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SPECTRAL VIRIAL EXPANSION
FOR COLLISION-INDUCED LIGHT SCATTERING IN GASES

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Résumé. — On développe un formalisme général qui décrit la dépendance en fonction de la densité de la lumière dépolarisée diffusée par les fluctuations translationnelles dans les gaz. De plus, on a fait des mesures d’intensité absolue du spectre de diffusion de lumière dépolarisée de l’argon gazeux, dans le domaine de densité de 20 à 150 amagats et dans l’intervalle de fréquence de 7 à 150 cm\(^{-1}\). A toute fréquence, l’intensité \(I(\omega)\) peut être développée en série de puissances de densité

\[ I(\omega) = I_d(\omega) \rho^2 + I_3(\omega) \rho^3 + \cdots. \]

Le terme \(I_d(\omega)\) représente le spectre de la lumière diffusée, dû à l’anisotropie optique induite dans une paire d’atomes en collision, alors que \(I_3(\omega)\) représente la portion de l’anisotropie induite par une collision à trois centres qui ne peut être représentée comme une somme d’effets de collision à deux centres. Ceci est analogue au développement du viriel classique de \(pV\).

On présente les spectres pour les termes à deux et trois centres et on les compare avec les prévisions basées sur divers modèles pour l’anisotropie induite de polarisabilité.

Abstract. — A general formalism is developed for the density dependence of depolarized light scattered by translational fluctuations in gases. In addition, absolute intensity measurements have been made of the depolarized light scattering spectrum of argon gas in the density range 20-150 amagats for the frequency range \(\omega = 7-150\) cm\(^{-1}\). At any given frequency, the intensity \(I(\omega)\) can be expanded as a power series in the density

\[ I(\omega) = I_d(\omega) \rho^2 + I_3(\omega) \rho^3 + \cdots. \]

The term \(I_d(\omega)\) is the light scattering spectrum caused by the optical anisotropy induced in a pair of atoms on collision, while \(I_3(\omega)\) represents the portion of the induced anisotropy in a three-body collision which cannot be represented as a sum of two-body effects. This is analogous to the familiar \(pV\) virial expansion.

Spectra for the two- and three-body terms are reported and compared with predictions based on various models for the induced polarizability anisotropy.

1. Introduction. — Although it has been known for many years that the light scattered from fluids composed of even isotropic molecules is partially depolarized [1], only recently have there been detailed experimental investigations of this phenomenon [2]-[10], and the usefulness of these spectra in probing intermolecular interactions and dynamics has only begun to be explored [5], [7], [8], [11], [12]. Since the physical processes involved are simplest and most easily manipulated in the gas phase, it seems sensible to begin a systematic study there, although it should be kept in mind that one of the main goals is to develop a new tool for studying the dynamics of both isotropic and anisotropic liquids. In this paper, we give a preliminary report of a systematic investigation, both experimental and theoretical, of the depolarized light scattering spectrum of gases of isotropic molecules, emphasizing the low density region where only two- and three-body interactions are significant. We report comparison with data on gaseous argon at room temperature.

Consider first a monatomic gas which is so dilute that intermolecular interactions are negligible. Then the polarizability tensor of each molecule is isotropic, resulting in only a polarized Rayleigh-Brillouin spectrum with spectral width typically of order 0.1 cm\(^{-1}\). As the density is increased to the point where binary interactions are significant, however, the polarizability tensor associated with the interacting pairs is in general anisotropic and time dependent. The full details of this induced polarizability anisotropy are not yet known, but it can be shown that its long-range asymptotic form is caused by the dipolar fields induced by the external applied field [13]. Since the pair polarizability tensor is then a function of the time-dependent interatomic coordinates, one has an attendant Raman scattering process involving the relative translational states of the colliding pairs. In a pictorial sense, we

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may view these translational states as the vibration-rotation continuum of an unbound transient dimer. (In general, even for the rare gases there will be some bound states which will also contribute to the scattering [14].) Similar considerations hold for interacting triplets, etc.

The physical information contained in these translational or collision induced spectra (CIS) is twofold. First, the scattering is caused directly by intermolecular interactions. This is in contrast to the more familiar vibrational and rotational Raman effects which are usually influenced only perturbatively (lineshape changes, etc.) by these interactions. Thus, we may hope to use CIS as a probe of intermolecular interactions and dynamics. The second aspect is that, viewed as a Raman effect, there is associated with this scattering a change in polarizability tensor with a normal coordinate. Spectral intensities then contain information on the degree of distortion of the molecular electronic configurations, as a function of intermolecular distance.

Unfortunately, however, the observed spectra contain the dynamical and electronic information combined in such a manner that neither can be studied isolated from the other. The simplest way around this difficulty is to assume that one knows either the intermolecular potential [8] or the form of the induced polarizability [7] to sufficient accuracy and use the data as a phenomenological fit for the unknown item. In later sections, we use the former strategy, assuming the Lennard-Jones form of the intermolecular potential for simplicity and comparing observed spectra with a model for the form of the induced polarizability.

We first outline a general approach to the theory and then give recent results on gaseous argon.

2. Theory. — For sufficiently low densities we may expand the CIS spectrum in powers of the density:

\[ I(\omega) = I_2(\omega) \rho^2 + I_3(\omega) \rho^3 + \cdots \]

As in the familiar PV virial expansion the term \( I_2 \) involves the properties of pairs, \( I_3 \) reflects three body collisions, etc. Apart from constants which shall not interest us we may write for spherical top molecules [10]:

\[ I_2(\omega) = \int dt e^{i\omega t} C_2(t) \]

\[ = \int_{-\infty}^{\infty} dt e^{i\omega t} < B[r(0)] B[r(t)] P_{z}[\cos \theta(t)] >_0 \]

(1)

where \( P_{z} \) is the second order Legendre polynomial, \( \theta(t) \) is the angle in laboratory coordinates between the intermolecular axis at time \( t \) and that at \( t = 0 \), and \( B(r) \) is the effective anisotropy of the pair polarizability tensor as a function of intermolecular separation:

\[ B(r) = \alpha_0(r) - \alpha_z(r) \]

(2)

The principal components of the pair polarizability tensor are \( \alpha_0(r) \) and \( \alpha_z(r) \), \( \parallel \) indicating that component parallel to the intermolecular axis. \( \langle \parallel \rangle \) symbolizes a phase space average in the limit of zero density. We see here in explicit form the problem alluded to earlier. In general, we do not know to arbitrary accuracy either the induced anisotropy of the polarizability as a function of intermolecular separation nor do we know the collision dynamics \( \{ r(t), \theta(t) \} \), which are controlled by the intermolecular potential.

In order to simplify the problem we shall not consider here \( I_2(\omega) \), \( I_3(\omega) \) directly, but only their invariants, or spectral moments:

\[ I^{(n)} = \int_{-\infty}^{\infty} d\omega \omega^n I(\omega) \]

(3)

The advantage to this is, of course, that the dynamical problem is avoided since the moments involve ensemble averages at a single time only:

\[ I^{(n)} = 2 \pi (-i)^n \frac{d^n}{dt^n} < C(t) >_{t=0} \]

(4)

A. Integrated Intensity. — For simplicity let us consider the light scattered by \( N \) atoms contained in a volume element \( V \) of dimensions small compared with the wavelength of light but large compared with molecular interaction ranges and with average intermolecular distances. For incident light of amplitude \( E_0 \) polarized in the \( Z \) direction the \( X \) polarized scattered intensity \( I_{xx} \) is given by:

\[ I_{xx} = CE_0^2 \int | \alpha_{xz}(1 \ldots N) |^2 f(1 \ldots N) d1 \ldots dN \]

(5)

Where \( \alpha_{xz}(1 \ldots N) \) is the \( xz \) component of the polarizability tensor of the total system:

\[ \alpha_{xz}(1 \ldots N) = \frac{\partial M_{xz}(1 \ldots N)}{\partial E_{oz}} \]

(6)

\( M_x \) is the \( x \) component of the total electric moment, and \( 1 \ldots N \) signifies the coordinates of particles \( 1 \) through \( N \), \( C \) is a constant containing frequencies and geometric factors and \( f(1 \ldots N) \) is the \( N \) particle distribution function.

Closely paralleling Van Kranendonk’s cluster expansion of induced infrared absorption [15] we introduce a set of polarizability tensor components \( \alpha_{xz}(1 \ldots N) \), \( 1 \leq n \leq N \), where \( \alpha_{xz}(1 \ldots N) \) is the polarizability of \( n \) molecules if present in \( V \) without any other molecules therein. Each \( \alpha_{xz} \) can in turn be expanded in cluster functions:

\[ \alpha_{xz}(12) = U_{xz}(12) \]

\[ \alpha_{xz}(123) = U_{xz}(123) + U_{xz}(12) + U_{xz}(13) \]

(7)

Thus, \( U_{xz}(12) \) is the polarizability of two molecules alone, \( U_{xz}(123) \) is that part of the triplet polarizability which is not pairwise additive, etc. The \( U(1 \ldots N) \)’s possess the cluster property of being zero unless the molecules \( 2, \ldots, n \) are all sufficiently close to 1 to influence its polarizability.
We now expand the polarizability in terms of the \( U's \):
\[
U_{xa}(1 \ldots N) = \sum_{i=2}^{n} U_{ax}(1 \ i) + \sum_{i<j=2} U_{ax}(1 \ ij) + \cdots \tag{8}
\]
and substitute (8) in (5). On integrating, this gives
\[
I_{ax} = C E_{0x} N(N-1) V^{-2} \int |U_{ax}(12)|^2 f(12) \, d1 \, d2 +
+ N(N-1)(N-2) V^{-3} \int B(123) \, d1 \, d2 \, d3 + \cdots . \tag{9}
\]

The first term in \( B \) is the interference between the pair polarizabilities while the second is the interference between the pair polarizability and the non-additive triplet contribution. Given the form of the induced polarizability these can be written explicitly.

Furthermore, the distribution functions can be expanded in powers of the density:
\[
f(1 \ldots n) = f(0)(1 \ldots n) + \rho f(1)(1 \ldots n) + \cdots . \tag{11}
\]

Thus to third order in the density the scattering intensity is given by:
\[
I_{ax} = C E_{0x} \rho^2 \int |U_{ax}(12)|^2 f(0)(12) \, d1 \, d2 +
+ \rho^3 \int |U_{ax}(12)|^2 f(1)(12) \, d1 \, d2 +
+ \rho^3 \int B(123) f(0)(123) \, d1 \, d2 \, d3 . \tag{12}
\]

A similar, but more involved expression may be written for the frequency dependence. In order to proceed further we need the form of the intermolecular potential (for the \( f's \)) and the form of the induced polarizability anisotropy (for the \( U's \)). For the purposes of this paper we shall use the Lennard-Jones potential.

**B. Form of the Induced Polarizability Anisotropy.** — It is known that the asymptotic dependence of the pair anisotropy is given by [13].
\[
\beta(r) = 6 \alpha^2 r^{-3} , \tag{13}
\]
where \( \alpha \) is the polarizability of an isolated molecule. This is exact, both classically and quantum mechanically, and represents the effect of a neighboring-induced dipole on the local field at a given molecule. Equation (13) is just the leading term for the local field in a power series in \( \alpha r^{-3} \). Classically all terms are positive, the next term being \( + 6 \alpha^3 r^{-6} \) whose value is negligible for all thermally significant intermolecular distances, at least for the rare gases (for argon at \( r = \sigma \), the Lennard-Jones diameter, \( \alpha r^{-3} \sim 5 \times 10^{-3} \)). Although the coefficients of \( r^{-6} \) and higher order terms are not exact quantum mechanically, we assume that they are reasonable approximations, so we neglect all contributions to the local field other than the leading term.

Several measurements [16], [17], [7] point to the inadequacy of eq. (13) in describing the intensity. In all cases for the rare gases, the measured intensity is less than that predicted. This suggests an additional contribution to \( \beta \) and which must have a negative sign over a significant portion of \( r \). For convenience, we will label this the overlap contribution. As a first approximation, we assume that these two effects are additive:
\[
\beta(r) = 6 \alpha^2 r^{-3} + \beta_{ov}(r) . \tag{14}
\]

There have been two recent approximate calculations of \( \beta_{ov} \) for H-H [18] and He-He [19], but they are not considered to be accurate enough to reliably determine its form. They do, however, suggest that \( \beta_{ov} \) is relatively long range. In addition, for H-H, \( \beta_{ov} \) is significantly larger than \( 6 \alpha^2 r^{-3} \) and of opposite sign. Since the asymptotic dependence of overlap-type functions is exponential, we shall assume such a form for \( \beta_{ov} \):
\[
\beta_{ov}(r) = \lambda \exp[-\gamma r] . \tag{15}
\]

The zeroth and second moments of the \( \rho^2 \) term [14] in eq. (12) can be used to assign phenomenological values to \( \lambda \) and \( \gamma \) for gaseous argon (Section 4). In addition, the \( \rho^3 \) term has been investigated in part. A more complete treatment will be given elsewhere [20] and will only be outlined here. Nothing is known, in general, about \( U_{xa}(123) \), the non-pairwise additive term. However, for the local field term it can be shown to be insignificant. We thus consider only the pair interference term in \( B(123) \) and the first density correction to the pair distribution function. For the induced dipole term, the expressions obtained agree with those previously reported by Gray and Ralph [21].

Numerical evaluations of the leading terms of the three-body scattering can be made using integrals tabulated by Levine and McQuarrie [22].

We find that
\[
I_3 = 4 \pi J_4 + J_5 , \quad I_2 = \frac{4 \pi J_4 + J_5}{\sigma^2 I_2'} , \tag{16}
\]
where \( \sigma \) is the Lennard-Jones diameter, and where \( J_4 \), \( J_5 \), and \( I_2' \) are defined by Levine and McQuarrie. \( J_4 \) accounts for the density correction to the pair distribution function, while \( J_5 \) represents the interference in the two pair polarizabilities in a triplet. \( I_2' \) is proportional to the scattering intensity of isolated
pairs. For argon at room temperature, the reported values are

\[ J_4 = 0.000152 \]
\[ J_5 = -0.116 \]
\[ I'_2 = +0.437 \]

Thus the \( \rho^3 \) term is negative and is overwhelmingly dominated by the interference term, at least in this case. We find from eq. (16) that the induced dipole contribution due to the cubic term should cancel the two-body induced dipole term at a density of 284 amagats, about 40% of the liquid density. Of course, at this density higher order terms \( \rho^4 \), etc., will be significant, assuming that the series in \( \rho^n \) converges.

3. Experimental. — Spectra were recorded digitally by counting photons for a set time period at a given frequency and gas density and then varying the density without changing frequency. Following Lallemand [7], we used a small amount of \( \text{H}_2 \) gas as an internal intensity standard, recording both the \( S_0(0) \) and \( S_4(0) \) rotational bands. Since the absolute scattering cross sections of these bands are accurately known, a comparison with the CIS spectrum allows the latter to be given on an absolute basis. Gas densities were determined using the \( pV \) measurements of Whalley, Lupien, and Schneider [23]. The 5 145 \( \AA \) line of a Spectra-Physics Model 165 argon ion laser (\( \sim 1 \) W) was used as the exciting source, with a Spex double monochromator as the frequency analyzer. Frequencies were calibrated to \( \pm 0.1 \text{ cm}^{-1} \) with a Fabry-Perot light comb [24].

4. Results and discussion. — Two and three-body contributions to the intensity at a given frequency were evaluated by a least squares fit to the linear equation:

\[ \frac{I_3(\omega)}{\rho^3} = I_3(\omega) + I_3(\omega) \rho . \] (18)

Typical plots are shown in figure 1. \( I_3 \) was found to be negative at all frequencies

\[ 7.5 \text{ cm}^{-1} \leq v \leq 50 \text{ cm}^{-1} . \]

At higher frequencies the scatter in data points prevented assigning a value to \( I_3 \), although the values for \( I_2 \) are significant out to at least 150 cm\(^{-1}\). Relative values of \( I_3(v) \) and \( I_2(v) \) are listed in Table I in terms of the density

\[ \rho^*(v) = -\frac{I_3(v)}{I_2(v)} , \]

at which for a given frequency the 2- and 3-body terms would cancel each other. For reference, the normal liquid density is \( \sim 750 \) amagats. No 4- or higher-body terms were observed in the present study, although they probably would have been significant at the highest densities for frequencies less than \( \sim 5 \text{ cm}^{-1} \).

The three body spectrum reconstructed from the data is shown in figure 2. Over the observed frequency range this spectrum can be approximated by an exponential shape:

\[ I_3(v) \approx I_3(0) \exp \left( -\frac{v}{\nu_0} \right) , \]

where a value of 8.3 cm\(^{-1}\) was found for \( \nu_0 \).

The experimental two body spectrum is shown in figure 3. It has two exponential-like regions [25], as previously noted by Volterra, Bucaro and Litovitz [9]. In fact the intensity over the whole observed frequency
range is well represented as a sum of two exponentials with characteristic frequencies 12.55 cm\(^{-1}\) and 22.6 cm\(^{-1}\).

Note that these results imply that the three body correlation time is \(\sim 50\%\) longer than the two body correlation time! That the three body spectrum should have a lower characteristic frequency can be accounted for heuristically by noting that steric restrictions make hard collisions in which all molecules are very close to each other and which contain more high frequency components, relatively less important for three bodies. Similar observations have been made for collision induced absorption in CO\(_2\) [26].

By assuming that observed 2 and 3 body lineshapes can be smoothly extrapolated between 7 and 0 cm\(^{-1}\) one can obtain estimates of the absolute scattering intensities using H\(_2\) as an internal standard as previously noted. We find that the relative intensities are such that the two and three body terms will cancel at a density of 410 amagats. Quantitatively we find that

\[
I_2(\text{experimental}) = 0.62 \; I_2(\text{induced dipole})
\]

and

\[
I_3(\text{experimental}) = 0.43 \; I_3(\text{induced dipole}).
\]

Table II compares the present value of \(I_2\) with those of other workers.

### Table II

<table>
<thead>
<tr>
<th>(I_2(\text{exp})/I_2(6;\alpha^2;r^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62 ± 0.06</td>
<td>Present work.</td>
</tr>
<tr>
<td>0.73 ± 0.11</td>
<td>Buckingham and Dunmur [16] (Kerr measurement)</td>
</tr>
<tr>
<td>0.81 ± 0.12</td>
<td>Lallemand [7]</td>
</tr>
<tr>
<td>0.67 ± 0.03</td>
<td>Thibau et al. [17].</td>
</tr>
</tbody>
</table>

The zeroth second and fourth moments of \(I_2(\omega)\) are found to be compatible with the following form of the induced pair anisotropy [20]:

\[
\beta(r) = 6 \alpha^2[r^{-3} - 0.72 \exp(-0.80\; r)], \quad (19)
\]

where \(r\) is in angstrom units. A preliminary estimate suggests that \(I_2\) is also compatible with this form. For comparison, we note that self-consistent field calculations [28] of the repulsive energy of two argon atoms shows an exponential dropoff (\(\sim \exp(-3\; r(\text{Å}))\)). If eq. (19) does indeed approximate the behavior of \(\beta\), it implies that the overlap portion dominates the scattering process. This seems consistent with Kerr [16] and CIS [10] measurements on the series Ar, Kr, Xe at room temperature. In this series, the reduced temperature is decreasing, so one would expect the longer \(r^{-3}\) term to be relatively more important for Xe than for Ar. However, \(I_2(\text{exp})/I_2(\text{induced dipole})\) is lower for Xe than for Ar, as would be predicted if the above magnitudes are correct. Before much reliance is placed on this form, however, further experimental and theoretical checks must be made. However, if the overlap contribution is approximately as given by eq. (19), it is indeed of quite long range. (From eq. (19), \(\beta(\text{induced dipole}) = \beta_0\), at \(r \approx 5.6\; \text{Å}\) and is greater at shorter range.) Thus, the liquid spectrum cannot be considered to be reflecting merely binary collisions, and a collective mode picture, as originally postulated by McTague, Fleurby, and DuPré, is required.

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