PHYSICAL REVIEW A VOLUME 33, NUMBER 2 FEBRUARY 1986

Interaction-induced translational Raman scattering of liquid argon: The spectral moments

Marco Zoppi and Giovacchino Spinelli
Consiglio Nazionale delle Ricerche, Istituto di Elettronica Quantistica, Via Panciatichi 56/30, I-50127 Firenze, Italy

(Received 29 July 1985)

The depolarized interaction-induced light scattering spectra of liquid argon have been measured, along the coexistence curve, at four different temperatures in the range 84.1—110.7 K. The experimental spectral moments have been evaluated, on an absolute scale, by means of a calibration procedure which makes use of a solution, in liquid argon, of about 1.4% hydrogen, whose rotational Raman lines are used as an intensity standard. The reproducibility of the calibration technique is very good and the present measurement fully confirms a previous experiment [D. Varshneya *et al.*, Phys. Rev. A **23**, 77 (1981)]. Molecular-dynamics computer simulation has been used to evaluate the first two even spectral moments in similar thermodynamic conditions. We used the pairwise additive potential of Barker, Fisher, and Watts and a model of the pair polarizability anisotropy which was derived from the low-density-gas collisional spectrum at room temperature. The overall agreement is good even if some refinements seem necessary. Since the effect of irreducible triple-dipole terms of both polarizability and potential is found to be smaller than the present experimental uncertainty, the small observed inconsistencies between measurement and computer simulation might be attributable to minor defects of the pair functions. More experimental data taken at different temperatures would help in refining the models.

I. INTRODUCTION

After some initial controversy concerning the absolute value of the total depolarized interaction-induced light scattering (DILS) intensity in liquid argon, it is now established that the difference between molecular-dynamics (MD) computer simulations and experiments is considerably less dramatic than the factor of about 6, which was reported in the early days.[1,2]

Two recent measurements,[3,4] performed with liquid argon close to the triple point, give results which are quite similar and not very far from the MD calculations,[5] even if their respective standard error bars do not always overlap. The situation, therefore, resembles that of the low-density gases for which absolute measurements of different laboratories are now fully consistent.[6–13]

A careful analysis of the liquid-argon data, however, reveals that the small remaining differences between recent measurements[3,4] (footnotes b and d in Table I) are larger than it seems at first sight. The two experiments were performed in slightly different thermodynamic states and, if one tries to correct the data to account for the differences, primarily of density, it turns out that the discrepancy tends to increase because a higher density implies a more symmetric structure and therefore a smaller amount of depolarized scattering. In addition, the two measurements were performed with two different calibration techniques both of which could be questioned in principle.

The measurement of Clarke and Bruining[4] was made on liquid argon at 86±2 K and was initially referred to the depolarized Rayleigh line of liquid nitrogen at 77 K. This intermediate standard was then calibrated with respect to the 991-cm^{-1} (Stokes) Raman band of benzene at 292 K. The corrections for the change of refractive index were made by assuming a known law for the change of the local field.

In order to avoid problems inherent to refractive-index corrections, our technique[3] made use of an internal standard. A small amount of hydrogen (in the order of 1%) was dissolved in liquid argon and its rotational Raman lines were used for intensity calibration. This method avoids any correction for refractive-index change, but it assumes that the presence of a little impurity of hydrogen does not affect the DILS spectrum of argon. Basically the assumption is twofold: first that the depolarized spectrum of argon is not affected by the impurity, and second that hydrogen molecules are freely rotating and sense the same local field as the argon scattering centers.

Without entering into the details of the calibration procedures, which have been discussed elsewhere,[14] we have reasons to believe that both the experiments were performed in the most careful way. However, in view of the inconsistencies, we decided to measure once more the DILS spectral moments of liquid argon in order (1) to check further this particular point and (2) to add more experimental data with, possibly, improved accuracy.

II. THE EXPERIMENT

Our experimental setup is quite standard for Raman spectroscopy. It is composed of the following.

(1) An argon-ion laser (Coherent Radiation model CR 10) which can supply more than 4 W at 5145 Å.

(2) A double monochromator (Spex model 1401) equipped with holographic gratings (1800 lines/mm).

(3) A photomultiplier (EMI model 9893 QA/100) selected for low noise and cooled down to −20 °C by a thermal housing from Products for Research (model TE 104). The measured level of dark counts is close to 0.1 count/s.

(4) A phase-sensitive photon counting system (EG&G Brookdeal model 5Cl) used with a chopper (PAR model 192) in the laser beam, for automatic subtraction of the dark noise.

A microcomputer (PET-CBM) controlled the setting of the spectrometer, the collection of data from the photon counting system, and the storage on a magnetic cassette support. The experimental data were then analyzed on another, similar, microcomputer.

The optical cell, which has been described in detail elsewhere,[15] can hold gas or liquid of pressure up to 1000 atm and any temperature below 300 K. It was fitted to a closed-loop helium refrigerator (Air Products model CSA 202) equipped with a temperature control which allows a stability of the sample within 0.2 K in the range from 10 to 300 K. The temperature reading was done by means of two platinum resistors (NBS calibrated) placed on top and bottom of the optical cell. At thermal equilibrium the agreement between the two readings was better than 0.2 K.

In order to compensate for a possible optical activity of the entrance window, induced by either pressure or temperature stress, we used a Babinet-Soleil compensator. This device also permitted us to rotate the polarization plane of the laser beam inside the cell. The scattering angle was set at 90° and the collection solid angle was measured to give an f number of 8.2, i.e., very similar to the 7.8 of the spectrometer.

An important calibration to be performed on the apparatus before starting the experiments was that of the response function of the detection system (spectrometer plus photomultiplier), for both polarizations of the incident light. We have used a calibrated blackbody radiation source (Infrared Industries model 443) operating at a temperature of 1040 ± 1 K. The blackbody radiation was polarized either parallel or perpendicular to the ruling of the gratings and both response functions, $F_V(\nu)$ and $F_H(\nu)$, were measured. To give an idea of the importance of this calibration procedure, we report the measured ratio between the $S(0)$ and $S(1)$ rotational lines of normal hydrogen at room temperature. The crude ratio of the two integrated intensities was obtained as 0.439, while the corrected value becomes 0.338. This compares favorably with the theoretical value of 0.339.

Almost all spectra were recorded in "horizontal configuration" (i.e., with the polarization plane in the incident laser beam parallel to the scattering plane), and the superposition of both polarization components (I_{HH} and I_{HV}) was collected by the spectrometer. Sometimes we have also recorded spectra in "vertical configuration" (i.e., with the polarization plane of the incident beam perpendicular to the scattering plane). The frequency range of these spectra was always limited to the first 90—100 cm^{-1} and the ratio of the two was found very close to $\frac{7}{6}$. Within the accuracy of our experiment (i.e., a few percent) we were unable to detect any trace scattering in liquid argon. This is consistent with the experimental results of Proffitt *et al.*[10] who have found evidence of trace scattering in low-density gaseous argon in the frequency range *above* 100 cm^{-1}.

Depolarized spectra of liquid argon were recorded at three different temperatures, along the coexistence curve, namely at 92.6, 102.0, and 110.7 K. Every single spectrum was collected in arbitrary units (counts/s) and corrected for the response function. The spectral moments, too, were calculated in arbitrary units.

The scattering cell was then evacuated in preparation for the absolute calibration procedure. Gaseous argon was introduced into the cell which was already cooled at the lowest temperature of 92.6 K. When the system was thermally stable, and the pressure of liquefied argon was equal to the expected vapor pressure, then hydrogen was slowly bubbled into the cell up to a total pressure of 12.9 bars. After an overnight equilibration, the system was ready for the measurement. The presence of a clearly visible meniscus made sure that we had a saturated solution of hydrogen in argon, and the concentration of hydrogen in the liquid was evaluated by means of the measurements of Mullins and Ziegler.[16]

We measured the scattering intensity at 20 and 40 cm^{-1} (Stokes side) and the integrated intensity of the rotational Raman lines $S(0)$ and $S(1)$ of hydrogen. This measurement was used for the absolute calibration of the DILS spectra and moments of liquid argon.

Since the solubility of hydrogen in liquid argon decreases by increasing temperature, it was easy to repeat the measurement at 102.0 and 110.7 K.

The measurement at 84.1 K was added at a later time to extend the range of densities of the present experiment as closely as possible to the triple point.

The results of the experiment are summarized in Table I.

The notations are the same as in Refs. 3 and 5 and have the following meaning:

$$G_{yx}^{(0)}=\frac{1}{V}\left\langle \sum_{P,Q}(\hat{\mathbf{y}}\cdot\overleftrightarrow{\alpha}(P,0)\cdot\hat{\mathbf{x}})(\hat{\mathbf{y}}\cdot\overleftrightarrow{\alpha}(Q,0)\cdot\hat{\mathbf{x}})\right\rangle , \tag{2.1}$$

$$G_{yx}^{(2)}=\frac{1}{V}\left\langle \sum_{P,Q}(\hat{\mathbf{y}}\cdot\dot{\overleftrightarrow{\alpha}}(P,0)\cdot\hat{\mathbf{x}})(\hat{\mathbf{y}}\cdot\dot{\overleftrightarrow{\alpha}}(Q,0)\cdot\hat{\mathbf{x}})\right\rangle , \tag{2.2}$$

$$G_{yx}^{(4)}=\frac{1}{V}\left\langle \sum_{P,Q}(\hat{\mathbf{y}}\cdot\ddot{\overleftrightarrow{\alpha}}(P,0)\cdot\hat{\mathbf{x}})(\hat{\mathbf{y}}\cdot\ddot{\overleftrightarrow{\alpha}}(Q,0)\cdot\hat{\mathbf{x}})\right\rangle , \tag{2.3}$$

where $\overleftrightarrow{\alpha}(P,t)$ is the total electric polarizability, at time t, of the local configuration P which produces the scattering process. The dots mean time derivative and the summations are extended over all possible configurations within the scattering volume, V. In the case of argon, which is monatomic, the local configurations which produce depolarized scattering are composed of clusters of at least two atoms.

As it is seen from Table I, the agreement between the present experiment (footnote a) and our previous one (footnote b) is very good. The comparison with the experiment of Clarke and Bruining[4] is also satisfactory in spite of the two different calibration procedures. We will comment further on this particular point below in the discussion section.

TABLE I. Experimental results relative to the first two even moments of liquid argon. The symbols are defined by Eqs. (2.1)—(2.3). χ_2 is the concentration of H_2 in argon.

T (K)	ρ (amagat)	χ_2 (%)	$G^{(0)}/\rho$ (10^{-8} Å^3/amagat)	$G^{(2)}/\rho$ (10^{-5} Å^3/amagat cm^2)	$G^{(4)}/\rho$ (10^{-2} Å^3/amagat cm^4)
84.1±0.1	793	1.03	1.84±0.24[a]	1.42±0.14[a]	5.5±1.3[a]
92.6±0.1	763	1.37	1.58±0.10[a]	1.21±0.07[a]	5.1±0.5[a]
102.0±0.2	728	1.40	2.13±0.17[a]	1.51±0.09[a]	7.3±1.5[a]
110.7±0.2	692	1.36	2.99±0.45[a]	1.90±0.27[a]	7.2±1.3[a]
90.8±1.5	770	0.73	1.57±0.22[b]	1.13±0.10[c]	
103.5±1.0	721	1.55	2.52±0.26[b]	1.60±0.17[c]	
86 ±2	784		1.90±0.18[d]		

[a] Present experiment.
[b] Reference 3.
[c] Reference 20.
[d] Reference 4.

III. THE COMPUTER SIMULATION

In order to evaluate from theory the DILS spectral moments under the same thermodynamic conditions as the experiments, we have executed a set of four molecular dynamics runs which simulate the behavior of liquid argon to the best of our knowledge.

The system was composed of 864 atoms interacting according to the pairwise additive potential of Barker, Fisher, and Watts (BFW),[17] truncated at 2.5σ, in a cubic box, whose dimensions are given by the experimental density, with periodic boundary conditions. We used Verlet's algorithm with a time step of 0.02 ps to numerically integrate Newton's equations, and the system was then equilibrated at a temperature as close as possible to the experimental one.

The zeroth moment (integrated intensity) was calculated from the quantity

$$S_{\alpha\beta}=\frac{\sigma_p^6}{N}\left\langle \left[\sum_{i=1}^{N}\sum_{j\neq i} T_{\alpha\beta}(i,j)\right]^2\right\rangle , \tag{3.1}$$

where σ_p is the pair distance at zero interaction potential, N is the total number of particles, and $T_{\alpha\beta}(i,j)$ represents the $\alpha\beta$ component of the pair collisional field propagator,

$$\overleftrightarrow{\mathrm{T}}(i,j)=f(r_{ij})\left[\overleftrightarrow{\mathrm{I}}-3\frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2}\right] , \tag{3.2}$$

where $\overleftrightarrow{\mathrm{I}}$ is the unit second-rank tensor, $\mathbf{r}_{ij}$ is the vector from the ith to the jth particle, and $\mathbf{rr}$ is a second-order dyadic.

The traceless, angular part, which multiplies the function $f(r_{ij})$, is imposed by the experimental evidence of a totally depolarized spectrum. If only first-order dipole-induced dipole (DID) is taken into account, then the function $f(r_{ij})$ reduces to $1/r_{ij}^3$.[2]

More generally, the function $f(r_{ij})$ is proportional to the pair anisotropy, $\beta(r_{ij})$, and is not exactly described by the DID mechanism alone. Consistently with our previous calculations,[5] we have used the following expressions for $\beta(r)$ and $f(r)$ (the labels i,j have been dropped when this does not generate confusion):

$$\beta(r)=\frac{6\alpha_0^2}{r^3}+\frac{A}{r^6}+B\exp(-r/r_0) , \tag{3.3}$$

$$f(r)=\beta(r)/6\alpha_0^2 . \tag{3.4}$$

In Eq. (3.3) the first term is the lowest-order DID, the second effectively accounts for all the following terms of the multipolar expansion, and the third one accounts for the overlap contributions. This model is very flexible. Moreover, if one uses for the parameters A, B, and r_0 the most probable values, obtained from the pair data (very low-density gas) at room temperature, the agreement with the experiments is good, even at densities and temperatures pertaining to the liquid state.[5]

From the definition of $S_{\alpha\beta}$, Eq. (3.1), it is clear that its numerical value depends on the choice of σ_p. Since for historical reasons this quantity was first calculated by using the Lennard-Jones (LJ) potential, it is useful, in order to compare the present MD results with the previous ones, to normalize our $S_{\alpha\beta}$ by multiplying it by the factor $f=(\sigma_{\mathrm{LJ}}/\sigma_p)^6$.

In order to get better statistics, we used the standard technique of evaluating the average,

$$S_{zz}=\tfrac{1}{6}[S_{xx}+S_{yy}+S_{zz}+\tfrac{4}{3}(S_{xy}+S_{xz}+S_{yz})] , \tag{3.5}$$

instead of a single component $S_{\alpha\beta}$.

Different from our previous calculations, in which the second spectral moment was evaluated from the short time (parabolic) expansion of the correlation function, we now have evaluated this quantity as an equilibrium average of the scalar product of the gradients:[18,19]

$$S_{\alpha\beta}^{(2)}=\frac{T^*\sigma_p^8}{N}\left\langle \sum_{k=1}^{N}\sum_{\gamma=1}^{3}\left[\nabla_{k,\gamma}\left[\sum_{i=1}^{N}\sum_{j\neq i}T_{\alpha\beta}(i,j)\right]\right]^2\right\rangle . \tag{3.6}$$

This quantity is then multiplied by the normalization factor f and by $\epsilon/m\sigma_p^2$ to give the second moment in units of s^{-2}.

In order to have an estimate of the computational errors, we have divided our averages in subgroups of 500 time steps each and evaluated a rms error. The S_{zz}, which corresponds to the integrated intensity, was averaged over 4000 time steps while the second moment, whose conver-

TABLE II. Molecular-dynamics simulation results for the first two even moments. The symbols are defined by Eqs. (3.1) and (3.6) and normalized as explained in text.

T (K)	Molecular volume (cm^3)	Reference	S_{zz}	$S_{zz}^{(2)}$ 10^{25} (s^{-2})
83.7±1.1	28.24	a	0.150±0.021	0.389±0.003
91.7±1.2	29.35	a	0.194±0.029	0.420±0.002
100.3±1.2	30.76	a	0.228±0.023	0.438±0.002
110.1±1.4	32.32	a	0.366±0.076	0.451±0.003
92	28.30	b	0.21	
90.8±1.5	29.08	c	0.210±0.057	0.472±0.042
89	28.71	d	0.26	
88.8	29.08	e(1)	0.162±0.020	0.406±0.003
95.0	29.08	e(2)	0.172±0.020	0.409±0.003

[a] Present MD calculation with BFW potential.

[b] Reference 21 with BB potential.

[c] Reference 5 with BB potential.

[d] Reference 3, DID with LJ potential.

[e] Reference 23 with (1) BFW only and (2) BFW and AT.

gence turned out to be much faster, was averaged only over 2000 time steps. The four simulations were undertaken for densities of 793, 763, 728, and 692 amagats and the results are summarized in Table II.

As is clear from Table II, the fluctuations of $S_{zz}^{(2)}$ (second moment) are of the same order of magnitude as those of the temperature, while for S_{zz} they are much bigger. This reflects the fact that in contrast to the zeroth moment, which is a static property of the system, both temperature and second moment are averages of dynamic quantities. A second important difference, which may also explain the different behavior between S_{zz} and $S_{zz}^{(2)}$, is that in the second moment the correlations between four particles are averaged to zero by the velocity distribution function, and only terms originating from two- and three-body correlations are important.[20]

For the sake of completeness we have also reported, in Table II, two calculations,[21,5] made with the same polarizability and the Bobetic-Barker (BB) potential,[22] and a calculation,[3] made with first-order DID polarizability model and Lennard-Jones potential. With reference to the calculations made with the same polarizability and different interaction potentials (footnotes a and b plus c, in Table II), not very much can be said about the effect, on the integrated intensity, of changing the potential, since the numerical fluctuations are of the same order of magnitude, or even larger, than the differences. Nevertheless, by comparing the second moment data, it seems confirmed that the BFW potential tends to decrease the value of the spectral moments of some 10%. This fact indicates that the BFW potential imposes a slightly more symmetrical structure (and therefore less anisotropy) around each argon atom than does the BB one. The two pair potentials are very similar. However the hard core, and part of the well, of the BFW potential are systematically below the corresponding quantities of the BB one. This implies that the pair correlation function for the BFW system has a slightly higher peak value and its raising edge is shifted toward shorter r values. As a consequence the coordination number of BFW atoms is slightly higher than that of the BB ones, which, in turn, implies a more symmetrical structure, on the average, for the BFW systems.

In Table II we have also included a calculation in which the potential energy was modeled either by using only the pairwise additive potential of BFW, and its contribution plus the three-body irreducible term of Axilrod and Teller (AT). The comparison of lines e(1) and e(2) in Table II shows what was already noticed,[23] that the effect of the inclusion of the triple-dipole irreducible term in the potential function is quite small and in any case within the statistical uncertainties of the MD calculations.

No attempt was made of evaluating the fourth moment from classical MD simulations. In fact, while quantum corrections do not affect significantly the DILS zeroth moment of liquid argon, their effect on the second moment is bigger and is estimated to be of the same order of magnitude of the present experimental accuracy.[19] To our knowledge, no quantitative calculation exists on the magnitude of quantum corrections to the fourth moment, but by a simple extrapolation of the results relative to the first two, one might expect a large effect, perhaps as big as the classical value itself.

IV. DISCUSSION

The available experimental results and MD calculations are summarized in Table III in comparable units. The data have been divided into four sets with very similar temperatures to make the comparison more meaningful.

Let us consider first the consistency of the experimental data. In the first set the agreement is very good. Even a correction for the difference in density would be in the right direction. Nevertheless one might speculate that the result by Clarke and Bruining,[4] footnote d in the table, is perhaps too high. In fact, these authors used an uncommon function to account for the effect of the local field and if we correct their result by using the more trustworthy[14] Lorentz-Lorenz local field (LF) factor,

TABLE III. Comparison of experimental and simulation results. The conversion constant for S_{zz} is 1.031×10^{-7} (Å^3/amagat), while the one for $S_{zz}^{(2)}$ is 2.906×10^{-30} (Å^3 s^2/amagat cm^2).

T (K)	ρ (amagat)	$G^{(0)}/\rho$ (10^{-8} Å^3/amagat) Expt.	$G^{(0)}/\rho$ (10^{-8} Å^3/amagat) MD	$G^{(2)}/\rho$ (10^{-5} Å^2/amagat cm^2) Expt.	$G^{(2)}/\rho$ (10^{-5} Å^3/amagat cm^2) MD
84.1±0.1	793	1.84±0.24[a]		1.42±0.14[a]	
83.7±1.1	793		1.55±0.21		1.130±0.009
86±2	784	1.90±0.18[d] (1.56±0.18)			
88.8±1.5	770		1.67±0.20		1.180±0.010
90.8±1.5	770	1.57±0.22[b]		1.13±0.10[c]	
92.6±0.1	763	1.58±0.10[a]		1.21±0.07[a]	
91.7±1.2	763		2.00±0.30		1.220±0.006
103.5±1.0	721	2.52±0.26[b]		1.60±0.17[c]	
102.0±0.2	728	21.3±0.17[a]		1.51±0.09[a]	
100.3±1.2	728		2.35±0.24		1.273±0.006
110.7±0.2	692	2.99±0.45[a]		1.90±0.27[a]	
110.1±1.4	692		3.77±0.78		1.310±0.009

[a] Present experiment.

[b] From Ref. 3.

[c] From Ref. 20.

[d] From Ref. 4.

$$\mathcal{F}_{\mathrm{LF}}=\left[\frac{n^2+2}{3}\right]^4, \tag{4.1}$$

we obtain a value which is 18% lower than theirs. This result is reported in parentheses in Table III. With that, the agreement of set one is somewhat poorer but still within the respective standard deviations.

The consistency in the second and third sets is very good. The previous results have been confirmed by the present experiment and the experimental errors reduced. The small differences are in part explained by the density dependence of the moments. No other experimental data exist for comparison with our measurement in the fourth set.

As it is seen from Table III, the temperature ranges from 83.7 to 110.7 K and the density from 692 to 793 amagats, i.e., a variation of about 30% and 15%, respectively. However, density is the more significant parameter. In fact, because of the strong cancellation among the two-, three-, and four-body correlation terms in the zeroth moment,[24] and that between the two- and three-body terms in the second moment,[20] it is the density, much more than temperature, which plays the principal role in the determination of the DILS spectral properties of liquid argon.

Figure 1 shows the reduced zeroth moment, $G^{(0)}/\rho$, as a function of density, ρ. The points are taken at different temperatures and the temperature variation is the same as for the coexistence curve.

The experimental data are represented by circles while the MD data are represented by triangles. The uncorrected value of Ref. 4 is represented by a cross. There is a substantial agreement between experiment and simulation even if the experimental data are mostly below the calculated ones.

Similarly, the reduced second moment, $G^{(2)}/\rho$, is depicted as a function of ρ in Fig. 2(a). Again, the comparison between experiment and simulation is quite good on the absolute scale, but the experimental points are now, on

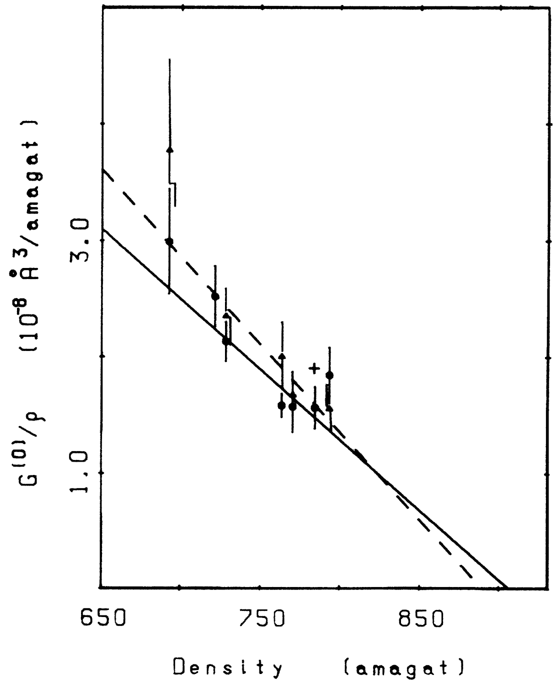

FIG. 1. Experimental zeroth moment per molecule, $G^{(0)}/\rho$, vs density. The circles are the values reported in Table III while the triangles represent the MD data. The cross is the uncorrected experimental zeroth moment of Ref. 4. The full line is the best fit to the experimental points while the dashed line is relative to the MD results.

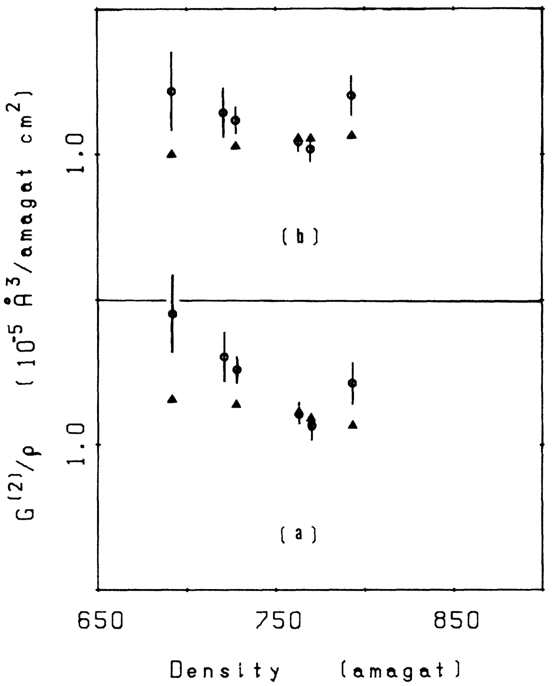

FIG. 2. (a) Experimental second moment per molecule, $G^{(2)}/\rho$, vs density. The circles are the values reported in Table III while the triangles represent the MD data. (b) Same as above reduced by the factor (T_0/T). The temperature T_0 has been chosen as $T_0=83.7$ K.

the average, above the computed results.

One might speculate that the differences, between calculations and experiments, are attributable to irreducible many-body terms, either in the potential or in the polarizability functions. Our feeling is that minor corrections, in the models of both polarizability and potential pair functions, might also give good agreement. In fact, in a recent calculation, Weis and Alder[25] have pointed out that n-body $(n>2)$ irreducible DID terms in the anisotropy have a very small effect and reduce the integrated intensity by no more than a few percent, which is not enough for explaining the actual differences. Moreover, in our MD calculations, we have tested the effect of introducing the Axilrod-Teller three-body term in the potential function, and have found no significant change in the DILS spectral moments.[23] These two calculations deal with irreducible terms which are relatively long ranged (triple-dipole) and do not tell us much about the effect of short-range corrections. On the other hand, to our knowledge, no calculation exists in which irreducible terms, of shorter range than DID, have been taken into account, either in the potential or in the polarizability anisotropy, for evaluating their effect on the DILS spectra. By contrast, as was noted above, the small variation of the pair potential, from BB to BFW, might affect the spectral moments by as much as 10%.

The pairwise additive models for both the potential and the polarizability anisotropy, have been tested and give results which reproduce the experimental data within two standard deviations or better. This small difference can, presumably, be accounted for by minor adjustments of the pair functions. We thus see that, in order to investigate in more detail the effect of many-body terms, in the liquid state, either in the potential or in the induced polarizability, the present accuracy of the experiments and the MD calculations should be drastically increased by 1 order of magnitude or more.

We have estimated the density, ρ_0, for which the integrated intensity vanishes by a linear extrapolation of the data points of Fig. 1. We find that the experimental points give an intercept at 905 amagats while the MD results point to 890 amagats. For comparison, we mention that the density of the solid at triple point is 910 amagats. As a matter of fact, the depolarized integrated intensity is a measure of the global anisotropy of the sample. The ratio of the intensity to the density is therefore related to the anisotropy "per atom." In both the low-density and high-density limit, the system is isotropic, as it can be easily seen by symmetry reasons. As density is increased from zero up, the anisotropy centers (i.e., collisions), whose number "per atom" increases linearly with density, depolarize the scattered radiation. In a perfectly complementary way, by decreasing the density from the close packing value, ρ_0, the rate of depolarized scattering should increase as $\rho_0-\rho$.[26,27] Of course at intermediate densities the depolarized cross section should go through a maximum and this is what is seen in compressed gas experiments.[5]

For the second moment this simple picture does not hold. Being related to the dynamical behavior of the liquid, the second spectral moment is not expected to vanish, *at finite temperature,* even in a symmetric structure. In fact, in an isotropic solid, thermal fluctuations around the equilibrium positions do not contribute to an averaged static property like the zeroth moment. However, they do contribute to a dynamical quantity like the second moment since this is related to the average squared time derivative of the anisotropy and therefore to the rms fluctuation of the displacements. This interpretation is supported by the smooth behavior of the experimental function $G^{(2)}/\rho$, whose slope tends to flatten if the leading temperature dependence is eliminated by considering the reduced quantity, $(T_0/T)G^{(2)}/\rho$, as a function of density [Fig. 2(b)].

Moreover it should be noted that the last experimental point in Fig. 2(b) is well outside the ideal straight line which fits the first five points. Since the temperature for this point (84.1 K) is very close to the triple point temperature (83.7 K), it is possible that the value of this reduced second moment has some contribution from the solidlike dynamics, which is not fully taken into account by the simulation, due to the limited dimensions of the box. It would be quite interesting to follow the behavior of the reduced second moment through the liquid-solid transition, but this is a matter beyond the scope of the present work.

V. CONCLUSIONS

The method of the internal standard, for calibration of the DILS spectra of noble gases, has been demonstrated to have a good reproducibility. However, in the case of liquids, the method is limited by the lack of solubility data of hydrogen in the heavier noble gases. The comparison with the other calibration technique, which makes use of an external standard, is favorable if the data are corrected for the local field factor by using the Lorentz-Lorenz function [Eq. (4.1)]. It would be very interesting to compare more experimental data, taken with the two different calibration techniques, since the two methods are somewhat complementary.

We have shown evidence that the integrated intensity "per atom" is an almost linear function of density. This fact appears to be plausible in terms of free volume in the liquid. Accordingly, near the high-density limit, the role of the scattering centers is assumed by the voids in the structure instead of single particles.[27] The density at which the reduced zeroth moment should vanish is very close to the density of the solid. Finally, it would be very interesting to follow experimentally the behavior of the spectral moments through the liquid-solid transition, since the experimental data points of the liquid, at a temperature very close to that of the triple point, seem to show some features which perhaps mimic the solid phase. This is more evident in the second moment where the solidlike dynamics might play an important role even in the liquid phase.

The use of DILS spectroscopy for investigating three-body effects of both the interaction potential and the polarizability, can be made provided that the present accuracy of experiment and MD simulation is drastically increased. From the experimental point of view, this goal does not seem very close. In fact, the statistical errors, which affect the photon counting and which can be easily reduced by increasing the observation time, are the least important in the total balance, while, on the one hand the solubility data and, on the other the refractive index correction,[28] introduce errors which are difficult to avoid. Also the computer simulation is limited from this point of view. To reduce the statistical uncertainties, one should increase the number of atoms in the box, and therefore the computer time, by a big factor and this would make the calculations lengthy and too expensive. Alternatively, one could collect experimental data at constant temperature, and analyze them as function of the density. By repeating this procedure at various temperatures one could be able to have separate information on the potential and polarizability whose error would be reduced by the great number of data.

In conclusion, within the present accuracy, there is a substantial agreement between the experiments and the MD calculations of DILS spectral moments of liquid argon with the pairwise additivity approximations. Small refinements of the present pair models would perhaps enable one to obtain complete agreement.

---

[1] P. A. Fleury and J. P. McTague, Opt. Commun. **1**, 164 (1969).

[2] B. J. Alder, J. J. Weis, and H. L. Strauss, Phys. Rev. A **7**, 281 (1973).

[3] D. Varshneya, S. F. Shirron, T. A. Litovitz, M. Zoppi, and F. Barocchi, Phys. Rev. A **23**, 77 (1981).

[4] J. H. R. Clarke and J. Bruining, Chem. Phys. Lett. **80**, 42 (1981).

[5] F. Barocchi, G. Spinelli, and M. Zoppi, Chem. Phys. Lett. **90**, 22 (1982).

[6] F. Barocchi and M. Zoppi, Phys. Lett. **66A**, 99 (1978).

[7] L. Frommhold, K. H. Hong, and M. H. Proffitt, Mol. Phys. **35**, 665 (1978).

[8] F. Barocchi, M. Zoppi, M. H. Proffitt, and L. Frommhold, Can. J. Phys. **59**, 1418 (1981).

[9] D. P. Shelton and G. C. Tabisz, Mol. Phys. **40**, 285 (1980).

[10] M. H. Proffitt, J. W. Keto, and L. Frommhold, Can. J. Phys. **59**, 1459 (1981).

[11] M. Zoppi, M. Moraldi, F. Barocchi, R. Magli, and U. Bafile, Chem. Phys. Lett. **83**, 294 (1981).

[12] M. S. Brown, M. H. Proffitt, and L. Frommhold, Chem. Phys. Lett. **117**, 243 (1985).

[13] U. Bafile, L. Ulivi, M. Zoppi, and F. Barocchi, Chem. Phys. Lett. **117**, 247 (1985).

[14] F. Barocchi and M. Zoppi, in *Proceedings of the NATO Advanced Research Workshop: Phenomena Induced by Intermolecular Interactions,* edited by G. Birnbaum (Plenum, New York, 1985).

[15] P.Mazzinghi and M. Zoppi, Rev. Sci. Instrum. **54**, 1585 (1983).

[16] J. C. Mullins and W. T. Ziegler, Adv. Cryog. Eng. **10**, 171 (1965).

[17] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971).

[18] F. Barocchi, M. Moraldi, and M. Zoppi, Phys. Rev. A **26**, 2168 (1982).

[19] F. Barocchi, M. Zoppi, and M. Neumann, Phys. Rev. A **27**, 1587 (1983).

[20] M. Zoppi, F. Barocchi, D. Varshneya, M. Neumann, and T. A. Litovitz, Can. J. Phys. **59**, 1475 (1981).

[21] J. Vermesse, D. Levesque, and J. J. Weis, Chem. Phys. Lett. **85**, 120 (1982).

[22] M. V. Bobetic and J. A. Barker, Phys. Rev. B **2**, 4169 (1970).

[23] M. Zoppi and G. Spinelli, Proceedings of the IXth International Conference on Raman Spectroscopy, Tokyo, 1984, edited by M. Tsuboi.

[24] A. J. C. Ladd, T. A. Litovitz, and C. J. Montrose, J. Chem. Phys. **71**, 4242 (1979).

[25] J. J. Weis and B. J. Alder, Chem. Phys. Lett. **81**, 113 (1981).

[26] M. Thibeau, B. Oksengorn, and B. Vodar, J. Phys. (Paris) **29**, 287 (1968); M. Thibeau, G. C. Tabisz, B. Oksengorn, and B. Vodar, J. Quant. Spectrosc. Radiat. Transfer **10**, 839 (1970).

[27] T. Keyes and P. A. Madden, Can. J. Phys. **59**, 1560 (1981).

[28] J. R. Nestor and E. R. Lippincot, J. Raman Spectrosc. **1**, 305 (1973).