a helium buffer gas pressure of 0.2 Torr to 85 kHz at 1.0 Torr at reduced rf field strengths. If we assume that the primary contribution to the linewidth at the higher pressure occurs as a result of collisions with the $^1S_0$ helium atoms, the disorientation cross section can be calculated from the relationship

$$\Delta\nu = 1/\pi\tau = \sigma v N/\pi,$$

where $\Delta\nu$ is the width of the resonance absorption signal at the half-maximum points in frequency units, τ is the mean time between depolarizing collisions, v is the relative velocity between the colliding neon and helium atoms, and N is the helium ground-state density. At room temperature we find $\sigma(\mathrm{Ne}^m\text{-He}) \leq 5.4\times10^{-17}$ cm^2. This must be regarded as an upper limit on the depolarization cross section since the effects of field gradients, Ne^m-Ne collisions, and the rf field were not taken into account.

The g factor can be determined from the magnetic resonance frequency and the magnetic field intensity. Sicne the cell used in this experiment contained helium, it is a simple matter to permit a small amount of helium resonance radiation at 1.083μ to align the metastable helium atoms. The location of the helium 2^3S_1 and $^3P_2$ resonances can then be observed in the same cell. From the ratio of the resonance frequencies at constant field and the measured g factor for metastable helium[8] we obtain $g_J = 1.501\,52 \pm 0.000\,64$ for the 2^3P_2 levels of neon, in good agreement with the value obtained by Lurio et al. using an atomic-beam resonance method.[9]

The results of this experiment suggest the possibility of optically pumping the other noble gas metastable atoms such as argon, xenon, and krypton. The use of isotopes having a nuclear spin would also permit the measurement of metastability-exchange cross section as well as a variety of other collisional effects and g factors.

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[1] F. D. Colegrove and P. A. Franken, Phys. Rev. 119, 680 (1960).

[2] G. K. Walters, F. D. Colegrove, and L. D. Schearer, Phys. Rev. Letters 8, 439 (1962).

[3] R. J. McNeal, R. A. Bernheim, R. Bersohn, and M. Dorfman, J. Chem. Phys. 40, 1678 (1964).

[4] T. Hadeishi, O. A. McHarris, and W. A. Nierenberg, Phys. Rev. 138, A983 (1965).

[5] Max Baumann, Z. Physik 173, 519 (1963).

[6] J. R. Dixon and F. A. Grant, Phys. Rev. 107, 118 (1957).

[7] F. D. Colegrove, L. D. Schearer, and G. K. Walters, Phys. Rev. 132, 2561 (1963).

[8] V. W. Hughes, G. Tucker, E. Rhoderick, and G. Weinreich, Phys. Rev. 91, 828 (1953).

[9] A. Lurio, G. Weinreich, C. W. Drake, V. W. Hughes, and J. A. White, Phys. Rev. 120, 153 (1960).

COLLISION-INDUCED LIGHT SCATTERING IN GASEOUS Ar AND Kr

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Light scattering attributable to a change in polarizability produced in colliding pairs of atoms is observed in gaseous Ar and Kr. The experimental results are qualitatively accounted for by relations between the integrated intensity and the collision-induced polarizability.

In a recent Letter, Levine and Birnbaum[1] discussed the scattering of light arising from the change in polarizability produced in a pair of atoms or spherical molecules by the distortion of the electronic structure during collision. This transient polarizability should scatter light into a broad frequency band whose width is related to the duration of collision and whose intensity should vary at low densities as the square of the density. Because the polarizability increment is anisotropic, it should depolarize the incident light although the isolated scatterers are spherically symmetric. In this Letter we report the observation of such scattering in gaseous Ar and Kr, and qualitatively account for the experimental results by relations between the integrated intensity and the spherical and anisotropic polarizabilities of the interacting pair.

Right-angle scattering was observed with the experimental geometry defined by a coordinate system with the y axis parallel to the direction of the incident light and the x axis parallel to that of the scattered light. The experimental arrangement consisted of a 6328-Å He-Ne laser (~80 mW), a device for rotating the polarized laser light in the x and z directions, a scattering cell, a double-grating monochromator, and photoelectric detection. The best signal-to-noise ratio, 25, was obtained with Kr at the highest gas pressure used, namely 150 atm. The scattering cell, designed to withstand pressures up to 170 atm, was machined from stainless steel and was fitted with three quartz windows 6 mm thick, two for the incident beam and one for the scattered beam. To reduce background scattering, the inside walls were blackened and a number of diaphragms were fixed inside the cell along the path of the incident light. Since no analyzer followed the scattering cell, both the y- and z-polarized components of the scattered radiation were measured.

Semilogarithmic plots of the scattered intensity versus deviation from the laser frequency for the laser beam polarized in the x direction are shown in Fig. 1 for Ar and Kr at a pressure of 150 atm. Within experimental error, the line shape in the wings was independent of the polarization of the incident beam, gas pressure, as well as slit width. It is seen that the frequency dependence in the wings is approximately exponential [roughly $\exp(-|\nu|/10)$] in accordance with the prediction of Levine and Birnbaum.[1] Near the center of the band the line intensity increases with frequency more rapidly than in the wings, possibly due to background scattering at the laser frequency which is detected because of the finite slit width. The density dependence[2] for the scattered light is plotted in Fig. 2 at two frequencies. In the limit that $\rho\to 0$, the intensity varies as ρ^2, indicating that the scattering is due to atomic pairs. The departure from a ρ^2 dependence at the higher densities can be attributed to interactions of three or more atoms. The nonzero intercept obtained at the lower frequency may arise from ordinary Rayleigh scattering from individual atoms whose intensity varies as ρ.

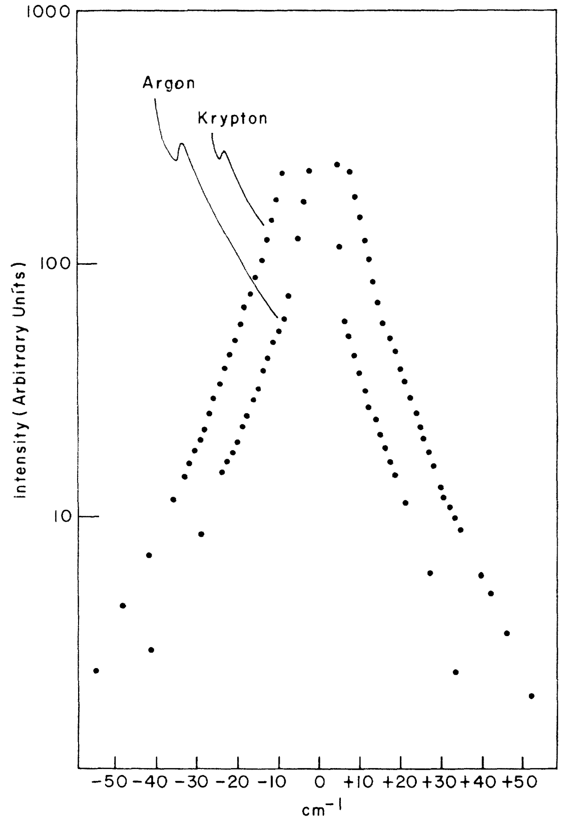

FIG. 1. Relative intensity of scattered light versus wave number for Kr and Ar at 150 atm. The laser beam was polarized in the x direction. Spectral slit width is roughly 4 cm^{-1}.

The calculation of Levine and Birnbaum[1] is based on a model which enabled them to discuss the spectral shape of the scattered light but which is not directly related to atomic parameters. To obtain expressions suitable for analyzing the experimental results, we start with the usual expressions for the intensity per unit volume scattered by axially symmetric molecules into a solid-angle element $d\Omega$. For the case where the detector measures both the y- and z-polarized components of the scattered radiation,[3] one has

$$\frac{dI_z}{d\Omega}=I_0\rho\frac{\omega^4}{c^4}\left(\alpha^2+\frac{7}{45}\beta^2\right), \tag{1}$$

$$\frac{dI_x}{d\Omega}=I_0\rho\frac{\omega^4}{c^4}\frac{2\beta^2}{15}, \tag{2}$$

where ρ is the number of scatterers per cc, and I_0 is the incident light flux. The average polarizability α and anisotropy β are defined by

$$\alpha=\tfrac{1}{3}(\alpha_\parallel+2\alpha_\perp), \tag{3}$$

$$\beta=(\alpha_\parallel-\alpha_\perp), \tag{4}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are, respectively, the polarizabilities parallel and perpendicular to the symmetry axis. The subscripts z and x refer to the direction of polarization of the incident light.

These expressions are easily modified for collision-indiced light scattering by noting that in this case α and β are functions of R. Then by replacing ρ by the probability $2\pi\rho^2 g(R)R^2dR$ of finding two atoms between the distance R and $R+dR$, where

$$g(R)=\exp[-u(R)/kT] \tag{5}$$

and $u(R)$ is the interaction energy between two atoms, Eqs. (1) and (2) become

$$\frac{dI_z}{d\Omega}=2\pi I_0\rho^2\frac{\omega^4}{c^4} \times\int_0^\infty\left[\alpha^2(R)+\frac{7}{45}\beta^2(R)\right]g(R)R^2dR, \tag{6}$$

$$\frac{dI_x}{d\Omega}=2\pi I_0\rho^2\frac{\omega^4}{c^4}\frac{2}{15}\int_0^\infty \beta^2(R)g(R)R_2dR, \tag{7}$$

where $\alpha(R)$ and $\beta(R)$ refer to the polarizability increments relative to $R=\infty$.[4]

In investigating the Kerr constant of gases composed of atoms or spherical molecules, Buckingham and Dunmur[5] found a density-squared dependence which they interpreted as arising from the induced polarization in molecular pairs. This contribution is characterized by the second Kerr virial coefficient

$$B_{\rm K}=\frac{8\pi^2N_0^2}{405kT}\int_0^\infty \beta^2(R)g(R)R_2dR, \tag{8}$$

provided, as is sufficiently correct in the present case, that the optical and static values of β are taken to be equal. Then comparing Eqs. (7) and (8) we see that

$$dI_x/d\Omega=(27kTI_0\rho^2\omega^4/2\pi N_0^2c^4)B_{\rm K}. \tag{9}$$

The (relative) integrated intensity[6] can be obtained only roughly because the experimental curves must be extrapolated into the region near the laser frequency where strong background scattering precluded measuring the much weaker scattering due to the induce polarizabilities. We find that the ratio $(dI_x/d\Omega)_{\rm Kr}/(dI_x/d\Omega)_{\rm Ar}$ is in the range 1.5-3.5, which is within the experimental error of the ratio

$$B_{\rm K}({\rm Kr})/B_{\rm K}({\rm Ar})=(16\pm14)/(4.1\pm0.6).$$

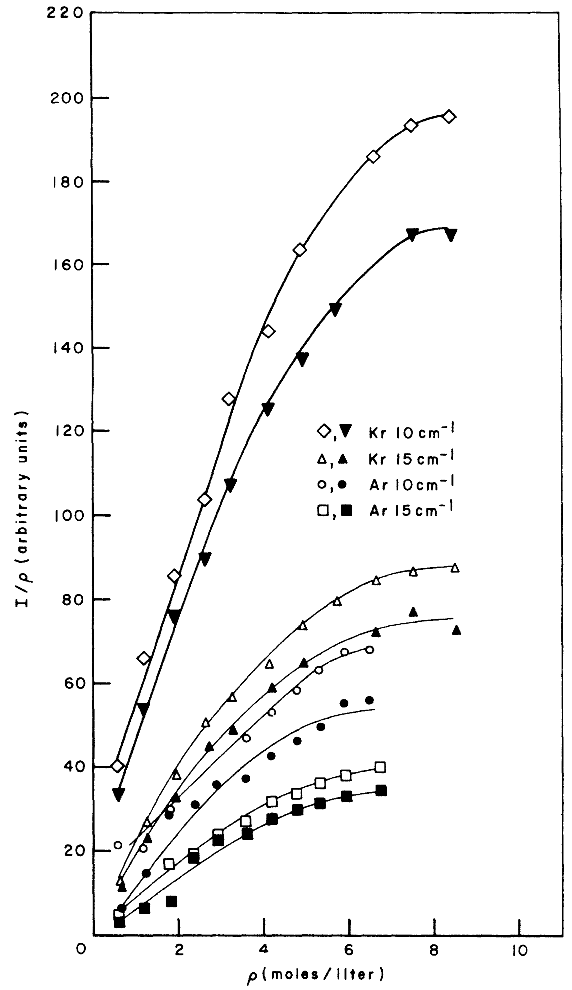

FIG. 2. Density dependence of scattering intensity at two frequencies. Spectral slit width is roughly 4 cm^{-1}. z-polarized intensity is indicated by open symbols, x-polarized intensity by filled symbols.

The depolarization ratio at a given frequency, defined by $(d^2I_x/d\Omega d\bar{\nu})/(d^2I_z/d\Omega d\bar{\nu})$, is 0.86 ± 0.04 for Ar[7] and Kr at $\bar{\nu}=10$ and 15 cm^{-1}. Estimating the integrated intensities on the basis that the line shapes for the x and z polarizations are the same, these results mean that $\langle\alpha^2(R)\rangle\ll\langle\beta^2(R)\rangle$,[8] where $\langle\rangle$ represent the average over R indicated in Eqs. (6)-(8). As far as we know, there is no experiment other than the one discussed here which measures $\langle\alpha^2(R)\rangle$. However, the second dielectric virial coefficient for rare gases measures $\langle\alpha(R)\rangle$, and one can relate $\langle\alpha^2(R)\rangle$ to $\langle\alpha(R)\rangle$ by means of a model for the induction process which includes an overlap contribution varying as r^{-12} and a dispersion contribution varying as r^{-6}. A preliminary estimate shows, in agreement with experiment, that $\langle\alpha^2(R)\rangle$ is negligible compared with $\langle\beta^2(R)\rangle$.[9] Work is in progress to extend the experiments to other gases and gas mixtures, and over a range of temperatures. Experiments of this type are expected to contribute to the understanding of intermolecular forces as well as the scattering mechanism itself, which should be present to a greater or lesser degree in all systems.

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

[2] The density of Ar was calculated from the data of A. Michels, Hub. Wijker, and Hk. Wijker, Physica 15, 627 (1949). The density of Kr was calculated from the data of J. A. Beattie, J. S. Brierley, and R. J. Barriault, J. Chem. Phys. 20, 1613 (1952).

[3] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc., New York, 1955), pp. 43-48.

[4] Anisotropic light scattering in systems composed of spherically symmetric particles has been discussed by S. Kielich, J. Chem. Phys. 46, 4090 (1967); O. Theimer and R. Paul, J. Chem. Phys. 42, 2508 (1965); and A. D. Buckingham and M. J. Stephen, Trans. Faraday Soc. 53, 884 (1957).

[5] A. D. Buckingham and D. A. Dunmur, to be published.

[6] The intensities refer to the low-density region where $I \propto \rho^2$.

[7] M. Thibeau, B. Oksengorn, and B. Vodar, Compt. Rend. 265B, 722 (1967), measured the integrated light intensity scattered from compressed Ar. Their data indicate that the depolarized component varies as ρ^2, which they interpreted as due to fluctuations of the effective molecular field.

[8] Indeed, if $\langle\alpha^2(R)\rangle \ll \langle\beta^2(R)\rangle$, then $d^2I_x/d\Omega d\bar{\nu}$ and $d^2I_z/d\Omega d\bar{\nu}$ depend only on the anisotropy polarization and should, therefore, have the same line shape.

[9] G. Birnbaum and J. P. McTague, to be published.

MEASUREMENT OF THE CROSS SECTION FOR THE REACTIONS $H^- + H_2O \rightarrow OH^- + H_2$ AND $D^- + D_2O \rightarrow OD^- + D_2$ AT INCIDENT ION ENERGIES NEAR 2 eV*

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H^- and D^- ions produced by dissociative attachment of electrons to H_2O and D_2O have been used as primary ions in the measurement of a cross section of $(1.6 \pm 0.3) \times 10^{-14}$ cm^2 for the negative-ion–molecule reaction $H^- + H_2O \rightarrow OH^- + H_2$ at an H^- energy of 1.93 ± 0.45 eV and $(5.8 \pm 1.2) \times 10^{-14}$ cm^2 for the reaction $D^- + D_2O \rightarrow OD^- + D_2$ at a D^- energy of 1.84 ± 0.38 eV. The method is quite generally applicable to the study of negative-ion reactions in the energy region from thermal energies to ~3 eV.

Previously reported measurements of negative-ion charge exchange and negative-ion–molecule reaction rates were made at incident ion energies above 2 eV with beam techniques[1] or at thermal energies with afterglows.[2] Paulson[3] has used dissociative attachment in D_2O and O_2 to produce D^- and O^- ions in the source region of a mass spectrometer and has reported reaction rates for a number of negative-ion processes as a function of the ion extraction voltage. The constant repeller field induced a large energy spread in the initial ion-energy distribution and made difficult the accurate estimation of reaction rates as a function of ion energy, particularly in the low-energy region.[4] However, the initial energy distribution of the ions produced in dissociative attachment can in many cases be accurately determined experimentally or calculated from known bond dissociation energies and electron affinities. In the work described here we have used a pulsed electron beam to produce H^- or D^- ions of ~2-eV kinetic energy through the peaks at 6.5-eV electron energy in the dissociative attachment reactions $e + H_2O \rightarrow H^- + OH$ and $e + D_2O \rightarrow D^- + OD$.[5] The subsequent ion-molecule reactions[6]

$$H^- + H_2O \rightarrow OH^- + H_2, \tag{1}$$

$$D^- + D_2O \rightarrow OD^- + D_2 \tag{2}$$

were allowed to proceed under field-free conditions in the source region of a time-of-flight mass spectrometer for varying lengths of time before rapid ion extraction and measurement of the H^- and OH^- or D^- and OD^- currents. We are not reporting here a detailed study of these reactions as a function of ion energy but the following results show, firstly, that the Reactions (1) and (2) proceed extremely rapidly for ion energies near 2 eV with a large isotope effect; secondly, that the reaction cross section increases with decreasing electron energy; and,