kinetic energy, where the differential cross section for inelastic scattering is markedly dependent on the scattering angle. Also shown in Fig. 2 are ratios for the total cross section derived from the work of Vainstein, Opykhtin, and Presnyakov.[4] These theoretical values have been used for comparison with our differential cross-section ratios since no closer theoretical data are available. Although a comparison of total and differential cross sections is not completely satisfactory, we feel that it is justified for cross-section ratios for dipole transitions.

As can be expected, the theoretical curves agree well with our data at high incident-electron energies. Furthermore, at high incident energies we can use the Born approximation to obtain the differential cross section from the optical line-strength ratio. The latter has been determined experimentally and found to be 2.1 ± 0.2.[6] From this value we derive a differential cross-section ratio of 1.9 ± 0.2, which is in good agreement with our measurements at high energies.

At low incident-electron kinetic energies the Born approximation cannot be expected to agree with our differential cross-section ratios. However, calculations based on the Vainstein model[4] are also constant over the range of our measurements. Only when the excess energy of the scattered electrons is comparable with the difference in energy of the thresholds of the two states do the Born approximation and the Vainstein model[4] predict a decrease in the cross-section ratio. It should be remembered that the lowest energy of the electrons after scattering in our experiment was 1.5 eV, and probably higher (see above for correction), and that this is approximately 20 times the difference in threshold energy for the $6^2P_{1/2}$ and $6^2P_{3/2}$ states. It seems possible that some improvement could be made in the theoretical calculations by the inclusion of spin-dependent forces in the Schrödinger equation.

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ROLE OF DISPERSION IN COLLISION-INDUCED ABSORPTION

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It is shown that theoretical calculations which use the exponential model $\vec{\mu} = \mu_0(\vec{r}/r)$ $\times \exp(-r/\rho)$ for the variation of the dipole moment $\vec{\mu}$ with internuclear separation $\vec{r}$ can be forced into agreement with experiment only if one uses dipole parameters μ_0, ρ which are in serious disagreement with values computed by the molecular Hartree-Fock approximation. On the basis of a Drude model calculation, it is concluded that the exponential model is an inadequate representation of the true physical situation because of its neglect of electron correlation effects.

The elegant experiment by Bosomworth and Gush[1] has aroused considerable interest on the part of theoreticians, and several papers have appeared recently[2-9] in which theoretical calculations of the spectral line shape for collision-induced absorption in rare-gas mixtures or related systems have been made. In the first four of these papers (Refs. 2-5) a heuristic model was employed for the variation of the collision-induced dipole moment of a heteropolar rare-gas diatom with internuclear separation, which yields good agreement with experiment when certain parameters are suitably adjusted. We shall not discuss these calculations further here. In the second four papers (Refs. 6-9), the dipole moment was assumed to vary in what apparently is a physically realistic way:

$$\vec{\mu} = \mu_0(\vec{r}/r) \exp(-r/\rho). \tag{1}$$

A similar form has been suggested in theoretical papers dealing with the integrated absorption.[10,11] A calculation of $\bar{\mu}$ as a function of $\bar{r}$ has been performed by Matcha and Nesbet,[12] using the molecular Hartree-Fock approximation, which at first sight tends to confirm (1). We shall show, however, that the contrary is true, and that a critical comparison of exponential-model calculations with Ref. 12 shows that the exponential model represents at best only a part of the dipole moment, and that another part of about equal importance must exist. This second part is easily accounted for by appeal to a long-range dispersion interaction, which the Hartree-Fock calculation by its nature cannot obtain.[12]

Consider the moments of the absorption spectrum $\alpha(\omega)$:

$$\gamma_{2n} \equiv \frac{3\hbar c}{4\pi^2 n_A n_B} \int_0^\infty \omega^{2n-1} \alpha(\omega) \times \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega, \tag{2}$$

as defined by Sears,[8] where n_A, n_B are the number densities of the two species in the gas mixture, c is the speed of light, and the other symbols have their usual meanings. It can be shown that these moments also are given by[8]

$$\gamma_{2n} = V\langle |d^n \bar{\mu}/dt^n|^2\rangle, \tag{3}$$

where V is the sample volume, and the brackets denote a canonical average. In the classical limit, the canonical averaging gives in particular[2]

$$\gamma_0 = 4\pi \int_0^\infty r^2 g(r)[\mu(r)]^2 dr, \tag{4}$$

and[10]

$$\gamma_2 = \frac{4\pi kT}{m} \int_0^\infty g(r)\left[\left(\frac{d\mu}{dr}\right)^2 + 2\mu^2\right] dr, \tag{5}$$

where $g(r)$ is the radial distribution function, and $\mu(r)$ is the scalar dependence of the collision-induced dipole upon distance. It has been pointed out by Futrelle[13] that the ratio γ_2/γ_0 from (4) and (5) is virtually independent of the interatomic potential for the exponential model (1), and comparison of the theoretical ratio with the experimental value, determined by (2) and (3), allows one to determine unambiguously the value of the range ρ. To illustrate the point, let us approximate $g(r)$ by

$$g(r) = 0, \quad r < r_0; \quad g(r) = 1, \quad r \geq r_0; \tag{6}$$

where the effective collision diameter r_0 is given

as a function of temperature by the condition

$$\tfrac{1}{2}m\langle v_x^2\rangle = \tfrac{1}{2}kT = \varphi(r_0), \tag{7}$$

where m is the reduced mass, and $\varphi(r)$ is the interatomic potential. Substituting (1) and (6) into (4) and (5), one finds

$$\frac{\gamma_2}{\gamma_0} = \frac{kT}{\rho^2 m}\left\{\frac{\xi^2 + \xi + \frac{5}{2}}{\xi^2 + \xi + \frac{1}{2}}\right\}, \tag{8}$$

where $\xi = r_0/\rho$. For He-Ar mixtures at room temperature and typical potentials, $r_0 \simeq 2.7$ Å; in addition, $\rho \simeq 0.32$ Å is consistent with the exponential model, so that $\xi \simeq 8.4$. Then the bracketed expression in (8) is $\simeq 1.03$, and varies only very slowly with temperature because of the slow variation of r_0. A similar result applies for Ne-Ar mixtures. Thus we can write

$$\rho \simeq (kT\gamma_0/m\gamma_2)^{1/2}, \tag{9}$$

which is independent of potential. To show this more precisely, we have determined ρ for various potentials by adjusting it so that the ratio of (5) to (4) agrees with the experimental value. The latter was obtained by analytically integrating the line-shape formula of Levine[3] for He-Ar and by numerically integrating the empirical line-shape formula of Bosomworth and Gush[1] for Ne-Ar. The numerical values are given in Table I. It is to be stressed that the close agreement of the former line-shape formula[3] with the experiment makes it a convenient empirical representation of the experimental data, and it is only in that sense that it has been used. Given the value of ρ, we then obtain the value of μ_0 by adjusting it so that the experimental and theoretical values of γ_2 are in agreement. Using two different potentials[14,15] for He-Ar, we compare in Fig. 1 the result of such a calculation with the results in Ref. 12. The disagreement is greater than can be attributed to the uncertainty in the experimental values[16] of γ_0 and γ_2, or to numerical errors in Ref. 12. A number of other potentials[14,17-19] lead to curves lying between the two shown, and a similar plot holds for Ne-Ar. Reference 12 gives a dipole moment less than the experimental curves indicate, suggesting that an additional contribution to the dipole moment must exist. The difference is most easily accounted for by the fact that Ref. 12, being a molecular Hartree-Fock calculation, by its nature does not include electron correlation effects, which become dominant in the dispersive long-range limit.

Table I. The spectral moments γ_0, γ_2.

| Gas | Moment[a] | Experiment | Theory, Eqs. (4), (5), (18), (19) | | | | | |
| | | | LJ (6-12) potential | | | Exp-6 potential | | |
			b	c	d	e	f	g
He-Ne	γ_0	...	0.0331	0.0335	0.0391	0.0371	0.0321	0.0319
	γ_2	...	0.0205	0.0208	0.0251	0.0243	0.0203	0.0201
He-Ar	γ_0	1.70	1.29	1.38	1.49	0.979	1.35	1.37
	γ_2	1.17	0.540	0.575	0.640	0.401	0.580	0.587
Ne-Ar	γ_0	2.38	...	1.10	1.22	0.879	1.30	1.13
	γ_2	0.550	...	0.107	0.121	0.0838	0.132	0.112

[a]Units of γ_0, 10^{-62} erg cm^6; of γ_2, 10^{-35} erg cm^6 sec^{-2}.

[b]Ref. 17, p. 466.

[c]Ref. 14, p. 1110 (viscosity potential), using empirical combining rules.

[d]Ref. 14, p. 1110 (virial coefficient potential), using empirical combining rules.

[e]Ref. 15.

[f]Ref. 18.

[g]Ref. 19.

Insofar as the dipole moment of a rare-gas diatom is concerned, Buckingham[20] has shown by quantum-mechanical perturbation theory that at large separations the variation of the dipole moment is of the form $\mu \sim r^{-7}$. We can estimate the magnitude of this dispersive term by a straightforward semiclassical calculation based upon the Drude model.[14]

Consider two coupled harmonic oscillators with a Hamiltonian

$$H = \tfrac{1}{2}(m_1 \ddot{\vec{r}}_1{}^2 + m_2 \ddot{\vec{r}}_2{}^2 + k_1 r_1{}^2 + k_2 r_2{}^2)$$
$$+ e^2 \left[\frac{1}{r} + \frac{1}{|\vec{r} - \vec{r}_1 + \vec{r}_2|} - \frac{1}{|\vec{r} - \vec{r}_1|} - \frac{1}{|\vec{r} + \vec{r}_2|} \right], \quad (10)$$

where $\vec{r}_1$, $\vec{r}_2$ are the displacements of the oscillators from their equilibrium positions. In the limit of large r we may expand the equations of motion in powers of r^{-1}. This leads to a set of coupled linear differential equations for $\vec{r}_1$ and $\vec{r}_2$, which can be solved successively. The dipole moment of the interacting oscillators is then obtained by averaging $-e(\vec{r}_1 + \vec{r}_2)$ over time and phase. We find that

$$\mu(r) = \sum_{n=0}^{\infty} \mu_n r^{-(2n+7)}, \quad (11)$$

where in particular

$$\mu_7 = 60 e^5 (\omega_2{}^2 - \omega_1{}^2)$$
$$\times \left(\frac{1}{m_2 \omega_2{}^2} - \frac{1}{m_1 \omega_1{}^2} \right) \left(\frac{|A_{1z}|^2}{m} - \frac{|A_{2z}|^2}{m_1} \right). \quad (12)$$

In (12), the A's are the amplitudes and the ω's the frequencies of the unperturbed motion. The

polarity is 1^+2^-. The amplitude can be related to the mean square extension by

$$6|A_{iz}|^2 = \langle r_i{}^2 \rangle. \quad (13)$$

and the product $m_i \omega_i{}^2$ can be related to the polarizability α_i by[14]
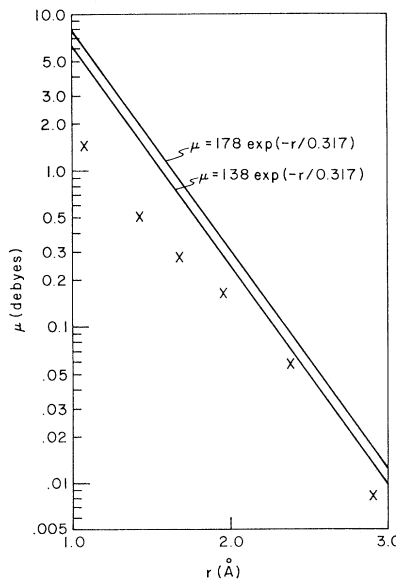
$$\alpha_i = e^2 / m_i \omega_i{}^2. \quad (14)$$

FIG. 1. Dipole moment for He-Ar based upon assuming the form of Eq. (1) and adjusting μ_0, ρ to match the experimental values of γ_0, γ_2 (solid curves). The upper curve is based upon the potential of Ref. 15, and the lower upon the potential given in Ref. 14, p. 1110, using second virial coefficient data and empirical combining rules. The crosses are the results of the calculation of Ref. 12.

If we assume equal effective masses, the use of (13) and (14) reduces (12) to

$$\mu_7 = 10e\,\alpha_1\alpha_2\{\langle r_1^2\rangle - \langle r_2^2\rangle\}. \tag{15}$$

As a further approximation, we can use

$$\langle r_i^2\rangle \simeq \alpha_i^{2/3}, \tag{16}$$

a relation which can be tested on atomic hydrogen,[14] where it is easily shown to be correct to within 10%. Thus, we finally write

$$\mu_7 = 10e\,\alpha_1\alpha_2(\alpha_1^{2/3} - \alpha_2^{2/3}), \tag{17}$$

as an approximation for the dispersive part of the dipole moment in terms of the atomic polarizabilities. Using the experimental polarizabilities, we obtain

$$\mu_7(\mathrm{He^+Ne^-}) = 0.17 \times 10^{-73}\ \mathrm{esu\ cm^8},$$

$$\mu_7(\mathrm{He^+Ar^-}) = 2.43 \times 10^{-73}\ \mathrm{esu\ cm^8},$$

$$\mu_7(\mathrm{Ne^+Ar^-}) = 3.07 \times 10^{-73}\ \mathrm{esu\ cm^8}. \tag{18}$$

To assess the importance of these values, we can compute the moments γ_0, γ_2 assuming the dipole moment to be of the form

$$\mu = \mu_7(\vec{r}/r)r^{-7}, \tag{19}$$

with μ_7 given by (18). Using (4) and (5), we obtain the values listed in Table I. These values represent a considerable fraction of the experimental values for He-Ar and Ne-Ar. For HeNe, Bosomworth and Gush[1] were unable to see any spectrum experimentally and the small values listed for this case are in keeping with their negative result.

Despite the crudity of our estimate of μ_7, the above results suggest that a dispersive term of the form (19) goes a long way toward explaining the discrepancy indicated in Fig. 1. This means that none of the calculations of Refs. 6-9 provides a definitive explanation of the experimental results. Further theoretical work must be carried out with consideration of the fact that the

simple exponential model (1) does not adequately describe the dipole moment in mixed rare gases. What is clearly called for is an empirical form constructed by analogy with the well-known exp-6 potential, which assumes the form (1) for small r and the form (19) for large r, and undergoes a smooth transition between the two forms for intermediate distances.

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