

⁹S. J. Buchsbaum, *Bull. Am. Phys. Soc.* **7**, 151 (1962); S. J. Buchsbaum, L. Mower, and S. C. Brown, *Phys. Fluids* **3**, 806 (1960).

¹⁰When ω lies in the band of upper hybrid frequencies, the integrand of Eq. (1) has a simple pole for some value of x ($|x| \leq a$). The inclusion of electron collisions removes this singularity from the path of integration. Taking the limit of zero collision frequency tells one how to integrate around the pole. This limit is equivalent to the Dirac formulation of such integrals and is responsible for giving Z_p a real part.

¹¹R. S. Harp, R. L. Bruce, and F. W. Crawford, *J. Appl. Phys.* **38**, 3385 (1967).

¹²See, for example, G. A. Pearson, *Phys. Fluids* **9**, 2454 (1966); H. L. Frisch and G. A. Pearson, *Phys. Fluids* **9**, 2464 (1966).

¹³For a discussion of this problem, see G. Bekefi, *Radiation Processes in Plasmas* (John Wiley & Sons, Inc., New York, 1966), p. 223.

¹⁴D. E. Kaplan, R. M. Hill, and A. Y. Wong, *Phys. Letters* **22**, 585 (1966).

¹⁵L. O. Bauer, F. A. Blum, and R. W. Gould, in the Ninth Annual Meeting of the Division of Plasma Physics of the American Physical Society, Austin, Texas, 8-11 November 1967 (unpublished); R. M. Hill and D. E. Kaplan, private communication.

COLLISION-INDUCED LIGHT SCATTERING

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We consider here a new type of light scattering in gases and liquids which arises as a result of molecular collisions. Because of the distortion of the electronic structure during collision, the polarizability of colliding molecules is not the sum of the individual polarizabilities. For binary collisions, this incremental polarizability scatters light into a broad frequency band whose width is controlled by the duration of collision and whose intensity varies as the square of the density. Such scattering can be viewed as Rayleigh scattering by the collision-induced polarizability, or as Raman scattering involving a change in the translational state of the relative kinetic energy of a pair of colliding molecules. Our purpose is to derive a simple analytic expression for the spectrum of scattered light which provides a framework for discussing the nature of the effect, to consider what systems are most suitable for observation, and to indicate experiments in which the effect may have been seen although not clearly recognized as such.

Following our previous work in collision-induced absorption,¹ we (1) consider binary collisions, (2) assume straight line paths, and (3) assume the variation of the incremental polarizability with interatomic separation to be of the form

$$\alpha(r) = A_1 \exp(-\gamma_1^2 r^2), \quad (1)$$

$$\beta(r) = A_2 (\gamma_2 r)^2 \exp(-\gamma_2^2 r^2), \quad (2)$$

where $\alpha(r)$ and $\beta(r)$ are, respectively, the spher-

ical and anisotropic parts of the induced polarizability, defined in the usual way in terms of $\alpha_{\parallel}(r)$ and $\alpha_{\perp}(r)$. These equations exhibit the proper asymptotic behavior: (1) $\alpha(r) \rightarrow 0$ as $r \rightarrow \infty$, and $\alpha(r)$ assumes a finite limit as $r \rightarrow 0$; and (2) $\beta(r) \rightarrow 0$ as $r \rightarrow \infty$, and $\beta(r) \rightarrow 0$ as $r \rightarrow 0$ by reason of the spherical symmetry of the united atom.²

Assuming a plane-polarized incident light beam with an electric vector, $\vec{E} = \vec{E}_0 \cos[\omega_0(t - z/c)]$, we apply classical radiation theory³ to compute the energy spectrum of the light scattered by the induced dipole moments, which are proportional to $\alpha(r)$ and $\beta(r)$, during a single collision. The assumptions stated above mean that the energy pulses dominantly have a Gaussian envelope in time. Multiplication by the collision rate⁴ and integration over the relative velocity and impact parameter then yields the power spectrum of the scattered light. For the noble gases, it is found to be the sum of two contributions:

$$\frac{d^2 J_{\kappa}^{(1)}}{d\Omega d\omega} = \frac{2A_1^2 N_0^2}{c^4 V_0^2} \left(\frac{\pi k T}{2m} \right)^{3/2} \times x_1^4 P_{\kappa}^{(2)}(|x_2 - x_{02}|) \quad (3)$$

due to the spherical term $\alpha(r)$ and

$$\frac{d^2 J_{\kappa}^{(2)}}{d\Omega d\omega} = \frac{2A_2^2 N_0^2}{15c^4 V_0^2} \left(\frac{\pi k T}{2m} \right)^{3/2} \times x_2^4 P_{\kappa}^{(2)}(|x_2 - x_{02}|) \quad (4)$$

due to the anisotropy $\beta(r)$. The quantity $d^2J_\kappa^{(i)}/d\Omega d\omega$ is the scattered power per unit volume per unit solid angle (Ω) per unit frequency interval (ω) per unit incident intensity per unit density squared (density in amagats), polarized with the electric vector in the direction κ ($\kappa = x, y, \text{ or } z$). N_0 is Avogadro's number, V_0 is the mol volume, c is the speed of light, k is Boltzmann's constant, T is the absolute temperature, m is the reduced mass of an atomic pair, and the x 's are reduced frequency variables defined by $x_i = (\omega/\gamma_i)(m/kT)^{1/2}$ and $x_{0i} = (\omega_0/\gamma_i)(m/kT)^{1/2}$ ($i = 1, 2$). The P 's contain the dependence of the intensity upon the scattering angle, which is the same as that for vibrational Raman scattering by diatomic molecules. For the direction along the magnetic vector of the incident beam, we find

$$P_x^{(1)} = Q_1, \quad P_y^{(1)} = 0, \quad P_z^{(1)} = 0, \quad (5)$$

$$P_x^{(2)} = Q_2, \quad P_y^{(2)} = 0, \quad P_z^{(2)} = \frac{3}{4}Q_2, \quad (6)$$

where

$$Q_1(x) = xK_1(x), \quad (7)$$

$$Q_2(x) = x\left\{(1 + x^2/384)K_1(x) + \frac{1}{6}xK_0(x)\right\}, \quad (8)$$

and K_0, K_1 are modified Bessel functions of the second kind. Equations (3) and (4) above neglect additional terms involving $P_\kappa^{(i)}(x_i + x_{0i})$, which are extremely small at optical frequencies. Thus, scattering due to $\beta(r)$ has a component which is z polarized, while that due to $\alpha(r)$ does not, so that their contributions can be separated by observations in different polarizations. Since for $x \gg 1$, $K_n(x) \sim (\pi/2x)^{1/2} \times \exp(-x)$, these equations predict that the scattered intensity should fall off exponentially in the wings. The shapes of the spectra are plotted semilogarithmically in Fig. 1.

The depolarization ratio \mathcal{D} , defined⁵ as the ratio of the z -polarized intensity to the x -polarized intensity, is given by

$$\mathcal{D} = \frac{3}{4} \frac{A_2^2 x_2^4 Q_2}{15A_1^2 x_1^4 Q_1 + A_2^2 x_2^4 Q_2}. \quad (9)$$

The frequency-dependent behavior of \mathcal{D} is plotted in Fig. 2 for the case $\gamma_1 = \gamma_2$ and $A_1 = A_2$ which appears to be a reasonable guess from the calculations in Ref. 2. Except for a region of slight curvature near $\omega = \omega_0$, \mathcal{D} increases linearly with $\Delta = |\omega_0 - \omega|$ well out into the wings of the spectrum.⁶

To determine whether collision-induced scat-

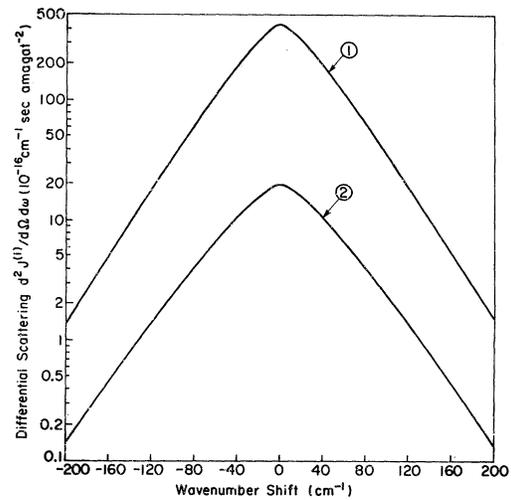


FIG. 1. Scattered intensity along the magnetic vector of the incident light wave, according to Eqs. (3)-(8) of the text. The constants used are $A_1 = A_2 = 2.1 \times 10^{-24} \text{ cm}^3$, $\gamma_1 = \gamma_2 = 0.67 \times 10^8 \text{ cm}^{-1}$, $T = 300^\circ\text{K}$, $m = 3.316 \times 10^{-23} \text{ g}$ (Ar), $x_{01} = x_{02} = 744.9$ (argon ion laser λ 4880 Å). Curves 1 and 2 correspond to $i = 1$ and $i = 2$, respectively.

tering is observable, we integrate Eq. (3) over all frequencies and sum over all polarizations to obtain

$$\sum_K \frac{dJ_\kappa^{(1)}}{d\Omega} = \frac{\gamma_1 A_1^2 N_0^2 E_0^2 (\pi/2)^{1/2} (kT)^2}{4v_0^2 c^3} \left(\frac{m}{m}\right) x_0^4, \quad (10)$$

and compare this with the integrated intensity due to the usual Rayleigh scattering. For lack of more specific information we take $\gamma_1 = 0.67 \text{ \AA}^{-1}$, the average value of γ deduced from collision-induced absorption at 295°K for He-Ar and Ne-Ar gas mixtures.^{1,7} The factor A_1

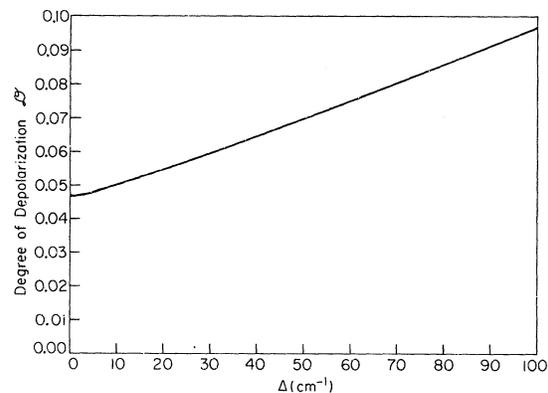


FIG. 2. Depolarization ratio for collision-induced scattering versus frequency shift. The constants assumed are the same as for Fig. 1.

may be related to the second dielectric virial coefficient, B ,⁸ by using⁹

$$B = \frac{8\pi^2}{3} \int_0^\infty \alpha(r) \exp[-V(r)/kT] r^2 dr. \quad (11)$$

Setting the intermolecular potential $V(r)$ equal to zero, which is consistent with the assumption of straight line trajectories, and again using Eq. (1), we find that

$$B = 2A_1 \pi^{5/2} / 3\gamma_1^3. \quad (12)$$

From the experimental value¹⁰ $B(\text{Ar}) = 2.6 \text{ cm}^6 \text{ mole}^{-2}$, Eq. (12) gives $A_1(\text{Ar}) = 2.1 \times 10^{-24} \text{ cm}^3$, and we find that at a density ρ of 100 amagats the integrated collision-induced scattering (which varies as ρ^2) is weaker than the Rayleigh scattering (which varies as ρ) by about a factor of 100. This value is similar to the ratio of the intensity of vibrational Raman lines to the Rayleigh scattering by typical diatomic molecules.¹¹ In the same way, we estimate that for Kr, where the second dielectric virial coefficient is much larger,¹⁰ i.e., $B = 5.6 \text{ cm}^6 \text{ mole}^{-2}$, that at a density of 100 amagats the integrated collision-induced scattering is weaker than the Rayleigh scattering by only about a factor of 2. Similarly for neon and especially for helium the effect should be very small; in the latter case it may be unobservable. Thus, particularly in the case of Kr, a detailed examination of the spectrum produced by collision-induced scattering should be possible.

Although we have been considering noble gases, it is clear that collision-induced scattering is a general phenomenon and should occur for all molecules and in liquids as well as in gases. We mention several recent experiments where the data suggest the presence of collision-induced scattering in molecular liquids. (1) Recently, Shapiro and Broida¹² studied Rayleigh scattering in liquid CS_2 as a function of a frequency as far as 160 cm^{-1} away from the exciting line and found a higher intensity than given by theories predicting a Lorentzian line shape. We find that their data correspond to an exponential line shape in the deep wings, which agrees with the predictions of our equations. (2) Rayleigh scattering up to 110 cm^{-1} from the excitation frequency has been observed in liquid C_6H_6 , CHCl_3 , and CCl_4 ,¹³ which all show the exponential behavior. (3) Murphy, Evans, and Bender¹⁴ measured the depolarization ratio for the Raman line of CCl_4 arising from the totally symmetric vibration to

be 0.0039. For spherical molecules acting as independent scattering centers, the depolarization ratio for such a line should be zero. Using Fig. 2 as a rough guess, and including also the Rayleigh scattering seen in the experiment, we can account for the observed depolarization.

Other experiments could be cited which provide evidence for the effect discussed here. It seems appropriate now, however, to focus attention on the simplest systems, i.e., the rare gases where it would appear that scattering at frequencies well removed from the exciting frequency can be due only to the effect we have discussed. When seen, experimental study of such scattering, coupled with theoretical analyses which incorporate the effect of intermolecular forces, should provide new information about such forces and collision dynamics.

¹H. B. Levine and G. Birnbaum, *Phys. Rev.* **154**, 86 (1967); H. B. Levine, *Phys. Rev.* **160**, 159 (1967).

²A recent calculation for molecular H_2 confirms this general behavior. See W. Kólos and L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

³J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962), Chap. 14.

⁴R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1958), p. 145.

⁵G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), pp. 246-249.

⁶The depolarization of Rayleigh scattered light has recently been considered by S. Kielich, *J. Chem. Phys.* **46**, 4090 (1967). He does not treat the translational Raman scattering considered in this paper.

⁷This is not a true physical range, but rather an effective range which results from a complex compounding of the effects of the real intermolecular potential and the real range of polarizability. Since the effect we consider here is similar to the infrared case, it seems reasonable that the effective ranges should be roughly equal.

⁸D. A. McQuarrie and H. B. Levine, *Physica* **31**, 749 (1965); *J. Chem. Phys.* **44**, 3500 (1966).

⁹H. B. Levine and D. A. McQuarrie, to be published.
¹⁰R. H. Orcutt and R. H. Cole, *J. Chem. Phys.* **46**, 697 (1967).

¹¹T. Yoshino and H. J. Bernstein, *J. Mol. Spectry.* **2**, 213 (1958).

¹²S. L. Shapiro and H. P. Broida, *Phys. Rev.* **154**, 129 (1967).

¹³D. O. Landon, private communication. These spectra so far have been measured only at a few points, so that additional structure which is possible in the wings has not yet been seen.

¹⁴W. F. Murphy, M. V. Evans, and P. Bender, *J. Chem. Phys.* **47**, 1836 (1967).