Moment analysis of collision-induced light scattering from compressed CF$_4$[†]

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The method of moments is used to determine a functional form of the induced polarizability increment β, which gives rise to collision-induced light scattering from compressed CF$_4$. Based upon the zeroth and second moments, two expressions are found to be acceptable: $\beta(x) = 6\alpha^2\sigma^{-3}(x^{-3} - 2.85x^{-4.05})$ and $\beta(x) = 6\alpha^2\sigma^{-3}(x^{-3} + 0.757x^{-8.51})$, where $x = r/\sigma$. Both expressions result in calculated fourth moments consistent with the experimental estimate. This is the first experimental evidence in which a positive non-dipole-induced-dipole term is shown to be a possibility. In other respects, however, the results are similar to those obtained from rare-gas spectra.

I. INTRODUCTION

Light scattering, arising through the polarizability induced in a cluster of interacting molecules, may provide detailed information on molecular motion in dense media.[1-3] The primary impediment to progress concerns the intermolecular potential and the induction mechanism, which determine the collision dynamics and the nature of the induced polarizability, respectively. Their roles in the scattering process must be clearly specified before reliable interpretation of the spectra can be made.

In a recent paper,[4] we reported the collision-induced Rayleigh scattering from compressed gaseous CF$_4$ and CF$_4$-He mixtures. The spectra were discussed in terms of empirical models for the line profile, namely, sums of functions exponential in frequency. The principal conclusions were (i) that the profile at low frequencies (5–20 cm^{-1}) evolves with density according to the scaling law found appropriate for rare-gas spectra,[5,6] and (ii) that the tail at high frequencies (>20 cm^{-1}), which is prominent at densities higher than 50 amagat, is due to close binary collisions. In an effort to derive more details on the form of the induced polarizability, the spectra have now been analyzed by the method of moments. The results of this analysis are the subject of the present paper.

II. THE METHOD OF MOMENTS

Collision-induced scattering has been treated previously through moment analysis by Lallemand[7] and Levine.[8,9] A functional form for the induced pair polarizability is assumed and its characteristic parameters are determined from the moments of the experimental spectra.

Suppose $\phi^{(2n)}$ is the $(2n)$th moment of the frequency distribution of the scattered intensity $I(\omega)$, i.e.,

$$\phi^{(2n)} \propto (-1)^n \int \omega^{2n} I(\omega)\, d\omega . \tag{1}$$

It is straightforward[7,9] to calculate $\phi^{(2n)}$ in terms of $\beta(r)$, the induced-pair-polarizability anisotropy, which is a function of the intermolecular distance r:

$$\phi^{(0)} = 4\pi \int_0^\infty (\beta(r))^2 g(r) r^2 dr , \tag{2}$$

$$\phi^{(2)} = -4\pi \frac{kT}{\mu} \int_0^\infty \left[\left(\frac{d\beta}{dr}\right)^2 + 6\left(\frac{\beta(r)}{r}\right)^2 \right] g(r) r^2 dr, \tag{3}$$

$$\phi^{(4)} = 4\pi \left\{ \left(\frac{kT}{\mu}\right)^2 \int_0^\infty \left[72\left(\frac{\beta}{r^2}\right)^2 + 8\left(\frac{1}{r}\frac{d\beta}{dr}\right)^2 - \frac{36}{r^2}\beta\frac{d^2\beta}{dr^2} + \frac{4}{r}\frac{d\beta}{dr}\frac{d^2\beta}{dr^2} + 3\left(\frac{d^2\beta}{dr^2}\right)^2 \right] g(r) r^2 dr \right.$$
$$\left. - \frac{kT}{\mu^2}\int_0^\infty \left[\left(\frac{d\beta}{dr}\frac{dV}{dr}\right)\left(2\frac{d^2\beta}{dr^2}+\frac{4}{r}\frac{d\beta}{dr}-\frac{36}{r^2}\beta\right) + 48\frac{\beta^2}{r^3}\frac{dV}{dr} \right] g(r) r^2 dr + \frac{1}{\mu^2}\int_0^\infty \left(\frac{d\beta}{dr}\frac{dV}{dr}\right)^2 g(r) r^2 dr \right\}. \tag{4}$$

μ is the reduced mass of two colliding molecules and $g(r)$ is the radial distribution function,

$$g(r) = e^{-V(r)/kT} , \tag{5}$$

where $V(r)$ is the intermolecular pair potential.

Levine and Birnbaum[8] considered a pair polarizability function,

$$\beta(r) = (6\alpha^2/r^3) + (B/r^p) , \tag{6}$$

which may be written in dimensionless form,

$$\beta(x) = 6\alpha^2\sigma^{-3}[x^{-3} + (\tfrac{1}{6}y)x^{-p}] , \tag{7}$$

where $x = r/\sigma$ and $y = B\alpha^{-2}\sigma^{3-p}$. α is the molecular polarizability and σ is the molecular diameter; p and y (or B) are the parameters to be determined. $\beta(x)$ is thus represented as the sum of a long-range dipole-induced–dipole term,[1] $6\alpha^2/r^3$, and another contribution B/r^p thought to be of much shorter range. Using the Lennard-Jones 12-6 potential for $V(r)$, they found that, for argon, two sets of values of p and $\tfrac{1}{6}y$ gave satisfactory solutions to (2) and (3), the left-hand sides of which are experimentally determined through Eq. (1). These solutions are (i) $p \sim 6$ and $\tfrac{1}{6}y \sim -0.25$ and (ii) $p \sim 10$ and $\tfrac{1}{6}y \sim -0.40$. They considered the smaller value of p to be physically unrealistic for a short-range interaction and rejected it. Similar results were obtained for krypton and xenon, except that the smaller p was about 3.5. In all cases, y is less than zero, giving credence to the contention that short-range interactions lower the induced anisotropy from the contribution due to the dipole-induced–dipole mechanism alone, at least over the range of r sampled in the experiments.

Lallemand[7] has made a much more extensive analysis for argon. He considered several potentials—Kihara, Barker-Pompe, and Dymond-Alder—in addition to the Lennard-Jones 16-6. Also, he treated both $(\tfrac{1}{6}y)x^{-p}$ and $\lambda e^{-x/d}$ as possible forms for the second term in the expression for $\beta(r)$. Again for the Lennard-Jones and x^{-p} cases, with p and y determined from the zeroth and second moments, two solutions were acceptable: (i) $p = 4.15$ and $\tfrac{1}{6}y = -0.23$ and (ii) $p = 10.75$ and $\tfrac{1}{6}y = -0.51$. However, only the *first* set gave reasonable values for the fourth and sixth moments. Thus only the first set was retained; the second shorter-range solution was rejected. Calculations with the other potentials and trial polarizability functions yielded similar conclusions. In contradiction to the reasoning adopted by Levine and Birnbaum, the shorter-range solution was always discarded in favor of a long-range term.

Three aspects to the CF_4 data suggest that a moment analysis would yield a form for $\beta(r)$ differing from the rare-gas cases. First, a high-frequency tail of significantly different slope from the low-frequency profile appears above 50 amagat in the case of CF_4 (Fig. 1). This break in the profile occurs at about $\tfrac{1}{10}$ of the triple-point density, in contrast to argon, where a similar break is observed at about the triple-point density.[5] Moreover, for CF_4, the slope of this tail remains constant in the range 50-100 amagat (the highest density studied), indicating that it arises from binary encounters. Second, in the case of molecules, frame distortion may contribute to the induced anisotropy. It has

been proposed[10] that this interaction would give a term in $\beta(r)$ varying as r^{-13}, somewhat shorter in range than the r^{-9} expected from electron overlap interactions between rare-gas atoms.[10,11] Third, the Kerr-effect measurements suggest a difference in the magnitude of $\beta(r)$ between CF_4 and the rare gases (Table I). For the rare gases, the experimental values of the second virial Kerr coefficient B_k are all less than the calculated values; for CF_4, the experimental value is greater. The calculated values have been obtained from the relation[12,13]

$$B_k = \frac{8\pi^2 N_0^2}{405kT} \int_0^\infty [\beta(r)]^2 g(r) r^2 \, dr , \tag{8}$$

where N_0 is Avogadro's number. Here $\beta(r)$ consists only of the dipole-induced–dipole term $6\alpha^2/r^3$ and the Lennard-Jones potential appears in $g(r)$.

III. ANALYSIS

The experimental and theoretical zeroth and second moments were found following the method of Levine and Birnbaum.[8] Spectra taken in the density range 50-100 amagat were considered. The intensity was extrapolated to zero frequency from 5 cm^{-1} by fitting an empirical line-shape function consisting of the sum of the two exponentials.[4] Irwin and May[14] have shown that such an extrapolation does not introduce gross errors in the case of argon. The moments were then determined by calculating $\int I(\omega)\,d\omega$ and $\int \omega^2 I(\omega)\,d\omega$. Since relative rather than absolute measurements are in fact made, the experimental moments must
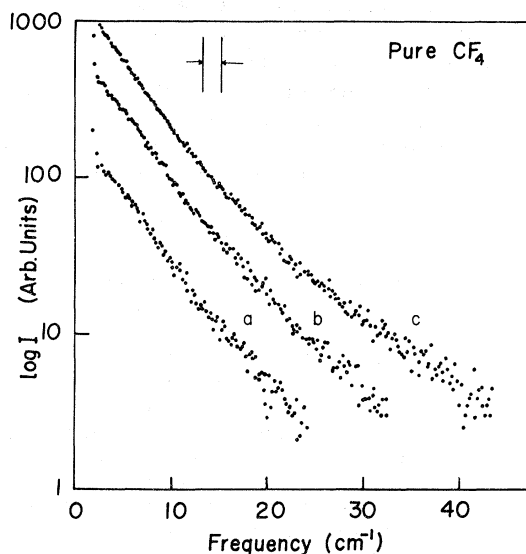

FIG. 1. Collision-induced light scattering from pure CF_4 at 18 (a), 37 (b), and 57 amagat (c) at 295 K. The vertical bars represent the spectral slit width of 2 cm^{-1}.

first be normalized in some manner. A direct method utilizes measured values of the second virial Kerr coefficient B_k through Eqs. (2) and (8). This Kerr coefficient determined by Buckingham and Orr[13] was used. The average values obtained for $\phi^{(0)}$ and $-\phi^{(0)}/\phi^{(2)}$ are presented in Table I together with the results for rare gases.[8] As one might suspect from the polarizabilities and masses alone, the moments of CF_4 fall between those for krypton and xenon.

Next, the unspecified parameters in the polarizability function (7) were determined. Equations (2) and (3) are quadratic in the unknown y, when p is specified. The right-hand sides were evaluated for a large number of values of p. For each p, (2) and (3) were solved for y. A search was then made for the values of y which simultaneously satisfied (2) and (3). For all densities, two sets of the parameters p, y were acceptable. For the lower value of p, in the range 3–5, y was always less than zero; for the higher value of p, 7–9, y was always greater than zero. The average values are (i) $p = 4.05 \pm 0.1$ and $\frac{1}{6}y = 2.85 \pm 0.03$ and (ii) $p = 8.51 \pm 0.2$ and $\frac{1}{6}y = 0.757 \pm 0.02$. Therefore two forms of the polarizability function are possible:

$$\beta(x) = \frac{6\alpha^2}{\sigma^3}\left[x^{-3} - \frac{2.85}{x^{4.05}}\right] \tag{9}$$

or

$$\beta(x) = \frac{6\alpha^2}{\sigma^3}\left[x^{-3} + \frac{0.757}{x^{8.51}}\right]. \tag{10}$$

IV. DISCUSSION

The important question is to decide if a distinction may be made between these two functions. The obvious test is to verify whether these polarizability parameters give reasonable values for the higher moments. When the right-hand sides of Eqs. (2) and (4) are evaluated with $p = 4.05$, one obtains $\phi^{(4)}/\phi^{(0)} = 3.38 \times 10^{50}$ sec^{-4}. With $p = 8.51$,

$\phi^{(4)}/\phi^{(0)} = 4.36 \times 10^{50}$ sec^{-4}. This differs from the result of Lallemand for argon, where the fourth moment is an order of magnitude larger with the short-range term ($p = 10.75$) than with the long-range term ($p = 4.15$). For CF_4 there seems to be little possibility of distinguishing experimentally between the two rather similar values. In order to estimate the fourth moment from our results, we elected to work with the function fitted to the line profile,[4] rather than to use directly the measured intensities which are not known precisely for large frequency shifts. Integrating this sum of two exponentials from zero to infinity, one finds $\phi^{(4)}/\phi^{(0)} = 1.1 \times 10^{50}$ sec^{-4}; therefore the measured fourth moment is of the same order as the two theoretical values. This estimate is a lower bound on the true value, as the fitted line-profile expression appears to lie slightly lower than the observed intensities at high frequency. Therefore, the fact that the experimental estimate is closer to the calculated value for $p = 4.05$ than that for $p = 8.51$ is of little significance. The experimental data are not of sufficient quality to permit the determination of still higher moments.

Most of the initial work on collision-induced scattering assumed that $\beta(r)$ would contain the long-range dipole-induced–dipole term together with a short-range overlap term. Thus, Bucaro and Litovitz[10] were able to propose an isolated binary-collision model for the scattering from liquids. The foundations of the model are that, at liquid densities, interference effects are expected to severely reduce the intensity of the scattering due to the dipole-induced–dipole interaction and that, even at such high density, the probability for more than two molecules to overlap strongly is small. Under these assumptions, they determined that a $\beta(r)$ which varies as r^{-9}, and arises from electron overlap, is consistent with the scattering from atomic fluids. For molecular liquids, they argued that the induced polarizability anisotropy is

TABLE I. Comparison of CF_4 and rare-gas data.

Gas	B_k (esu × 10^{-12}) Expt.[a]	Calc.[a]	σ (Å)[b]	ϵ/k (K)[b]	α (Å)^3	Mass (amu)	$\phi^{(0)}$[d] (Å)^9	$-\phi^{(0)}/\phi^{(2)}$[d] (10^{-26} sec^2)
Ar	4.1 ± 0.6	5.6	3.41	119.8	1.642	40	30.2 ± 4.4	12.5
Kr	16 ± 14	26	3.60	171	2.484	84	93.5 ± 13.9	12.5
Xe	65 ± 22	140	4.10	221	4.045	131	468 ± 69	19.8
CF_4	37.7 ± 3.6	25.2	4.70	152.5	3.84[c]	88	270 ± 30	17.6

[a] References 12 and 13.

[b] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[c] α at 6328 Å. Experiments on CF_4 were performed at 4880 Å.

[d] Rare-gas results from Ref. 8.

due mainly to a very-short-range interaction producing molecular frame distortion; an r^{-13} dependence of $\beta(r)$ was compatible with their data. Subsequent investigations[15,16] have shown that within the IBC model, r^{-13} is indeed appropriate for some anisotropic molecules (e.g., $CHCl_3$, C_6H_{12}, C_6H_6, but that r^{-9} is more in accord with experiment for isotropic molecules (e.g., CCl_4, $SiCl_4$, $GeCl_4$, $TeCl_4$).

The solution of $p = 8.51$ for gaseous CF_4 would be in agreement with these findings for liquids, particularly since the high-frequency tail is thought to be due to close binary collisions. However, the assumption regarding the existence of a short-range overlap term has been put in doubt, not only by the results of Lallemand on argon, but also by detailed calculations of pair polarizabilities. O'Brien et al.[17] have determined the $\beta(r)$ for He_2 using a fully self-consistent Hartree–Fock procedure. They find that $\beta(r)$ may be represented by a dipole-induced–dipole term and an exponential in r. For values of r sampled in these experiments, the exponential term is negative, reducing the anisotropy. However, it is not truly of short range, varying approximately as r^{-6} in the region of $r = \sigma$. While extrapolations to heavier atoms and polyatomic molecules are impossible, it is no longer reasonable to reject an r^{-4} term on the basis that it is physically unrealistic.

Because of the normalization procedure, both $p = 4.05$ and $p = 8.51$ are consistent with the Kerr-coefficient measurements. For $p = 4.05$, $\beta(r)$ is negative in the important region for r; while for $p = 8.51$, $\beta(r)$ is positive. For both values, $[\beta(r)]^2$ is greater than the dipole-induced–dipole term alone (Fig. 2).

In summary, despite the somewhat different density dependence of the CF_4 spectra and despite the size of B_k relative to the dipole-induced–dipole contribution, the analysis returns values of p quite similar to those found for rare gases. The one difference is the sign of the possible short-range term; it is positive for CF_4 but negative for rare gases. The two sets of values (p, y) give almost identical fourth moments, making further insight impossible on the basis of the available data. This
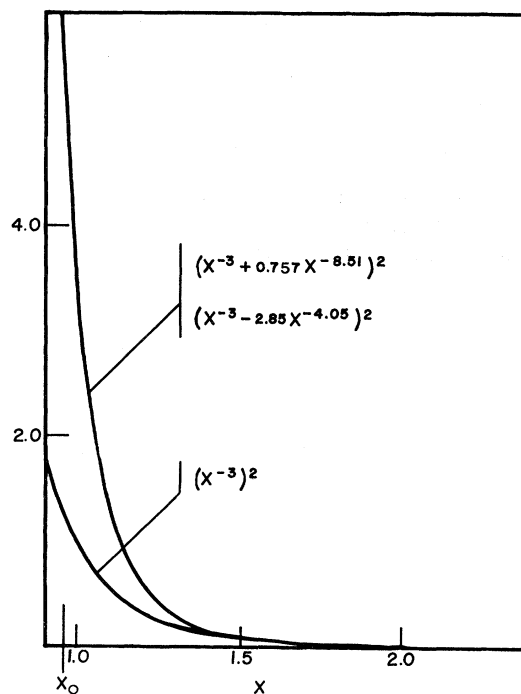

FIG. 2. Plot of $[\sigma^3\beta(x)/6\alpha^2]^2$ vs x for the dipole-induced –dipole term x^{-3} alone and for the cases in which the additional term varies as $x^{-4.05}$ and $x^{-8.51}$. Although it is not noticeable from the above scale, $[\beta(x)]^2$ does differ slightly between the two cases, $p = 4.05$ and 8.51, in the range $x > x_0$. x_0 is 0.962 and is the distance of closest approach at 295 K.

is the first experimental evidence that the sign of the additional term in $\beta(r)$ may be positive. While a detailed calculation of $\beta(r)$ for $(CF_4)_2$ such as O'Brien et al.[17] made for $(He)_2$ is impractical, perhaps a less rigorous approach would yield an indication of the sign of the contribution apart from the dipole-induced–dipole term. Then the possibilities (9) and (10) could be distinguished.

ACKNOWLEDGMENT

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