability from the DID as a function of $x = r/\sigma$.

$x = r/\sigma$	$\frac{\beta_{\mathrm{emp}}(x) - \beta_{\mathrm{DID}}(x)}{\beta\ (x)}$
0.8	−0.031
0.9	−0.073
1.0	−0.021
1.1	−0.046
1.2	+0.101
1.3	+0.135
1.4	+0.151
1.5	+0.155
1.6	+0.150
1.7	+0.140
1.8	+0.127
1.9	+0.115
2.0	+0.102

The explanation of such a large drop in the value of S^{zz} at this density can be understood if one takes into account the strong cancellation among the two-, three-, and four-body contribution.[26] At such a density, the ratio between the three contributions, $C_2:C_3:C_4$, is $1:-1.72:0.77$ (Ref. 33) and their sum is 0.05 (i.e., the local anisotropy around an atom is strongly reduced with respect to the two-body contribution). Thus, small changes in C_2, C_3, and C_4 can cause relatively large changes in their sum in the correlation function.

From Fig. 3 we see that the contribution to S^{zz} from the first shell, defined by the first minima of the $g(r)$, is almost equal to its limiting value. This implies that most of the physical information is contained in the configuration of the first shell. If it were completely symmetric, its anisotropy, S^{zz}, would be identically zero but, as the real configuration of the shell is slightly deformed from the ideal situation, therefore there is a finite contribution to it. In the neighborhood of every atom there are some irregular void spaces, which are too small to be filled but can alter the isotropy of the distribution. In this situation any kind of short-range interaction will experience less cancellation than a longer-range one. In fact, a very short-range interaction can be considered as predominantly described by a two-body term alone so that no cancellation effect can arise.

In conclusion, the short-range correction, which is much smaller than the leading DID term and is less affected by the cancellation effect, can result in contributing to the total anisotropy of the shell which is comparable to the DID one. This concept has interesting consequences in the case of a crystal where the DID anisotropy is even smaller and therefore even larger contributions to S^{zz} would come from the short-range terms of the polarizability.

We have found that the use of the empirical model of polarizability gives a ~−30% correction to S^{zz} at the triple point of argon whereas at the zero-density limit, it gave +7%. One should therefore expect some correction to S^{zz} in the intermediate-density region also. To check this point, we performed three short MD runs at 97, 299, and 487 amagat using only 108 atoms and 4 500 time steps. On comparing the results for both the DID and the empirical model of anisotropy (b set), we found no appreciable difference between the two values at the first two densities and a ~10% decrease at the third density. This confirms that the empirical model of polarizability can well describe the density behavior of the CILS integrated intensity of argon in the whole density range.

VIII. DISCUSSION AND CONCLUSION

The CILS integrated intensity of liquid argon measured in this experiment is greater than the value quoted in Refs. 5 and 6. Our result is in agreement with our MD calculation. The difference between the present experimental value and the previous one[5] cannot be attributed to the contribution from the very low frequency part of the spectrum (which was not detected in Ref. 5).since the extrapolation of the spectrum by extending the exponential portion of the wings from 20 cm^{-1} to the excitation frequency (see Fig. 2) gives a difference of only 11%. We suspect that a major problem in the previous experiment[5] was the use of an external intensity reference standard (namely the 459 cm^{-1} vibrational line of CCl_4) which brings in changes in the collection geometry of the experiment and in the local field due to the change in the refractive index. We have eliminated these problems by utilizing an internal intensity reference in both the liquid and gas phase .

The indicated agreement between the measured and calculated integrated intensity over the entire density range which is based on the use of the modified DID model of polarizability suggests strongly that a pair-wise additive polarizability can account for the integrated intensity even at liquid densities. Thus, the introduction of higher-order configurations in the cross section would contribute $\lesssim$10%, which is the accuracy of the present work.

Some further comments must be expressed on the use of the Lennard-Jones interaction potential in the MD calculations. It is quite well known that this potential is just a good first approximation to describe pair interactions and the use of a more realistic one can change the calculated results. This effect has been analyzed in the low-density gas phase of argon and it has been observed that the choice of the potential does change the calculated integrated intensity as much as 5% [Ref. 9(a)] at room temperature and about 10% at $T^* \sim 1.0$ [Ref. 28(b)]. However, the effect of the difference between the true interaction potential and the L-J one has been placed on the polarizability in the present work, explaining the good agreement between MD and experiment in the low density as well as in the liquid phase.

It would be useful to gain more insight into the collision-induced phenomenon if one uses a more realistic potential in the MD calculations. Unfortunately, these calculations with a Bobetic-Barker potential or a similar one would consume much more computer time which would make the method unaffordable.

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