

Scattering of Thermal Rare Gas Beams by Argon. Influence of the Long-Range Dispersion Forces*

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Total cross sections have been measured for scattering atomic beams of He, Ne, Ar, Kr, and Xe by argon. A modulated beam technique was employed. The apparatus had an angular resolution of 1.5 minutes of arc. The data were correlated using the Massey-Mohr theory, assuming an attractive interatomic potential $V(r) = -C/r^6$; in which case the cross section Q is given by $Q = b(C/v_r)^{2/5}$ where b is a constant and v_r is the relative velocity. Values of C may be estimated from theoretical expressions and from experimental data on transport properties in gases. By using these sources for C , we may calculate the corresponding Q 's. The cross sections obtained from our experiment were higher than those calculated. For the argon-argon interaction, for example, a theoretical expression for C (that of Kirkwood and Müller) indicates that $Q = 410 \text{ Å}^2$. From viscosity data we infer that Q should be 383 Å^2 . Our experimental value is 468 Å^2 . The discrepancy is beyond experimental error.

INTRODUCTION

THE scattering of molecular beams by other molecules is a relatively direct way to investigate intermolecular forces. In particular, measurements of the total cross section for scattering of thermal molecular beams are expected to yield information regarding the long-range van der Waals forces. Massey and Mohr¹ have derived a simple relationship between the intermolecular potential constant C , the relative velocity v_r , and the observed total scattering cross section Q . For the long-range potential $V(r) = -C/r^6$, the equation is

$$Q = 4.662 \times 10^{11} (C/v_r)^{2/5}, \quad (1)$$

when cgs units are employed.

Various aspects of this relationship have been investigated experimentally with beams of alkalis or their salts. Rosin and Rabi² performed experiments which indicated that the total scattering cross section is finite. In another experiment the ratios of cross sections for many scattering gases (with a given beam material) were measured.³ These ratios were in good agreement with the predictions of the Massey-Mohr theory. Measurements of the total cross section as a function of velocity,⁴⁻⁶ and of temperature,⁷ were in good agreement with Eq. (1), although deviations have been found for low mass beams.⁵

Massey and Mohr estimated that the cross sections predicted by their formula should be accurate within

5%. Bernstein⁸ has investigated the influence of the repulsive part of the potential upon Q and found it to be small (at reasonable thermal energies) except for the case of light atoms at low velocities. At very high velocities, the repulsive forces would become important.

We have studied the scattering of He, Ne, Ar, Kr, and Xe by argon. For these cases several theoretical calculations have been made for the interatomic potentials. The attractive potential constant has also been estimated from transport property data. A comparison of previous scattering data with theory and with gas properties has been more difficult because of the paucity of accurate physical constants of alkalis and alkali salts, but some early experiments appeared, with one exception, to agree with theory.⁹ Subsequent experimental results have indicated that the absolute cross section may be considerably higher than Eq. (1) would predict.^{3,6,10}

EXPERIMENTAL

In concept, this experiment was similar to a previous study of alkali beam scattering.³ The apparatus is shown in Fig. 1. It was divided into three separately pumped vacuum chambers. The beam atoms effused from a 0.075-mm wide slit constructed from 0.025-mm thick foil. The pressure behind the source slit was adjusted so that the mean free path was about twice the slit width. The beam passed through a collimating slit (also made from 0.025-mm thick foil) and then entered the scattering chamber. Finally the beam entered the detector through a 0.038-mm wide slit. Both the source and the detector slit could be translated for alignment. The detector was an electron bombardment ionizer of the Bayard-Alpert type. The beam passed through an elliptical grid (7.5-mm major axis, 4-mm minor axis) which was 5 cm long. The electron source was an oxide-coated cathode whose emission

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¹ H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc. (London)* **A144**, 188 (1934).

² S. Rosin and I. I. Rabi, *Phys. Rev.* **48**, 373 (1935).

³ E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.* **31**, 1619 (1959).

⁴ H. Pauly, *Z. Naturforsch.* **15a**, 277 (1960).

⁵ H. U. Hostettler and R. B. Bernstein, *Phys. Rev. Letters* **5**, 318 (1960).

⁶ R. C. Schoonmaker, *J. Phys. Chem.* **65**, 892 (1961).

⁷ H. Schumacher, R. B. Bernstein, and E. W. Rothe, *J. Chem. Phys.* **33**, 584 (1960).

⁸ R. B. Bernstein, *J. Chem. Phys.* **34**, 361 (1961).

⁹ A. Dalgarno and A. E. Kingston, *Proc. Phys. Soc. (London)* **73**, 455 (1959).

¹⁰ H. Pauly, *Z. angew. Phys.* **9**, 600 (1957).

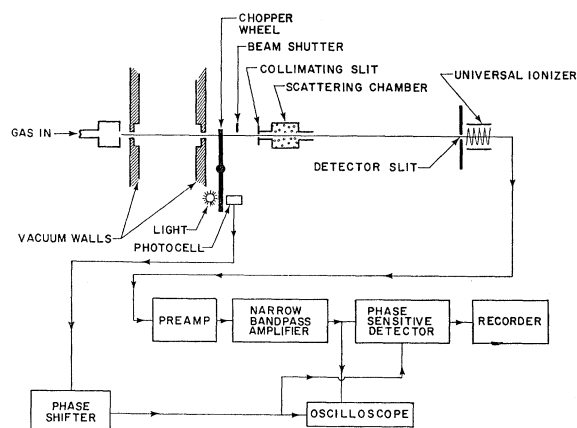


FIG. 1. Schematic of the experiment.

was regulated by a control grid. The grids and cathode were parts of a commercial 6L6 electron tube. Sensitivity of the detector to background gas (determined by comparison with an ion gage) was $10\mu\text{a}$ of ion current per micron of pressure per milliamper emission. Normal emission currents were about 40 ma. To discriminate the beam signal from background gas, the beam was mechanically chopped (101.8 cps) and phase-sensitive detection was employed.

The distance from the source to the collimating slit was 27.7 cm and from the collimating slit to the detector was 31.8 cm. The calculated half-width at the detector was 0.17 mm while that observed was 0.20 mm. Applying the Kusch criterion, described in reference 7, the angular resolution, at the 50% level, is calculated to be 90 sec of arc.

The pressure of the argon in the scattering chamber was measured by an ionization gage (I.G., Veeco RG75), which was connected to the scattering chamber by 5 cm of 18-mm i.d. Pyrex tubing. The I.G. was operated at an emission current of $800\mu\text{a}$. This gage was calibrated against a Consolidated Vacuum Corp. (CVC) GM-110 McLeod gage. The McLeod manufacturer claims 1.4% accuracy at 10^{-4} mm Hg. The calibration was checked by comparing this McLeod against another, which had been calibrated by mercury weighing. Within the 5% accuracy of the calibration procedure, the CVC model read correctly.

The scattering chamber is shown in Fig. 2. Each of the two beam channels has a length, l , of 12.7 mm, a width, a , of 0.80 mm, and a height, b , of 3.18 mm. The central volume has a length of 25.4 mm, and the depth and width are each 12.7 mm. The collimating slit, which is fastened over the center of one of the beam channels, also has a height, b , of 3.18 mm, and a width, c , of 0.081 mm. The pressure P' , just inside the collimating slit may be computed from three separate gas conductances. These are the conductance from the central volume into the rectangular tube, the conductance along that tube, and the conductance through

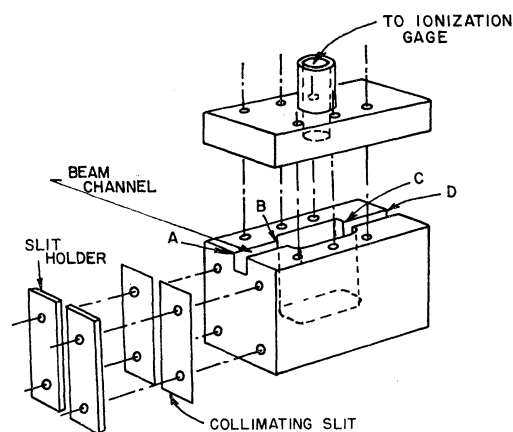


FIG. 2. Scattering chamber. The collimating slit is attached.

the collimating slit.¹¹ We derive the expression for the ratio:

$$P/P' = [a/(a-c)] + [3cl(a+b)/8abK(a-c)],$$

where P is the pressure in the central volume and K is the Clausing factor.¹¹ In the present case P'/P is 0.617. The pressure outside the slit, in the main vacuum chamber, is negligible compared to P and P' , and was taken to be zero. Thus to calculate an effective path d at the pressure P we take

$$Pd = d_{BC}P + d_{AB}0.5(P + 0.617P) + d_{CD}0.5P,$$

where the d_{ij} are the distances between points i and j . By using these expressions we find that $d = 42.0$ mm. No pressure rise in the surrounding vacuum chamber was observed ($\Delta P < 2 \times 10^{-8}$ mm Hg) with the highest scattering pressures used.

The beam intensity (I) was measured for about 10 to 15 values of the scattering gas pressure. The beam flag was frequently shut to measure the zero line and the scattering chamber was often evacuated to obtain the 100% transmission line (I_0). Almost all the data were obtained between 50 to 100% transmission. Plots of $\log(I/I_0)$ vs pressure were linear. From the slopes of these plots, the cross sections were obtained by using a procedure identical to that described by Rosin and Rabi,² except that a different beam velocity distribution was required. This modification is necessary, because the universal ionizer used here discriminates against the faster beam particles, while the surface ionizer employed by Rosin and Rabi does not. Furthermore, the phase-sensitive detection also alters the distribution of velocities. These points are discussed further in the Appendix.

The reproducibility of the data was quite good ($\pm 3\%$). The accuracy of the cross sections ($\pm 5\%$) was limited by the uncertainty of the McLeod calibration. This limit of accuracy does not apply to the

¹¹ A. Guthrie and R. K. Wakerling, *Vacuum Equipment and Techniques* (McGraw-Hill Book Company, Inc., New York, 1949).

TABLE I. Physical properties needed for various estimations of C .

	α (10^{-24} cm ³) ^a	IP (eV) ^b	χ (10^{-6} cm ³) ^b	Viscosity ^c		Mutual diffusion ^d with argon		N
				ϵ/k (°K)	σ (10^{-8} cm)	ϵ_{12}/k (°K)	σ_{12} (10^{-8} cm)	
He	0.206	24.56	— 1.94	10.22	2.576	33.8	2.99	2
Ne	0.408	21.56	— 7.2	35.7	2.789	64.5	3.098	8
Ar	1.64	15.76	— 19.4	124	3.418	8
Kr	2.49	14.0	— 28	190	3.61	155	3.526	8
Xe	4.02	12.13	— 43	229	4.055	171	3.693	8

^a H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc. (London) **A156**, 144 (1936).^b H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie* (Springer-Verlag, Berlin, 1950), 6th ed., Vol. I, Part 1 pp. 211, 394.^c See reference 18.^d See reference 19.

helium-argon scattering. Helium is difficult to detect because of its higher velocity and lower ionization cross section. Further, the small gas collision probability requires a high scattering gas pressure. The He-Ar cross section is uncertain by about 10%. For the same reasons, our preliminary measurement of the He-He cross section (45 Å²) is uncertain by about 10 to 15%. Another source of error is the possibility that still higher angular resolution would yield higher cross sections. Pauly recently measured the effect of angular resolution upon the total cross section, by scattering potassium from Hg, Ar, He, and N₂.¹² At an angular resolution of about 1.5 minutes, 99% of the value of the total cross section was obtained. It is not obvious that the present experiment should require better resolution.

DISCUSSION

The quantitative calculation of intermolecular dispersion forces has been of interest for many years. Margenau¹³ and Pitzer¹⁴ have reviewed the state of the problem. The following three formulas have been most widely used. London¹⁵ used second order perturbation theory to derive the expression

$$V(r) = \frac{-3\alpha_1\alpha_2}{2r^6} \frac{U_1U_2}{U_1+U_2}, \quad (2)$$

where α is the static atomic polarizability and U is some average excitation energy. The subscripts 1 and 2 represent different atoms. The ionization potentials (IP) of the atoms are often put equal to U . The variational method was applied by Slater and Kirkwood¹⁶ to obtain the expression

$$V(r) = \frac{-e^2a_0^3}{r^6} \frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}}, \quad (3)$$

where e is the electronic charge, a_0 is the Bohr radius, and N is the number of outer shell electrons. The

¹² H. Pauly, *Proceedings of the Atomic and Molecular Beams Conference* (University of Denver, Denver, Colorado, 1960); *Z. Physik* **157**, 54 (1959).

¹³ H. Margenau, *Revs. Modern Phys.* **11**, 1 (1939).

¹⁴ K. S. Pitzer, *Advances in Chem. Phys.* **2**, 59 (1959).

¹⁵ F. London, *Z. physik. Chem.* **B11**, 222 (1930); *Z. Physik* **63**, 245 (1930).

¹⁶ J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

variational approach was also used to obtain the Kirkwood-Müller¹⁷ formula,

$$V(r) = \frac{6mc^2}{N_0r^6} \frac{\alpha_1\alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)}, \quad (4)$$

where m is the electronic mass, c the velocity of light, N_0 is Avogadro's number, and χ is the diamagnetic susceptibility per mole. The values of C predicted by these three expressions are given in Table II.

Intermolecular potential functions have often been fitted to experimentally determined quantities, such as virial coefficients, mutual diffusion, and viscosity. The widely used 2-parameter (ϵ, σ) Lennard Jones potential is

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (5)$$

Here $C = 4\epsilon\sigma^6$. An extensive tabulation of ϵ and σ for various gases, based on second virial coefficient and viscosity data, is available.¹⁸

For unlike atoms, we apply the standard combination rules¹⁸ to values of ϵ and σ obtained from viscosity, i.e., $\sigma_{12} = 0.5(\sigma_1 + \sigma_2)$ and $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$. Evaluations of σ_{12} and ϵ_{12} are also obtained from mutual diffusion measurements.¹⁹

Salem²⁰ has recently used second order perturbation theory to obtain the dispersion energy. His expression contains an explicit two-electron correlation term; when this term is neglected it reduces to Eq. (4). That equation is said to provide an upper limit to the dispersion term.

Fontana²¹ has obtained the dispersion energy by using an irreducible tensor formalism. The values of C are about the same magnitude as those of London, and are smaller than any of the other estimates listed above.

Guggenheim and McGlashan,²² who have made a

¹⁷ J. G. Kirkwood, *Physik. Z.* **33**, 57 (1932); A. Müller, *Proc. Roy. Soc. (London)* **A154**, 624 (1936).

¹⁸ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

¹⁹ B. N. Srivastava and K. P. Srivastava, *J. Chem. Phys.* **30**, 984 (1959); K. P. Srivastava, *Physica* **25**, 571 (1959).

²⁰ L. Salem, *Mol. Phys.* **3**, 441 (1960).

²¹ P. R. Fontana, *Phys. Rev.* **123**, 1865 (1961).

²² E. A. Guggenheim and M. L. McGlashan, *Proc. Roy. Soc. (London)* **A255**, 456 (1960).

TABLE II. Potential constants for the interaction of atoms with argon. Units (10^{-60} erg cm⁶).

	He-Ar	Ne-Ar	Ar-Ar	Kr-Ar	Xe-Ar
Slater-Kirkwood	11.0	24.8	74.8	102	143
London	7.8	14.6	50.9	72.5	109
Kirkwood-Müller	14.4	38.6	130	192	302
Viscosity	14.2	32.8	109	160	253
Mutual diffusion	13.3	31.5	...	164	240
Present experiment	25	60	180	201	377

critical study of the entire argon-argon potential, suggest that the previous empirical data fitting may shed little light upon the true magnitude of the dispersion energy. They choose a quantum mechanical prediction as the "best" value, because "it is not possible to determine (C) even approximately from experiment alone."

Table I contains a number of atomic properties which were used for the estimations of C given in Table II. The "experimental" C is obtained from the observed cross sections by using Eq. (1). It should be remembered that the measured cross sections may be slightly smaller than the true total scattering cross section because the angular resolution may be inadequate. In addition, uncertainty of the ion gage calibration may lead to a cross section error of about 5%. In the computation of an experimental C from the cross section, approximations in the derivation of Eq. (1), as well as measurement errors, may lead to uncertainties as great as 15 to 20%. The value of C for He-Ar may be further in error, because of greater experimental difficulty, as well as the influence of repulsive forces in the scattering of light gases.

Table III shows the experimental values of Q as well as cross sections predicted by Eq. (1) using the various estimates of C .

Our values for C and Q are higher than those predicted by any of the estimates for the dispersion energy. Similarly, high cross sections and potential constants have previously been observed for alkali beam scattering, when the results were compared to the Slater-Kirkwood relation.^{3,6,10} The ratios of cross sections for the various gas pairs are in better agreement with theory than are the absolute values. For example, the ratio $Q_{\text{Xe-Ar}}/Q_{\text{Ar-Ar}}$ are calculated to be 1.41, 1.48, 1.53, and 1.52, using the Slater Kirkwood, London and

TABLE III. Cross sections for the scattering of atoms by argon. Units (10^{-16} cm²).

	He-Ar	Ne-Ar	Ar-Ar	Kr-Ar	Xe-Ar
Slater-Kirkwood	109	196	329	396	465
London	94.8	158	282	345	416
Kirkwood-Müller	122	234	410	510	627
Viscosity	121	219	383	474	584
Mutual diffusion	118	215	...	480	572
Present experiment	150	278	468	520	685

Kirkwood-Müller equations, and the viscosity data, respectively. The experimental ratio is 1.46. Similar agreement of theoretical and experimental ratios, with disagreement in absolute values, has been previously found in alkali beam scattering.³ The origin of these discrepancies is not clear but suggests the possibility of systematic error either in experimental or theoretical methods.

APPENDIX

When an atomic beam is formed by effusion, the velocity distribution is different from that in a normal gas, because the probability that a gas particle will emerge from a slit is proportional to its velocity.²³ However, in the present experiment, the beam was detected by an inefficient electron bombardment ionizer. Thus the probability that an atom would be ionized was proportional to the time it spent in the detector, i.e., inversely proportional to its velocity. Therefore the fraction of ions obtained from atoms in the beam which had velocities between v_2 and v_2+dv_2 is the same as that in a normal gas, i.e., proportional to

$$v_2^2 \exp(-\beta_2^2 v_2^2) dv_2, \quad (a)$$

where $\beta_2 \equiv (m_2/2kT_2)^{1/2}$.

There is still a further factor to be introduced in the distribution of detected velocities in the beam because we used phase-sensitive detection. The output of the electronics gave a signal proportional to the input signal multiplied by the cosine of the phase angle between it and an arbitrary phase reference signal. Since an atom requires a time s/v_2 to travel the distance s from the beam chopper to the detector, it is seen that the altered distribution for particles detected by phase-sensitive amplification is

$$A v_2^2 \cos[\phi + (2\pi\nu s/v_2)] \exp(-\beta_2^2 v_2^2) dv_2, \quad (b)$$

where ϕ is an arbitrary phase angle which depends upon the setting of a phase shifter dial on the electronics, ν is the chopping frequency, and A is the normalizing factor. In practice, the phase-shifter dial was adjusted so that a maximum signal was obtained. This adjustment is equivalent to setting $\phi = \phi_{\text{max}}$ so that the integral J is a maximum, where

$$J \equiv A \int_0^\infty v_2^2 \cos[\phi + (2\pi\nu s/v_2)] \exp(-\beta_2^2 v_2^2) dv_2. \quad (c)$$

The integral may be rewritten

$$J = E \cos\phi - F \sin\phi,$$

where

$$E \equiv \int_0^\infty A v_2^2 \cos(2\pi\nu s/v_2) \exp(-\beta_2^2 v_2^2) dv_2,$$

²³ See, for example, N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956).

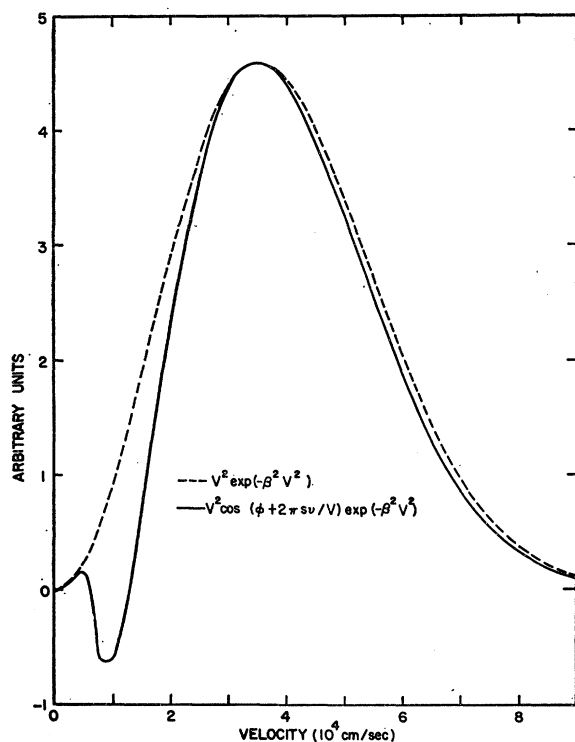


FIG. 3. Velocity distributions, before and after phase-sensitive detection.

and

$$F \equiv \int_0^\infty A v_2^2 \sin(2\pi \nu s / v_2) \exp(-\beta_2^2 v_2^2) dv_2.$$

To find the value of ϕ_{\max} we set $dJ/d\phi=0$, then $\tan\phi_{\max} = -(F/E)$. To obtain the normalizing factor A we replace ϕ by ϕ_{\max} in Eq. (c) and carry out the integration. This integration, as well as those required to evaluate E and F , were carried out by an IBM 7090 computer. Checks indicate that they are accurate to five significant figures. Figure 3 illustrates the argon velocity distribution given by expression (b), with $\phi = \phi_{\max}$. Distribution (a) is also shown for comparison. Some of the lower velocities make a negative contribu-

tion to the signal. This effect is more pronounced for xenon and krypton, but is almost non-existent for helium.

Now we follow the method of Rosin and Rabi² to obtain the cross section from the experimental data. Our only deviation from their approach is that we use the beam velocity distribution (b) rather than the distribution appropriate to their detector. This leads to the expression for the cross section

$$Q = -[\ln(I/I_0)f(z)]/nd,$$

where

$$f(z) \equiv \frac{A\pi^{\frac{1}{2}}}{\beta_1^{\frac{3}{2}}} \int_0^\infty \frac{x^4 \exp(-zx^2)}{\psi(x)} \cos\left(\phi_{\max} + \frac{2\pi\nu\beta_1 s}{x}\right) dx,$$

and

$$\psi(x) \equiv x \exp(-x^2) + (2x^2 + 1) \int_0^x \exp(-y^2) dy,$$

$$z \equiv (\beta_2/\beta_1)^2, \quad x \equiv v_2\beta_1, \quad \text{and} \quad \beta_1 \equiv (m_1/2kT_1)^{\frac{1}{2}},$$

where m_1 , m_2 are atomic masses of scattering gas (1) and beam (2), T_1 and T_2 are temperatures of gas and beam, v_2 is the beam atom speed, n is the scattering gas density, and d is the scattering path length. Integrations to obtain $f(z)$ were also performed on the computer, and are accurate to at least four significant figures. The experimental parameters were $s=50$ cm, $\nu=101.8$ cps, and $T_1=T_2=300^\circ\text{K}$. The calculated values of $F(z)$ for these parameters were 0.9384, 0.8050, 0.7124, 0.5948, and 0.5212, for the scattering of helium, neon, argon, krypton, and xenon beams, respectively.

The average relative velocity was calculated by using velocity distribution (a) for the beam. The result is given by standard kinetic theory texts²⁴ as

$$v_r = [(4/\pi\beta_1^2) + (4/\pi\beta_2^2)]^{\frac{1}{2}}.$$

Approximation (a) is adequate here, because the contribution of the beam velocity to v_r is large only for helium and neon. For these fast atoms the influence of the phase-sensitive detection upon the velocity distribution is small.

²⁴ See, for example, L. B. Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934).