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Collision-induced light scattering from fluid methane at high densities

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We have studied the collision-induced light-scattering spectrum of fluid methane at several densities between 75 and 780 amagat. The results indicate that only two- and three-body contributions are significant up to densities much higher than found in previous work. The two- and three-body intensities are found to have rather similar frequency dependences.

I. INTRODUCTION

Light scattered by a fluid of atoms or isotropic molecules is observed to include a depolarized component which extends as far as 300 cm^{-1} on either side of the laser frequency. This so-called collision-induced scattering (CIS) is attributed to the incremental polarizability associated with molecular collisions. The basic problem in interpreting the data is to separate the contributions of many-body dynamics from that of cluster polarizabilities.[1]

In the low-density limit, the observed CIS spectrum is exponential, while the integrated intensity is proportional to the square of the density.[2] These features were predicted on the basis of a binary-collision model, where the incremental polarizability results from electronic overlap during the collision.[3] Another mechanism proposed to explain CIS is the dipole-induced dipole mechanism, where the scattered spectrum is due to the fluctuating local field seen by each individual scatterer.[4]

In the binary-collision model, the exponential spectrum has a decay constant which is related to the duration of a collision and is independent of the density. Analytical calculations indicate that this decay constant is independent of the form chosen for the intermolecular potential or the pair polarizability.[5]

Departures from the binary-collision predictions are evident in the CIS spectrum of gases at densities as low as 50 amagat. The integrated intensity saturates as the density is increased as a result of the reduction in the polarizability anisotropy associated with colliding groups of three, four, or more molecules.[2] Also, an additional exponential region, with a different decay constant, has been observed at larger frequency shifts in the CIS spectrum of rare gases under moderate pressures.[6,7] The scattered intensity from argon within this new region was found to have a density-squared dependence up to a density of 220 amagat.[7] As concluded in Ref. 7, this might indicate that the longer-ranged dipole-induced dipole mechanism is responsible for the low-frequency region while the shorter-ranged electronic overlap is responsible for the region at large frequency shifts since the latter will not suffer cancellation effects at higher densities. The argument provided is that even in a multiple collision an atom has a low probability of overlapping more than one atom at the same time.[7] In any event, the exponential region at high-frequency shifts should be sensitive to the form of the short-range repulsive part of the intermolecular potential.

Similar exponential CIS spectra have been observed in liquids.[8-10] Since binary collisions are no longer predominant at such high densities, the intensities are lower and the decay constants are higher than expected from the binary-collision model. In fact, the decay constant Δ for argon has been shown to follow the empirical relation

$$\Delta = \Delta_0[1 + (\rho/\rho_0)^2] , \quad (1)$$

where ρ is the density in amagats, $\rho_0 = 500$ amagat, and Δ_0 depends on the temperature.[11] This expression was later written in a corresponding states form which was successfully applied to other fluids.[12]

The most fruitful attempt to extract information from CIS data has been carried out by McTague and co-workers, who studied gaseous argon and methane at densities where only two- and three-body collisions are important.[13,14] They could thus separate the two- and three-body contributions by fitting the observed intensity to a virial expansion with up-to-cubic terms in the density. In the case of methane, at a temperature of 293 K and densities to 110 amagat, Barocchi and McTague[14] found an exponential two-body intensity extending well beyond 300 cm^{-1} and having a drastic change of

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the decay constant around a frequency shift of 100 cm^{-1}, from 15.5 cm^{-1} below to 138 cm^{-1} above 100 cm^{-1}. This low-frequency decay constant agrees well with calculations using the dipole-induced dipole model for the polarizability anisotropy, and either a hard-sphere or a Lennard-Jones pair potential.[15,16]

Barocchi and McTague[14] found an exponential three-body intensity extending to frequency shifts of 120 cm^{-1}, with a decay constant of 11.8 cm^{-1}. A recent theoretical calculation[17] of this decay constant using the dipole-induced dipole model for the pair polarizability and neglecting three-body irreducible polarizabilities resulted in good agreement with experiment for both hard-sphere and Lennard-Jones pair potentials.

Finally, comparison of calculated and measured integrated intensities led Barocchi and McTague to the conclusion that there must be a short-range interaction, not present in the noble gases, which determines the high-frequency-shift region of the two-body spectrum in methane.[14] In this paper, we present additional data on the CIS spectrum of fluid methane at substantially higher densities.

II. EXPERIMENTAL DETAILS

The high-pressure optical cell, which is equipped with sapphire windows, has been previously described.[18] The gas under investigation, in this case high-purity methane gas from the Matheson Gas Co., was used as the pressure-transmitting fluid.

The CIS spectrum of fluid methane up to frequency shifts of nearly 200 cm^{-1} was recorded at 240 ± 0.1 K and pressures to 8 kbar, corresponding to densities from 75 to 780 amagat.[19] They were obtained with the 5145-Å line of an argon-ion laser in the usual 90° scattering geometry, a beam power of 0.5 W, a Chromatrix DS-40 double monochromator at a resolution of 2.2 cm^{-1}, and photon-counting techniques. Pressure was measured to better than 5 bars with a high-precision manganin gauge.

Even though the sapphire windows depolarize light to some extent, in an attempt to measure the density dependence of the scattered intensity, all spectra were recorded within two days, during which time the experimental setup remained untouched.

III. RESULTS AND DISCUSSION

Figure 1 shows the CIS spectrum of methane at 240 K and several densities between 75 and 780 amagat. The spectrum at frequency shifts below 20 cm^{-1}, not shown in the figure, has been discussed in a previous publication.[20] The CIS spectrum for this

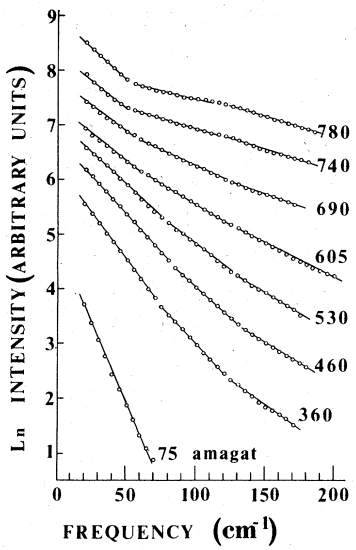

FIG. 1. CIS spectrum of fluid methane at several densities from 75 to 780 amagat. The spectra have been displaced upward for the sake of clarity. The circles are experimental points. The solid lines are least-squares fits to the data; the negatives of the slopes are the decay constants. The instrumental resolution was 2.2 cm^{-1}.

region cannot be adequately described classically and is complicated by the rotational spectrum of methane dimers.[21] Above 20 cm^{-1}, the CIS spectrum of Fig. 1 shows three exponential regions, with the exception of the spectrum taken at 75 amagat, where the spectrum is much weaker at high frequency shifts. The decay constants Δ_1, Δ_2, and Δ_3, associated with the low-, intermediate-, and high-frequency-shift exponential regions have quite different behavior at high densities. However, up to 530 amagat, all three decay constants follow the relation given by Eq. (1) with $\Delta_0 = 16.5$, 23.2, 44.2 cm^{-1}, and $\rho_0 = 425$, 480, and

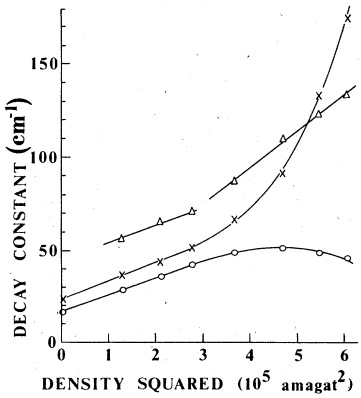

FIG. 2. Decay constants Δ_1 (circles), Δ_2 (crosses), and Δ_3 (triangles), associated with the low-, intermediate-, and high-frequency-shift exponential regions of the CIS spectrum in Fig. 1 vs density squared.

680 amagat, respectively. The decay constants are plotted versus density squared in Fig. 2. All decay constants are well represented, up to 530 amagat, by straight lines of nearly the same slope, given by Δ_0/ρ_0^2. This indicates that all three decay constants are affected in the same manner by three-body collisions and that higher-order collisions are not significant in the CIS spectrum of fluid methane at 240 K below 530 amagat. Although Δ_1 and Δ_2 clearly deviate from a density-squared dependence above 530 amagat, Δ_3 follows such a dependence to higher densities, but with a different slope. This change in slope might correspond to a change in the mechanism responsible for the light scattered in the high-frequency region. The electronic-overlap mechanism could be more important above 530 amagat while, at lower densities, the dominant mechanism could be the frame-distortion effect proposed by Bucaro and Litovitz for molecular liquids.[10] The short-range interaction alluded to by Barocchi and McTague[14] could well be frame distortion.

Some of the conclusions of the previous paragraphs are substantiated by an analysis of the intensity. However, at this point the reader should be reminded that, because of the depolarization of the sapphire windows and the lack of an internal standard, no conclusions can be made about absolute intensities from the data presented here.

Qualitatively, the intensity at a frequency shift of 30 cm^{-1} increases first, saturates around 400 amagat, and then decreases as the density is increased. At a frequency shift of 100 cm^{-1}, the intensity reaches a maximum around 550 amagat, while, at 150 cm^{-1}, the intensity is still increasing up to the maximum density reached, 780 amagat.

Following McTague, Ellenson, and Hall,[13] the observed intensity $I(\nu)$, which is a function of the frequency shift ν, is assumed to be given by a virial series in the density,

$$I(\nu)/\rho^2 = I_2(\nu) + I_3(\nu)\rho \ . \tag{2}$$

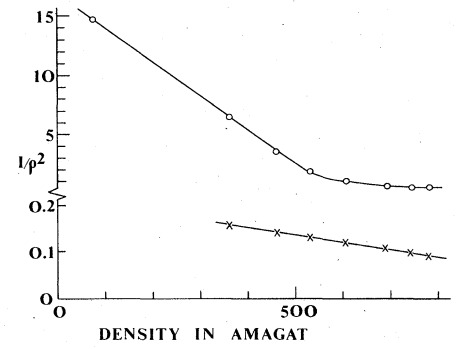

FIG. 3. Density dependence of I/ρ^2, the CIS intensity divided by the square of the density, at frequency shifts of 20 cm^{-1} (circles) and 150 cm^{-1} (crosses). Although the units of I/ρ^2 are arbitrary, all intensities have been properly scaled.

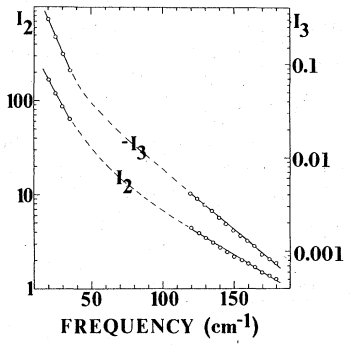

FIG. 4. Frequency dependence of I_2 and I_3, the two- and three-body contributions to the CIS intensity. Although the units of I_2 and I_3 are arbitrary, all intensities have been properly scaled.

Figure 3 then shows the quantity $I(\nu)/\rho^2$ versus density for frequency shifts of 20, and 150 cm^{-1}. For $\nu = 20$ cm^{-1}, the quantity $I(\nu)/\rho^2$ is linear in density up to 530 amagat. The intercept and slope resulting from a least-squares fit to Eq. (2) are $I_2(\nu)$ and $I_3(\nu)$, the two- and three-body contributions to the scattered intensity. Figure 4 shows the frequency dependence of $I_2(\nu)$ and $I_3(\nu)$. These quantities are well represented at frequency shifts between 20 and 40 cm^{-1} by the functions

$$I_2(\nu) = I_2'(0)e^{-\nu/14.9} \ ,$$
$$I_3(\nu) = -I_3'(0)e^{-\nu/11.7} \ ,$$

with

$$I_2'(0)/I_3'(0) \approx 400 \ .$$

The decay constants in these expressions are in good agreement with the values of 14.5 and 11.8 cm^{-1} obtained by Barocchi and McTague.[14] We can then conclude that only two- and three-body collisions are needed to account for the low-frequency region in the CIS spectrum of fluid methane at densities below 530 amagat. It is rather surprising that higher many-body collisions are not significant at such high density if one believes the commonly accepted view that this region of the spectrum is determined primarily by the longer-ranged dipole-induced dipole mechanism.

At intermediate frequency shifts the quantity $I(\nu)/\rho^2$ does not follow Eq. (2) in the density range studied. For instance, for $\nu = 60$ cm^{-1}, this quantity is nearly the same at 75 and 460 amagat, indicating that in this frequency region the polarizability anisotropy does not suffer the expected can-

cellation effects due to three-body collisions. Again, a frame-distortion mechanism can explain this result since it would tend to increase the polarizability anisotropy.

At frequency shifts above 120 cm^{-1}, the observed intensity is well represented by Eq. (2) in the density range 360–780 amagat, as shown in Fig. 3 for $\nu = 150$ cm^{-1}. The data points were least-squares fitted to Eq. (2). The frequency dependence of the resulting two- and three-body contributions are shown in Fig. 4. These are well represented by the functions

$$I_2(\nu) = I_2''(0)e^{-\nu/47.8} ,$$

$$I_3(\nu) = -I_3''(0)e^{-\nu/33.1} ,$$

with

$$I_2''(0)/I_3''(0) \approx 330 .$$

The high-frequency decay constant of the two-body intensity found in the present study is much smaller than that found by Barocchi and McTague.[14] This is the result of the fact that we have found a second exponential region in the three-body intensity, whereas the data in Ref. 14 showed a single exponential region at low frequency shifts. The failure of the latter study to detect any three-body contribution to the CIS spectrum above 120 cm^{-1} is probably due to the weak intensity in this frequency region at densities up to 110 amagat. Looking back at Fig. 1, it is obvious that the relative intensity of the high-frequency region of the spectrum increases dramatically when the density is increased from 75 to 360 amagat. In fact, the spectrum taken at a density of 75 amagat was, at a frequency shift of 80 cm^{-1}, already too weak to be observed in this study.

We would like to point out in Fig. 4 the similarity in the shapes of the two- and three-body spectra. The decay constant of the two-body intensity is roughly $\frac{4}{3}$ that of the three-body intensity, in both the high- and the low-frequency regions.

In summary, the present study indicates that only two- and three-body collisions are responsible for the CIS spectrum of fluid methane up to densities of 530 amagat for the low-frequency region and 780 amagat for the high-frequency region. The results also support the conclusion of Barocchi and McTague[14] that there is a short-range interaction, not present in the rare gases, which affects the high-frequency region of the CIS spectrum. We have suggested that this interaction might be the frame-distortion effect.[10] In addition, we have found a previously undetected exponential region at high frequency shifts which gives the three-body spectrum a striking resemblance to the two-body spectrum. We feel that a more detailed study of the absolute intensities will shed some additional light on the present results.

ACKNOWLEDGMENTS

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