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Three-body depolarized interaction-induced light-scattering spectrum of neon

Silvia Pestelli, Ubaldo Bafile, Lorenzo Ulivi, and Marco Zoppi
Istituto di Elettronica Quantistica, Consiglio Nazionale delle Ricerche, via Panciatichi 56/30, I-50127 Firenze, Italy

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We report the results of a depolarized interaction-induced light-scattering (DILS) experiment on gaseous neon at room temperature, from which the two- and three-body induced spectra have been extracted. The two-body spectrum is in excellent agreement (in absolute units) with a previous determination by Frommhold and Proffitt [Phys. Rev. A **21**, 1249 (1980)], while the three-body spectrum is a new result. The comparison of the three-body experimental spectral moments with a calculation performed within the pairwise additivity approximation shows a discrepancy which is of opposite sign to that observed in krypton. The calculations have been carried out including the first-order correction of the Wigner-Kirkwood expansion in order to take into account quantum effects. We suggest that the occurence of irreducible three-body effects may be due to more than one microscopic mechanism and these can be usefully investigated by means of DILS spectroscopy.

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I. INTRODUCTION

In principle, the microscopic properties of a system composed of a large number N of interacting particles can be described exactly by a N-body Hamilton function containing all the kinetic- and potential-energy terms. However, the formidable complexity of such an approach has prevented, so far, any application of this method to the study of the real systems. Very often, the overall behavior of the system has been described, to an excellent approximation, as that of a model system driven by the so-called standard Hamiltonian, whose interaction potential term is pairwise additive. The closest experimental equivalent to the standard model is represented by the dilute rare gases.

In condensed rare gases, while many properties are well reproduced by the standard Hamiltonian up to the liquid density (and over) [1], other properties show that irreducible many-body contributions to the potential energy may play a significant role. As an example, we remind that even the experimental third virial coefficient of argon does not agree with the one computed within the pairwise additivity (PA) approximation [2]. Moreover, all rare gases form fcc crystals, while pairwise additive models show a minimum free energy for the hcp structure, which is almost independent of the particular choice of the potential [3]. It is well known that introducing an irreducible triple-dipole term in the Hamiltonian significantly reduces the discrepancy, but the change in energy is not big enough to stabilize the fcc structure [4].

While the pair potentials of simple systems are now accurately known [5], still very little information is available about the irreducible three-body term. Moreover, the inclusion of many-body forces in the theory of fluids implies a great deal of complication, and even computer simulation becomes quite inefficient when irreducible triplet contributions are taken into account [6]. As a consequence, the whole body of the statistical mechanics of dense gases and liquids has been developed in the framework of the PA approximation. In recent times, as the accuracy of the available experiments has been steadily increasing, this simplified interaction model has shown its limitations.

A convenient and widely used method for studying the density evolution of the microscopic and macroscopic properties of fluids is based on their representation in the form of power series of the density. In general, starting from the ideal-gas limit (linear behavior), one finds deviations increasing first as the square of the density: at sufficiently low density the probability that a third particle falls within the interaction range of the other two can be considered negligible and the pair approximation applies. At larger densities, triplets contribute with a cubic term. This cubic dependence is due partly to the sum of pair terms and partly to irreducible three-body effects. When the latter begin to play a role, the pair approximation breaks down.

Experimental evidence of the breakdown of the PA model in dense gases and liquids has been highlighted, for example, by neutron-scattering experiments [7,8]. At the same time, depolarized interaction-induced light-scattering (DILS) experiments performed on krypton at room temperature [9,10] and on hydrogen at several temperatures [11–15] have pointed out the occurrence of the same situation. Of course, only experiments can give us information on where the cluster expansion should be truncated beyond the pair term, and this will depend on the thermodynamic state. However, due to the relatively good description that the PA approximation gives of a dense system, it is expected that the irreducible three-body term will be sufficient to bring good agreement between theory and experiments in condensed systems, even at rather high density, within the present precision of the experimental results.

The investigation has been carried out mainly by comparing the predictions of the pair approximation (often by means of computer simulation) with the experimental results. The DILS technique is of particular interest in the investigation of three-body effects in monatomic or spherically symmetric molecular systems because the zero-density limit, in this case, is the pair term of the density expansion and the first correction already contains the triplet effects. However, the interpretation of DILS experiments is more involved than for a neutron-scattering experiment, because the effects of the irreducible many-body interactions appear both in the potential energy function, which drives the microscopic dynamics of the particles, and in the induced polarizability, which produces the depolarized light spectrum. The two effects cannot be easily separated. The DILS technique has been widely studied in the past two decades, and a rather large amount of data is now available for the rare-gas fluids and some simple spherical molecular systems [16,17].

Argon has been the first system for which the PA approximation has been tested by means of DILS experiments. The spectral data, taken at 298 K between about 4 and 1000 bars, were used to evaluate the density dependence of the 0th and 2nd spectral moments with the corresponding classical computer-simulation results obtained within the PA model [18,19]. In the simulations, the same polarizability model which best fitted the low-density *pair* data was used and a substantially good agreement was found in the whole density range. The same comparison was extended to the liquid phase with similar results [18–20]. The conclusion is that for argon three-body irreducible effects are very small and below the limit of detectability with the present accuracy of DILS experiments. However, when the same experimental investigation was extended to krypton, different results were found. While for the 0th moment the discrepancy was small, and of the same size as the joint uncertainties in the experiment and in the calculations, a clear breakdown of the PA hypothesis was observed in the behavior of the second spectral moment. Here the discrepancy was clearly beyond the errors that could be attributed either to the experiment or to the simulation result, including a possible uncertainty in the polarizability model [10]. A similar conclusion was drawn by Egelstaff and coworkers, after analyzing a neutron-diffraction experiment on the same substance [7]. Therefore, it appears that for krypton the PA approximation fails at relatively low density and irreducible three-body interaction terms should be included in the theory in order to interpret correctly the density dependence of the measured properties.

The hydrogen molecule is diatomic and, therefore, its depolarized Raman spectrum results in a mixture of an *intermolecular* DILS band with the *intramolecular* rotational lines [14]. In spite of this fact, the translational interaction-induced Raman band of hydrogen is measurable between $\omega \approx 10$ and $\omega \approx 200$ cm^{-1} [11,12,15,21], and this allows a satisfactory determination of the first DILS spectral moments. The experimental determination of the cubic term in the virial expansion of the DILS hydrogen spectrum was done both at 50 and 297 K and the comparison with the theoretical results was carried out on the first two (0th and 1st) moments [22]. Here, the observed discrepancy, between calculations and experiments, is larger than the experimental error. Moreover, while at 50 K both the computed moments are larger (in absolute value) than the experimental ones, the situation is reversed at room temperature, where the calculation gives smaller values than the experiment.

Finally, there is a substantial difference between the effect found on krypton and that observed in hydrogen at room temperature. For krypton, the computed values of the second moment as a function of density are *larger* than the experimental ones. This implies that a possible irreducible three-body contribution has the *same* sign (and increases the absolute value) as the PA term. For room-temperature hydrogen the situation is reversed, and the computed values of the three-body components would give a density variation of the moments stronger than the experiment. This means that, for hydrogen, the likely irreducible contribution has an *opposite* sign with respect to the PA term. In order to gain more insight into this matter, it seems worthwhile extending the investigation to other systems, and, in particular, the rare gases with smaller mass than argon.

On a purely experimental basis, neon appears more manageable than helium for a light-scattering experiment: although the atomic polarizability of both systems is so small that the experimental determination of the DILS spectrum is obtained only with great efforts, the larger atomic polarizability of neon (almost twice than helium) and the fourth power dependence of the cross section on this quantity, make quite a difference between the two systems. Moreover, both neon and helium are expected to manifest non-negligible quantum effects [23]. However, as long as we deal with neon at room temperature, the first Wigner-Kirkwood correction is sufficient to take into account quantum effects up to the second spectral moment. Therefore, for this case, the interpretation of DILS results is less questionable [24]. In this paper, we report the results of an experiment from which the three-body spectrum of neon has been obtained for the first time. In Sec. II we will briefly recall the basic formulas of DILS theory, while the experimental work is described in Sec. III. The analysis of the results is reported in Sec. IV, and the conclusions are the arguments of Sec. V.

II. OUTLINE OF DILS THEORY

A more detailed account of DILS theory has been given elsewhere [10]. Here we simply recall the results which will be necessary for the discussion. The DILS spectrum is the time Fourier transform of the autocorrelation function of the total polarizability tensor **A** of the system, projected on the polarization directions of the incident and the scattered fields. These are usually orthogonal and will be denoted with x and y. The relevant correlation function for DILS is

$$G_{xy}(t)=(1/V)\langle A_{xy}(t)A_{xy}(0)\rangle \ , \tag{1}$$

where V is the scattering volume. It is important to point out that the statistical average, represented by the angular brackets in right-hand side (rhs) of Eq. (1), should be carried out using the *true* Hamiltonian whose potential-energy contribution can be cluster-expanded as

$$\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\sum_{i<j}\phi^{(2)}(\mathbf{r}_i,\mathbf{r}_j)+\sum_{i<j<k}\phi^{(3)}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)+\cdots\ , \tag{2}$$

where $\phi^{(2)}$ and $\phi^{(3)}$ represent the irreducible two- and three-body potential-energy terms. Also, the polarizability tensor $\mathbf{A}$ can be cluster-expanded as

$$\mathbf{A}=\sum_{i}\boldsymbol{\alpha}^{(1)}(\mathbf{r}_i)+\sum_{i<j}\boldsymbol{\alpha}^{(2)}(\mathbf{r}_i,\mathbf{r}_j)+\sum_{i<j<k}\boldsymbol{\alpha}^{(3)}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)+\cdots\ , \tag{3}$$

where $\boldsymbol{\alpha}^{(1)}(\mathbf{r}_i)$ is the polarizability tensor, in the laboratory reference frame, of the ith molecule whose center-of-mass position is $\mathbf{r}_i$. Correspondingly, $\boldsymbol{\alpha}^{(2)}(\mathbf{r}_i,\mathbf{r}_j)$ represents the excess polarizability of the pair (i,j), and so on. Within the PA approximation, all terms beyond $\phi^{(2)}$ and $\boldsymbol{\alpha}^{(2)}$ are neglected. For monatomic systems, like the rare gases, the single-molecule term does not contribute to the depolarized scattering because of the spherical symmetry. Therefore, the leading term of the correlation function (1) becomes simply what arises from pair interactions, namely,

$$G_{xy}(t)=(1/V)\left\langle \sum_{i<j}\alpha_{xy}^{(2)}(ij,t)\sum_{k<l}\alpha_{xy}^{(2)}(kl,0)\right\rangle\ , \tag{4}$$

where we shorten the notation writing (ij) in place of $(\mathbf{r}_i,\mathbf{r}_j)$. In the following, we will drop the subscript xy as well as the superscript (2) in the polarizabilities. Here, it is important to point out that the PA approximation requires not only to neglect the term $\boldsymbol{\alpha}^{(3)}$ in Eq. (3), but also to compute the N-body statistical average on the rhs of Eq. (4), discarding triplet and higher-order terms from the potential energy of the system.

When the sums in (4) are worked out, three terms are obtained, according to whether common indices appear in the pair labels of the two tensor elements or not

$$G(t)=G^{(2)}(12,t)+G^{(3)}(123,t)+G^{(4)}(1234,t)\ , \tag{5}$$

with

$$G^{(2)}(12,t)=[N(N-1)/2V]\langle\alpha(12,t)\alpha(12,0)\rangle\ , \tag{6}$$

$$G^{(3)}(123,t)=[N(N-1)(N-2)/V]\langle\alpha(12,t)\alpha(13,0)\rangle\ , \tag{7}$$

$$G^{(4)}(1234,t)=[N(N-1)(N-2)(N-3)/4V]\times\langle\alpha(12,t)\alpha(34,0)\rangle\ . \tag{8}$$

Although these three terms exhibit an explicit density dependence of the form n^2, n^3, and n^4 $(n=N/V)$, respectively, the implicit density dependence of the equilibrium distribution functions, which is used to perform the statistical averages, must be taken into account in order to write down the virial expansion for the correlation functions $G^{(i)}(t)$ $(i=2,3,4)$. For a homogeneous system, this information is contained in the distribution functions $g^{(i)}(\{\mathbf{r}_1,\ldots,\mathbf{r}_i\})$ [1]. For $i=2$, the pair distribution function is

$$g^{(2)}(1,2)=g_0^{(2)}(1,2)+ng_1^{(2)}(1,2)+\cdots \tag{9}$$

and analogous expressions hold for $i=3$ and $i=4$.

We have now all the ingredients to write the correlation function $G(t)$ in power series of the density within the PA approximation [25]. This is

$$G(t)=G_2(t)(n^2/2)+G_3(t)n^3+\cdots\ , \tag{10}$$

with

$$G_2(t)=V\langle\alpha(12,t)\alpha(12,0)\rangle_0^{(2)}\ , \tag{11}$$

and

$$G_3(t)=V^2[\langle\alpha(12,t)\alpha(13,0)\rangle_0^{(3)}+(\tfrac{1}{2})\langle\alpha(12,t)\alpha(12,0)\rangle_1^{(2)}]\ . \tag{12}$$

Taking into account that in an isotropic fluid, $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ depends only on the distance $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, it is straightforward to compute the angular averages in Eqs. (11) and (12). Then, the two-body average operator $\langle\cdots\rangle_0^{(2)}$ reduces to a one-dimensional integral and, in a similar way, it is easily shown that the three-body average operators $\langle\cdots\rangle_1^{(2)}$ and $\langle\cdots\rangle_0^{(3)}$ become triple integrals whose expressions are known [26].

The triplet correlation function $G_3(t)$, which is represented by Eq. (12) within the PA approximation, is then composed by two terms. The first one is given by the correlation between the induced polarizability (pairwise additive) within a triplet. The second term originates from polarizability correlations within a single pair which are dynamically influenced by the presence of a third particle nearby. The first term is expected to give rise to a cancellation effect (decrease of the depolarized spectrum) due to a lesser degree of anisotropy in a triplet than in a pair. This term is always negative for a dipole-induced-dipole Lennard-Jones (DID-LJ) model [27]. The second term, instead, tends to increase the depolarization, in general. This is positive, for a DID-LJ model, at almost all temperatures, apart from a limited region when the reduced temperature is around 1.5–2.0 [24]. Irreducible three-body contributions to DILS, when present, would add up to Eq. (12) and are provided *both* by irreducible three-body polarizability and three-body potential-energy terms. It appears very difficult, at present, to assess the relative weight of the two contributions to DILS.

III. THE EXPERIMENT

Collision-induced scattering results in a weak depolarized wing appearing at both sides of the polarized Rayleigh-Brillouin spectrum. The intensity profile is almost exponential and the signal falls off rapidly with increasing frequency shift (typical decay constants are from 10 to 20 cm^{-1}). Basically, the experimental apparatus employed for DILS measurements is a standard Raman setup. However, the close proximity of the much stronger elastic peak and the exponential decay of the DILS spectrum, make essential requirements an intense laser source, an efficient stray-light rejection of the monochromator and a detector with low and constant noise level.

The green ($\lambda_0 = 514.5$ nm) beam of an argon-ion laser was focused on the neon gas sample inside the pressure optical cell [28]. Depolarized scattered radiation was collected at right angle, dispersed by an 85-cm Czerny-Turner double monochromator (Spex 1401) and detected with a GaAs cathode photomultiplier tube (Hamamatsu R943-02). The detector noise was found stable enough to allow for a constant noise subtraction. Due to the small scattering cross section of neon, as many as 15 h were needed to acquire one spectrum keeping the statistical uncertainty (after noise subtraction) within a few percent. Thus, particular care was taken in controlling the stability of the system during this time.

DILS spectra of gaseous neon were measured at room temperature and seven different pressures up to 340 bar with numerical density ranging from 2 to 7 atom/nm^3 (*PVT* data were obtained from Ref. [29]). For each density the spectrum was recorded on the Stokes side at frequency shifts in the range 6–120 cm^{-1} with respect to the laser line; the sampling step was 4 cm^{-1} with an instrumental pass band of 2 cm^{-1}. The frequency dependence of the scattered signal was corrected for the relative efficiency of the apparatus and an absolute calibration was performed using the integrated intensity of the rotational *S*(0) and *S*(1) Raman lines of hydrogen as an external standard, according to

$$\frac{d^2\sigma_{\text{coll}}(\omega)}{d\Omega d\omega} = n_{\text{H}_2} \frac{D_{\text{coll}}(\omega)}{D_{\text{rot}}[S(J)]} \left[\frac{d\sigma}{d\Omega} \right]_{S(J)} , \tag{13}$$

where $D_{\text{coll}}(\omega)$ and $D_{\text{rot}}[S(J)]$ are the measured quantities [the DILS signal from the neon sample (counts/s) at frequency shift ω, and the integrated intensity of Raman scattering from hydrogen at density n_{H_2} (cm^{-1} counts/s), respectively], while $(d\sigma/d\Omega)_{S(J)}$ is the scattering cross section of the rotational Raman line $S(J)$ of hydrogen which is accurately known [18,30].

The result of the experiment is a two-dimensional sampling of the frequency and density dependence of the depolarized scattering cross section of neon in the range specified above. The estimated uncertainty, taking into account all the corrections and calibration procedures, goes from 5% to 15% increasing with frequency shift. Some of the measured spectra are shown in Fig. 1.

IV. DATA ANALYSIS

As already discussed in Sec. II, two- and three-body contributions to DILS can be separated by analyzing the density dependence of the spectra. In particular, a polynomial regression of the measured cross section as a function of density, at fixed frequency shift, allowed us to derive both the pair and triplet spectral components according to the virial expansion [31].

$$D_{\parallel}(\omega,n) = D_{2,\parallel}(\omega)n^2/2 + D_{3,\parallel}(\omega)n^3 , \tag{14}$$

where $D_{\parallel}(\omega) = (2/15)\ k_0 k_s^3 G(\omega)$, k_0 and k_s are the incident and the scattered wave vectors, respectively, and $G(\omega)$ is the time Fourier transform of $G(t)$ defined in Sec. II. It is worthwhile pointing out that, in the frequency range of the present experiment, no extra contribution with respect to those explicitly written in Eq. (10) were observed. This was proved by a careful analysis of the χ^2 values for different polynomial fittings.

Density analysis resulted in the determination, in the explored frequency region, of the two-body spectrum $D_{2,\parallel}(\omega)$ and the three-body spectrum $D_{3,\parallel}(\omega)$ in absolute units (nm^6 and nm^9, respectively). For frequency shift beyond 70 cm^{-1} the best fitting curves were quadratic so that the three-body spectrum was found to vanish within the errors. In Fig. 2 the two-body spectrum is plotted against a logarithmic scale and compared with an independent experimental result reported by Frommhold and Proffitt [32]. The comparison shows a good agreement both in shape and in absolute values. The three-body spectrum of neon is reported in Fig. 3.

Measurements of the two-body spectrum, which is rigorously described by the pair theory, allow the determination of a model for the pair polarizability, once a reliable pair interaction potential is given. The coincidence

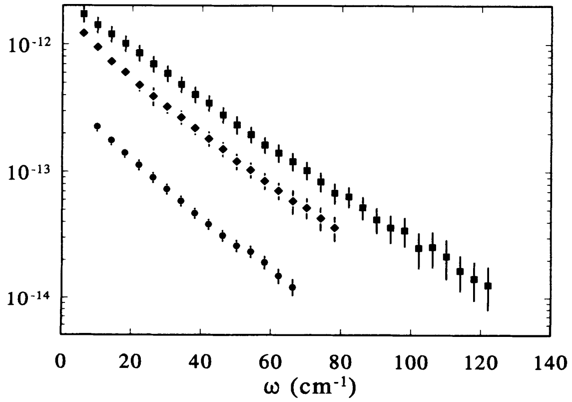

FIG. 1. DILS depolarized spectra of room-temperature neon at $n = 2.1$, 5.0, and 7.1 nm^{-3}. By expressing the frequency shift in units $1/\lambda$ (cm^{-1}), $D_{\parallel}$ turns out a dimensionless quantity.

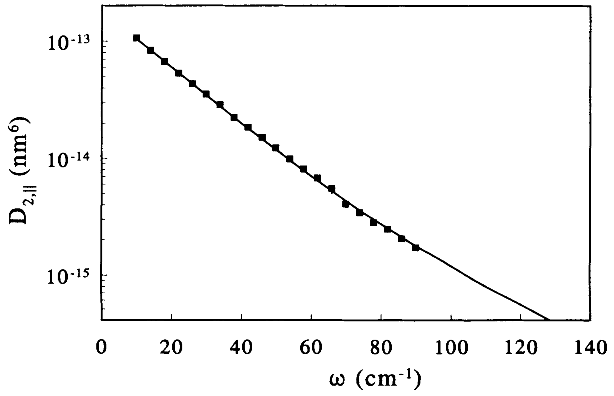

FIG. 2. Experimental two-body spectrum of neon, in absolute units, at $T = 296$ K. The full squares represent the present determination and are compared with the spectrum measured by Frommhold and Proffitt (full line) reported in Ref. [32].

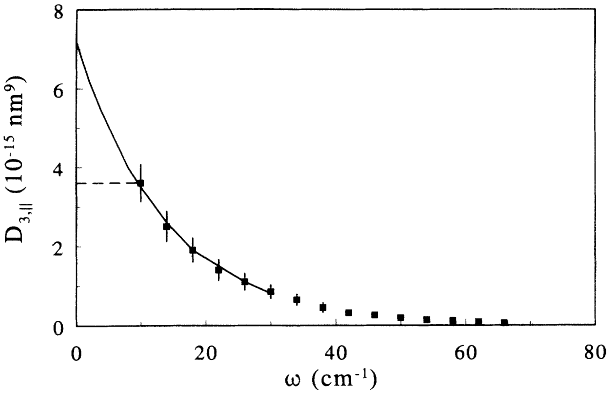

FIG. 3. Experimental three-body spectrum of neon, in absolute units, at $T=296$ K (full squares with error bars). The full line represents the low-frequency exponential extrapolation. One third of the area between the full and the dashed line represents the estimated extrapolation error on the integrated intensity (see text).

of the two pair spectra of Fig. 2 implies that the two-parameter empirical model for the pair polarizability derived by Frommhold and Proffitt [32] can be consistently used in the calculation of three-body spectral features in the PA approximation. With this information, it would be possible, in principle, to compute the three-body spectrum. However, while a theoretical calculation of the pair spectrum is possible, either classically or using quantum mechanics [33], this has not been exploited, to date, for the triplet contribution, even within the PA approximation. The calculation is feasible, at present, only for the first few spectral moments. The comparison with the theoretical models can be carried out, for these quantities, even for moderately quantum systems [24].

We recall that the ith moment of the n-body spectrum is defined as

$$ {}_nM_i=(-\sqrt{-1})^i[d^iG_n(t)/dt^i]_{t=0}=\int G_n(\omega)\omega^i d\omega \ , \qquad i=0,1,2,\dots \ , \tag{15}$$

where the definition of $G_n(\omega)$ follows immediately from the Fourier transform of Eq. (10). Three-body moments are obtained from the measured $G_3(\omega)$ and by calculation of the time derivative of the three-body correlation function [cf. Eq. (15)]. The comparison of the two determinations is a test of the PA approximation.

Following the procedure outlined here, we have evaluated the first three moments of the experimental three-body spectrum of neon. This is not a straightforward task, because the accuracy in the experimental determination of spectral moments is affected by the extrapolation of the spectrum in the frequency region where the measurement is not possible. The evaluation of the zeroth moment (the integrated intensity) is affected mainly by the extrapolation toward zero frequency. In fact, the spectrum is known to deviate, at very low frequencies, from the quasiexponential behavior, and a significant portion of the integrated intensity comes from the extrapolated region. On the other hand, at high frequency, a cutoff is imposed on the measured spectrum by the weakness of the signal in the wings, which is particularly severe in the case of neon. This requires to estimate an extrapolation to infinite frequency and limits the number of the experimentally accessible moments.

To deal with these difficulties, we used the same extrapolation procedure we have already tested on data from previous experiments [15]. The low-frequency contribution to the integral was evaluated using the exponential extrapolation as the best estimate for the zero-frequency limit and considering as a lower limit the intensity at the lowest measured frequency. One third of the difference between the two extrapolations was added to the estimated standard error. For the high-frequency region we have extrapolated to infinity by means of a two-parameter function which accounts for the observed curvature of the spectral shape in a semilog plot. A lower limit for the extrapolation is determined by imposing a purely exponential shape. The difference between the two distinct contributions to the moments was added to the estimated error. The contribution of low- and high-frequency extrapolations is shown, for the case of the zeroth and second spectral moment of the three-body spectrum, in Figs. 3 and 4, respectively.

An alternative procedure, which was used in order to check the internal consistency of our analysis, consists in evaluating, for each density, the first few spectral moments $M_i(n)$. For the spectral moments a virial expansion is possible (and rigorous) [25] so that experimental two- and three-body moments can be obtained through a density analysis analogous to that of Eq. (10). Best polynomial fitting curves were obtained in the form

$$M_i(n)={}_2M_i n^2/2+{}_3M_i n^3 \ . \tag{16}$$

Experimental points with error bars and the best fit are reported, for the three spectral moments, in Fig. 5. Here, the ratio of the spectral moments to the density is plotted as a function of density, so that three-body effects appear as deviations from a linear behavior. Such deviations de-

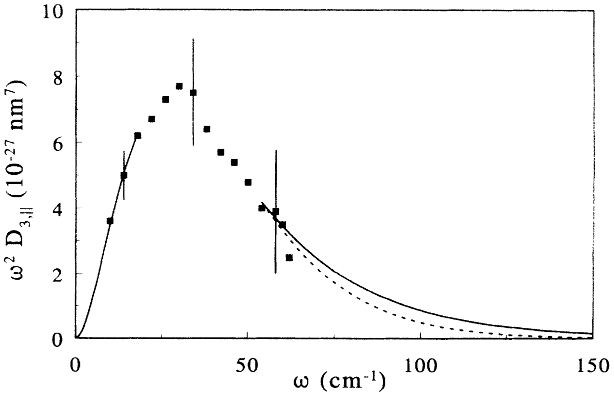

FIG. 4. The generating function of the second spectral moment for the three-body spectrum of neon. The full squares with error bars are the experimental points. The full line on the left is the low-frequency extrapolation. On the right side of the figure, the full line is the high-frequency extrapolation, while the lower (dotted) line represents the exponential extrapolation (see text).

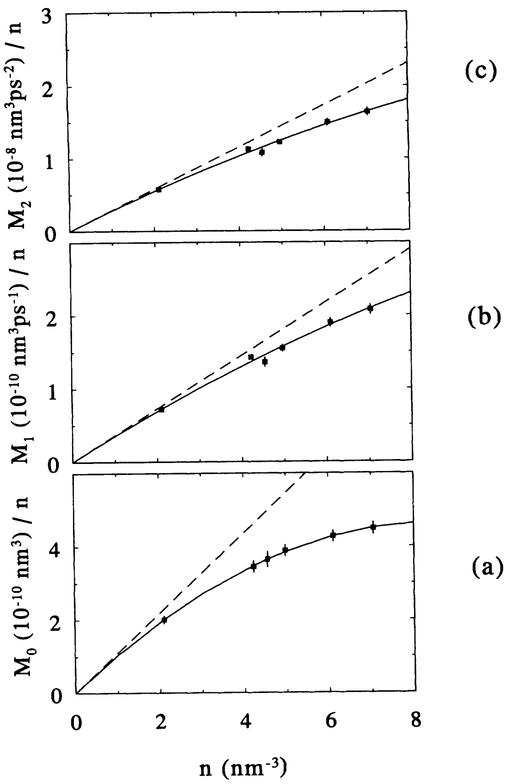

FIG. 5. Density behavior of the first three spectral moments. The plotted quantities are the ratio of the moments to the density (squares with error bars). The full lines represent the best fitting to the data. As explained in the text, the deviations from the pure pair contribution (dashed lines) decrease as the order of the moment increases.

crease with increasing the order of the moment. This is because of the increasing importance of the high-frequency portion of the spectrum, which is mainly produced by pair interactions.

A comparison *a posteriori* of the results of the two procedures showed good agreement, within their respective errors, and, therefore, we could proceed to the comparison of the experimental moments with the theoretical calculations obtained with the hypothesis of pair additivity of the interactions. As already stated, from this comparison valuable information can be obtained on the weight of three-body irreducible terms as well as their dependence on the system parameters or the thermodynamic state.

The results of the analysis are reported in Table I. The quoted errors on the experimental results are estimated standard deviations and include the uncertainty introduced by the extrapolations. Calculated quantities are also reported and include quantum corrections to the first order in the Wigner-Kirkwood expansion. The model chosen for the pair potential is of the Hartree-Fock-dispersion (HFD) type with parameters derived by Aziz [5]. For the induced polarizability, the two-parameter phenomenological model by Frommhold and Proffitt [32], the empirical model of Meinander, Tabisz, and Zoppi [16], and the long-range DID polarizability model are used, respectively. The comparison of the results for the various models confirms the well-known fact that the DID approximation reproduces the correct dynamics only at low frequency. In fact, as the order of the moment increases, the results for this model deviate more and more from those obtained with the more realistic phenomenological models. These, in turn, are in good agreement with each other, and the differences between their values may serve as an indication of the size of the uncertainty due to the particular choice of the polarizability model. In any case, the outcome of the comparison with the experimental values is hardly affected by such a choice. In particular, while the experimental zeroth moment is fully consistent with the PA calculation, a disagreement emerges clearly for the higher-order moments. Although the uncertainties of the measured values are quite large, mainly due to the magnitude of the extrapolated contributions, the difference with the calculation is well beyond the experimental uncertainty. It is very interesting to note that the deviation of the computed values from the measured ones has the opposite sign with respect to that observed in krypton, thus indicating that the irreducible three-body effects play a similar role in neon and in room-temperature hydrogen.

V. CONCLUSIONS

We have reported the results of a DILS experiment on gaseous neon at room temperature, from which we have extracted the two-body and three-body induced spectra. The two-body spectrum is in excellent agreement with the previous experimental determination by Frommhold and Proffitt [32]. The experimental three-body spectral moments have been compared with a calculation performed within the PA approximation, taking into account quantum corrections by means of the Wigner-Kirkwood asymptotic expansion. The comparison shows a clear disagreement at the level of the first and second moment, which can be accounted for neither by a possible uncertainty in the polarizability model used for the

TABLE I. Three-body spectral moments of neon. Experiment denotes this work. FP denotes the polarizability model of Frommhold and Proffitt (Ref. [32]). MTZ denotes the polarizability model of Meinander *et al.* (Ref. [16]). DID denotes the long-range dipole-induced-dipole polarizability model.

	Experiment	FP	MTZ	DID
$M_0(10^{-12}\ \mathrm{nm}^{12})$	-6.5 ± 1.3	-6.48	-6.45	-6.79
$M_1(10^{-12}\ \mathrm{nm}^{12}\,\mathrm{ps}^{-1})$	-1.12 ± 0.46	-0.469	-0.481	-0.357
$M_2(10^{-12}\ \mathrm{nm}^{12}\,\mathrm{ps}^{-2})$	-87.0 ± 37.0	-35.9	-36.8	-26.4

calculations, nor by the errors of the experimental results. Such discrepancies are not new. What is interesting to note here is that, in the case of neon, the absolute value of the experimental second moment is higher than the one computed within the PA approximation. Therefore, the observed difference is of *opposite sign* of that measured in room-temperature krypton. At the same time, the difference on the first spectral moment of neon has the *same sign* of the one observed in hydrogen at room temperature.

The available information on the irreducible three-body contributions to the microscopic dynamics of fluids, obtained from the comparison between DILS experiments and the calculations performed within the PA approximation, begins to provide a general picture of the importance of these effects for the rare gases and hydrogen. However, it appears clearly that more experimental results, on different systems, would contribute significantly to the elucidation of the mechanism leading to deviations from the PA approximation results. For instance, while the comparison between the cases of argon and krypton would suggest that irreducible three-body effects in rare gases might increase with the atomic polarizability, the first measurement of the three-body DILS spectrum of neon, here reported, shows that the situation is more complex than expected. An extensive calculation [24], carried out on the DID-LJ model as a function of the reduced temperature, has shown that a delicate balance between the two PA contributions to ${}_3M_i$ determines the size and the sign of the three-body DILS spectral moments. It is then reasonable to suggest that a change of sign in the effect attributed to the irreducible many-body terms can be determined by a change of balance among different physical effects. The case of hydrogen represents, somehow, a unifying key for interpreting the data. In fact, while room-temperature hydrogen data behave similarly to the present data of neon, the experiment at 50 K suggests a more close similarity with the case of krypton. This is an implicit demonstration that the temperature plays an important role in this phenomenology.

An extensive series of DILS experiment, carried out on various systems and at different temperatures, has provided the evidence of the importance of irreducible many-body effects. A correlation with experimental information from other sources (e.g., neutron spectroscopy) could be attempted. However, the amount of experimental data is not so extensive to go beyond a qualitative discussion. In any case, at present, the limitation appears more on the theoretical side. We expect that these experiments will induce more theoretical work in the field of irreducible many-body interactions.

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[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).
[2] J. A. Barker, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1976).
[3] R. J. Bell and I. J. Zucker, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1976).
[4] K. F. Niebel and J. A. Venables, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1976).
[5] R. A. Aziz, in *Inert Gases,* edited by M. L. Klein (Springer Verlag, Berlin, 1984).
[6] M. Zoppi and G. Spinelli, *Proceedings of the IXth International Conference on Raman Spectroscopy, Tokyo, Japan, 1984,* edited by M. Tsuboi (The Chemical Society of Japan, Tokyo, 1984).
[7] A. Teitsma and P. A. Egelstaff, Phys. Rev. A **21**, 367 (1980); P. A. Egelstaff, A. Teitsma, and S. S. Wang, *ibid.* **22**, 1702 (1980).
[8] P. A. Egelstaff, W. Glaser, D. Litchinsky, E. Schneider, and J. B. Suck, Phys. Rev. A **27**, 1106 (1983).
[9] F. Barocchi, M. Celli, and M. Zoppi, Europhys. Lett. **5**, 607 (1988).
[10] F. Barocchi, M. Celli, and M. Zoppi, Phys. Rev. A **38**, 3984 (1988).
[11] U. Bafile, L. Ulivi, M. Zoppi, and F. Barocchi, Chem. Phys. Lett. **117**, 247 (1985).
[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. **138**, 559 (1987).
[14] U. Bafile, L. Ulivi, M. Zoppi, F. Barocchi, M. Moraldi, and A. Borysow, Phys. Rev. A **42**, 6916 (1990).
[15] U. Bafile, L. Ulivi, M. Zoppi, and F. Barocchi, Phys. Rev. A **37**, 4133 (1988).
[16] N. Meinander, G. C. Tabisz, and M. Zoppi, J. Chem. Phys. **84**, 3005 (1986).
[17] U. Bafile, M. Zoppi, F. Barocchi, M. S. Brown, and L. Frommhold, Phys. Rev. A **40**, 1654 (1989).
[18] D. Varshneya, S. F. Shirron, T. A. Litovitz, M. Zoppi, and F. Barocchi, Phys. Rev. A **23**, 77 (1981).
[19] M. Zoppi, F. Barocchi, D. Varshneya, M. Neumann, and T. A. Litovitz, Can. J. Phys. **59**, 1475 (1981).
[20] M. Zoppi and G. Spinelli, Phys. Rev. A **33**, 939 (1986).
[21] M. S. Brown, S. K. Wang, and L. Frommhold, Phys. Rev. A **40**, 2276 (1989).
[22] U. Bafile, L. Ulivi, M. Zoppi, M. Moraldi, and L. Frommhold, Phys. Rev. A **44**, 4450 (1991).
[23] F. Barocchi, M. Zoppi, and M. Neumann, Phys. Rev. A **27**, 1587 (1983).
[24] U. Bafile, L. Ulivi, M. Zoppi, and S. Pestelli, Mol. Phys. **79**, 179 (1993).
[25] Rigorously, it should be pointed out that the virial expansion of a time-dependent dynamical quantity, like the correlation function $G(t)$, is not defined for every value of t, while a rigorous virial expansion of all the time derivatives $[d^nG(t)/dt^n]_{t=0}$ does exist. However, when the values of t are limited to the range which is experimentally accessible one may define a rigorous virial expansion, whose convergence radius is finite and depends on the actual value of t. For a more extensive treatment, refer to the paper by M. Moraldi, M. Celli, and F. Barocchi, Phys. Rev. A **40**, 1116 (1989).
[26] F. Barocchi, M. Neri, and M. Zoppi, Mol. Phys. **34**, 1391 (1977).
[27] D. P. Shelton, G. C. Tabisz, F. Barocchi, and M. Zoppi,

Mol. Phys. **46**, 21 (1982).

[28] P. Mazzinghi and M. Zoppi, Rev. Sci. Instrum. **54**, 11 (1983).

[29] A. Michels, T. Wassenaar, and P. Louwerse, Physica **26**, 539 (1960); V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton and Xenon* (Hemisphere, Washington, 1988).

[30] A. L. Ford and J. P. Browne, Phys. Rev. A **7**, 418 (1973).

[31] F. Barocchi and M. Zoppi, in *Phenomena Induced by Intermolecular Interactions,* edited by G. Birnbaum (Plenum, New York, 1985).

[32] L. Frommhold and M. H. Proffitt, Phys. Rev. A **21**, 1249 (1980).

[33] L. Frommhold, Adv. Chem. Phys. **46**, 1 (1981).