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SPECTRAL DISTRIBUTION OF DOUBLE LIGHT SCATTERING BY GASES

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We compute the spectral distribution for double light scattering by a pair of optically isotropic molecules in a gas. We obtain a good fit with experimental data in CH_4 when we use a Lennard-Jones potential to calculate classical relative trajectories of the two particles. Observed depolarized intensities are compared with calculated ones.

Light scattered by optically isotropic gases has long been known to be slightly depolarized. Several calculations of the depolarization ratio have been proposed, either using the concept of an anisotropic Lorentz local field acting on an atom[1] or considering double light scattering by two nearby atoms.[2] For low densities, these calculations yield a depolarized intensity varying as the square of the density. More recently, Levine and Birnbaum[3] have calculated the depolarized line shape using a pair polarizability varying exponentially with the separation of the two atoms in the pair. This was taken by analogy with far-infrared pressure-induced absorption spectra.[4] This depolarized component was first observed by McTague and Birnbaum[5] in Ar and Kr gas under pressure and later by a number of authors.[6]

This type of experiment should prove very valuable in studying short-range correlation functions in dense fluids where pair distribution functions as well as higher-order distribution functions are involved. This spectrum may be observed in any system, provided rotational Raman scattering or the usual Rayleigh wing scattering does not overcome it completely.

The purpose of this Letter is to make a detailed analysis of the line shape of the depolarized spectrum from low-density gases, both experimentally and theoretically, using the model of double light scattering in which we consider that the electric dipole induced in one atom by the incident field creates a dipolar field which is going to polarize a nearby atom that will in turn scatter light at great distances.

Let λ be the wavelength of the incident light field $\vec{E}_L$ and $\vec{R}$ the vector connecting two nearby atoms; provided $|R| \ll \lambda$, the scattering electric dipole is given by

$$P = -2\alpha^2 \operatorname{grad}(\vec{E}_L \cdot \vec{R}/|R|^3),$$

where α is the atomic polarizability. If we assume that only pairs of atoms need to be considered, which is true at low densities, the depolarized scattering cross section is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{zx} = \frac{72\pi}{15}\left(\frac{2\pi}{\lambda}\right)^4 N^2 \rho^2 \frac{\alpha^4}{\sigma^3} \times \int_0^\infty \frac{1}{x^6} \exp\left[-\frac{U(x)}{kT}\right] x^2 dx,$$

where $U(x)$ is the interatomic interaction potential in reduced units $x = R/\sigma$, N is the number of atoms per unit volume in standard conditions, and ρ the density in amagat units.

To calculate the power spectral density, we take the Fourier transform of the correlation function of the scattered field,

$$C(\tau) \propto \int_{-\infty}^{\infty} \langle \vec{E}_D(t+\tau) \cdot \vec{E}_D{}^*(t) \rangle \, dt,$$

where one takes a statistical ensemble average over all possible relative trajectories of the two

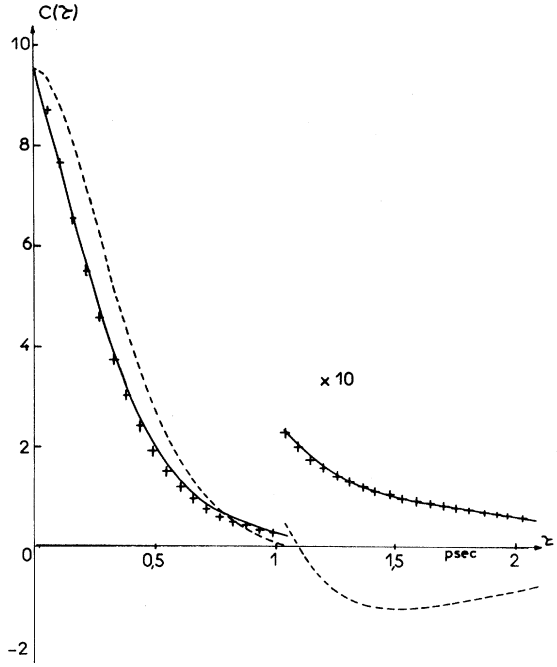

FIG. 1. Correlation function for double light scattering by pairs of CH_4 molecules with initial rms relative velocity. Dashed line is for the hard-sphere interaction potential, solid line is for the Lennard-Jones 6-12 potential, and crosses are for the modified Buckingham potential (Ref. 7). Notice a change of scale by a factor 10 for $t \geq 1.1$ psec.

particles. We neglect the motion of the center of mass as it corresponds to correlation times much longer than the duration of the collisions.

In the case of CH_4 molecules, we have performed numerical calculations of $C(\tau)$ taking as initial relative velocity in the collision the rms relative velocity $v=(3kT/\mu)^{1/2}$, μ being the reduced mass. Classical trajectories were determined for three intermolecular potentials[7]: (1) hard sphere; (2) Lennard-Jones, $U(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^6]$; and (3) modified Buckingham,

$$U(R)=\frac{\epsilon}{1-6/\alpha}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{R}{r_m}\right)\right]-\left(\frac{r_m}{R}\right)^6\right\}.$$

Integrations were performed on a computer over initial times t, impact parameters, and orientation of the initial relative velocity. The results are shown in Fig. 1. The results for (1) agree with those of Thibeau and Oksengorn.[8] Note the change of sign in $C(\tau)$. We see that there are slight differences between the results calculated with the two more realistic potentials (2) and (3).

The time scale being σ/v, we see that it is necessary to compute $C(\tau)$ for various values of the relative velocity v and to perform an integration over v. Assuming a Maxwellian velocity distribution, the average $C(\tau)$ we obtain is shown as the dashed curve in Fig. 2.

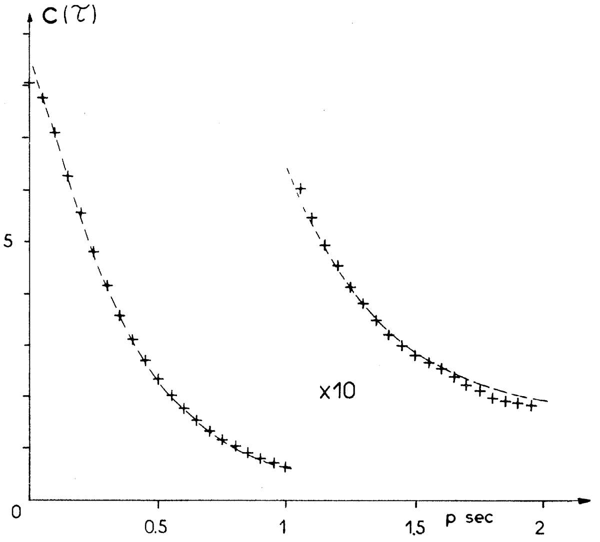

FIG. 2. Velocity-averaged correlation function. Dashed line is computed for a Lennard-Jones potential; crosses are calculated from the zx spectrum scattered by CH_4 at 70 amagats and 20°. Notice a change of scale by a factor 10 for $t \geq 1$ psec.

Experiments have been performed using a 1-W ionized argon laser, a 1-m double monochromator, and standard photon counting equipment. We have studied several gases at room temperature,[9] but we only present results for CH_4.

We first measured the depolarization ratio, which we find equal, to within 5%, to that of the rotational Raman lines of N_2 or H_2 that was used to calibrate our optics and detection system. We have measured the total depolarized intensity by comparison with the S_1 Raman line of a small quantity of hydrogen added to the gas in the pressure cell. This allows us to neglect the usual local-field correction factor $[\frac{1}{3}(n^2+2)]^2$, since we may expect it to have the same value for one hydrogen molecule and a pair of atoms of the gas. We find that at low density ($\rho < 30$ amagats) the depolarized intensity varies as ρ^2. We can therefore obtain an experimental value for the cross-section ratio

$$\mathcal{R}=\frac{(d\sigma/d\Omega)_{zx}\ (\text{depolarized at 1 amagat})}{(d\sigma/d\Omega)_{zx}\ (S_1 \text{ of } H_2 \text{ at 1 amagat})}.$$

Experimental values are shown in Table I together with theoretical values calculated for a Lennard-Jones $U(R)$, experimentally known optical polarizability,[10] and $\alpha_{\parallel}-\alpha_{\perp}=0.314\,\text{Å}^3$ for an H_2 molecule.[11]

Table I. Theoretical and experimental values for the ratio of the depolarized cross section at 1 amagat to that of the S_1 Raman line of hydrogen at 1 amagat.

Gas	Theory	Experiment
H_2	1.3×10^{-3}	$(1.7\pm0.2)\times10^{-3}$
Ar	1.6×10^{-2}	$(1.3\pm0.2)\times10^{-2}$
CH_4	0.68×10^{-1}	$(0.70\pm0.1)\times10^{-1}$
SF_6	2.1×10^{-1}	$(3.7\pm0.5)\times10^{-1}$

There exist other ways to determine the depolarized cross section. One of them is to measure the depolarization ratio of the scattered light as was done by Thibeau, Oksengorn, and Vodar,[12] who obtained a good agreement between experiment and the same theory for Ar gas. The other one is to measure the pressure-dependent part B_K of the Kerr coefficient,[13] as it is related to the depolarized cross section by

$$\frac{(d\sigma/d\Omega)_{zx}}{B_K}=\frac{27}{4\pi}\left(\frac{2\pi}{\lambda}\right)^4 kT\,\frac{\alpha^2}{(\alpha^{(0)})^2}$$

in the double-light-scattering theory. Here $\alpha^{(0)}$ is the static polarizability. In the case of SF_6, experiments performed by Buckingham and Dunmur[13] have shown that theory and experiment differ by about a factor of 0.6, as we present in Table I.

We see from Table I that the depolarized cross section varies roughly as α^4/σ^3. This will be tested further as more gases become available.

The line shape has been measured using an instrumental width of about 1 cm^{-1}. We have found no change in the spectrum when the pressure was varied from 10 to 100 atm in CH_4. No change was detected either for the other gases we studied. We find that within experimental error, the zx spectrum is identical to the zz spectrum. We have checked that the Stokes-anti-Stokes intensity ratio varies as $\exp(h\nu/kT)$ with T close to the operating temperature.

From the experimental data we obtained in CH_4 at 70 amagats and 20°C, we have calculated the experimental correlation function that is plotted as crosses in Fig. 2.

We see in Fig. 2 that the calculated correlation function (dashed line) is in good agreement with the experimental one (crosses). Here we adjusted the relative intensity, but as we mentioned before, the integrated observed intensity agrees well with the theoretical one. This result means that the term $6\alpha^2/R^3$ for the pair polarizability as a function of distance[14] is the dominant one. We have obtained the same kind of agreement for Ar and H_2. The fit is not as good for SF_6 when we use $\sigma=5.51$ Å.[7]

At higher densities, higher-order distribution functions become important. The next additional term to the ratio $\mathfrak{R}$ they give rise to is $-b\rho^3$.[9] They lead to spectra that ought to be broader as we expect higher-order distribution functions to vary faster in time. In addition our present calculations assume linear trajectories at large distances. They will not be adequate when the mean free path is no longer large compared with σ. This will lead to changes near the center of the line as was discussed by Lewis and Van Kranendonk.[15]

In conclusion, we see that for low-density gases, double light scattering leads to calculated spectra that fit quite well with the experimental depolarized spectra. Therefore, we think that a plausible test of molecular-dynamics models in dense media[16] would come from comparison of experimental depolarized spectra and spectra calculated using $6\alpha^2/R^3$ pair polarizability.

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[1] J. Yvon, Actual. Sci. Ind. Nos. 542-543 (1937); M. Fixman, J. Chem. Phys. 23, 2074 (1955).

[2] M. L. Frisch and J. McKenna, Phys. Rev. 139, A68 (1965).

[3] H. B. Levine and G. Birnbaum, Phys. Rev. Lett. 20, 439 (1968).

[4] See, for example, H. B. Levine and G. Birnbaum, Phys. Rev. 154, 86 (1967), and references therein.

[5] J. P. McTague and G. Birnbaum, Phys. Rev. Lett. 21, 661 (1968).

[6] J. P. McTague, P. A. Fleury, and D. B. DuPré, Phys. Rev. 188, 303 (1969).

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954). We used the values of σ, π_m, α, and ϵ given therein.

[8] M. Thibeau and B. Oksengorn, Mol. Phys. 15, 579 (1968).

[9] P. Lallemand, to be published.

[10] H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc., Ser. A 156, 144 (1936).

[11] N. J. Bridge and A. D. Buckingham, Proc. Roy. Soc., Ser. A 295, 334 (1968).

[12] M. Thibeau, B. Oksengorn, and B. Vodar, J. Phys. (Paris) 29, 287 (1968).

[13] A. D. Buckingham and D. A. Dunmur, Trans. Faraday Soc. 64, 1776 (1968).

[14] L. Silberstein, Phil. Mag. 33, 521 (1917).

[15] L. C. Lewis and J. Van Kranendonk, Phys. Rev. Lett. 24, 802 (1970).

[16] A. Rahman, Phys. Rev. 136, A405 (1964).