This method has the great advantage of insensitivity to errors in two quantities directly entering the evaluation: mass-absorption coefficients and absorption jumps. All their values are clearly below the curve (3). The deviation of their carbon value from the value $\omega_K = 0.0035$ measured by us is greater than is to be expected from the given errors. We are not able to state a reason for this great discrepancy. We think, however, that our result is correct, and that we have given good reasons. It must be reserved for further work to bring greater clarity into this field.

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Determination of Rotational *g* Factors from Gas Transport Properties

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A procedure is given whereby for simple diatomic molecules the rotational *g* factor can be determined from transport measurements alone. The values so obtained agree to within 15% with those obtained from molecular-beam techniques. For N_2 and CO, the values of g_{rot} obtained are -0.285 and -0.301, respectively, to be compared with, respectively, -0.2593 and -0.2691 as obtained from molecular-beam magnetic resonance.

I. INTRODUCTION

That all polyatomic molecules possess a magnetic moment due to their rotational motion has been known since the classic work of Wick[1] and Ramsey.[2] As for electronic and nuclear magnetic moments, the rotational magnetic moment is characterized by a quantity called the rotational (Landé) *g* factor. The determination of this rotational *g* factor g_{rot} has lain in the realm of molecular-beam magnetic resonance since a molecular beam of essentially pure rotational states can be prepared. Until the last decade, it appeared that the determination of such a molecular parameter was restricted to molecular-beam measurements. With the advent of studies of the Senftleben-Beenakker (SB) effect,[3] a second possible experimental source of *g* values became available. The use of these effects was not, however, trivial insofar as the *g* factor occurred together with certain collision cross sections and, in order to extract the *g* value, independent determinations or estimates of the

cross sections must be available. Certain of the SB measurements have already proven very useful in this respect because, although the determination of the magnitude of g_{rot} is nontrivial, the determination of the sign of g_{rot} is quite trivial, being directly related to the direction of transverse heat or momentum transport in the presence of a magnetic field.[4] The situation is reversed in the case of molecular-beam measurements since then[5] the sign must be inferred by comparison with molecular hydrogen (for which the sign is known to be positive from theoretical work), from a second-order asymmetry of the experimental curves, or it must be obtained from separate experiments which employ a rotating field.

Recently, Scott, Smith, and Fry[6] have attempted to extract values of g_{rot} for molecular gases from measurements of the thermomagnetic torque, a rarefied-gas phenomenon closely linked[7] with the aforementioned SB effects. In employing the thermomagnetic-torque, shear-viscosity, or thermal-conductivity SB measurements, care must be taken to ensure that the kinetic collision cross section entering into the calculation is the correct one for the transport or relaxation process being considered. The procedure employed in Ref. 6 makes use of their thermomagnetic-torque results for a variety of molecular gases. The relationship used to extract the g_{rot} values from the experimentally obtained positions (on an H axis) of the torque maxima was obtained on the basis of the mean-free-path description[8,9] of these effects. However, the mean-free-path description is inadequate for more than a qualitative understanding of the field-dependent transport phenomena occurring in polyatomic gases: This has been conclusively demonstrated by Knaap and Beenakker.[10] One of the major difficulties arising from the mean-free-path picture is the introduction of the (basically) elastic-collision cross section which determines the ordinary (field-free) shear viscosity of the gas. The authors of Ref. 6 have been careful to point out that when the collision process is mainly an inelastic one, their description would break down and, in particular, they note that such a simple picture is clearly inadequate for the hydrogen isotopes.

A more refined description of the gas torque phenomenon, based on the Waldmann-Snider[11] kinetic equation shows that the thermomagnetic torque can be explained as a Burnett effect depending upon the presence of a second temperature gradient $\vec{\nabla}\vec{\nabla}T$ which is found in the cylindrical geometry of the torque experiment.[7] Since the largest part of the torque seems to be due to such a (bulk) Burnett contribution of the form given by the above-mentioned theory,[7,12] the thermomagnetic torque can be calculated once the various parameters entering into the SB effects have been determined from experiment. In particular, one of these parameters is characterized by the rotational g factor for the molecule divided by an *inelastic* collision cross section. Now, if the g factor is available from another source, such as a molecular-beam magnetic-resonance experiment, the inelastic-collision cross section can be determined from the measurement of the position on the H/p axis at which the shear-viscosity field effect attains half its saturation value. This is, in fact, the procedure employed by the Leiden workers for the extraction of this particular inelastic-collision cross section for molecular gases.[3,4] It has been shown[7] that the major contribution (of the order of 70%) to the Burnett torque comes from one of the two *transverse* shear-viscosity coefficients appearing in the field-dependent shear-viscosity scheme (the so-called double-frequency coefficient η_4 of the deGroot-Mazur[13] scheme) so that the position of the thermomagnetic-torque maximum on an H/p plot is largely determined by the shear-viscosity SB effect. Because of this, it will be seen that, *in principle*, it is not possible to obtain the magnitude of g_{rot} from measurement of the shear-viscosity field effect and of the thermomagnetic torque alone unless further information is fed in. Indeed, these two experimentally measurable effects do not, in fact, constitute independent measurements.

The authors of Ref. 6 found order-of-magnitude agreement between g_{rot} values obtained from *static-field* transport properties and those obtained from molecular-beam magnetic-resonance measurements. This agreement is due to two factors. In the first place, Smith and Scott[9] found it necessary to introduce a relatively *ad hoc* factor Q (taken in Ref. 6 to be 4π) of the order of 10, relating the molecular precession frequency due to the applied magnetic field to the collision frequency. In the second place, it happens that for many of the heavier diatomic and most polyatomic molecules, the inelastic-collision cross section entering into the more refined theory of the shear-viscosity field effect is of approximately the same order of magnitude as the elastic cross section determining the ordinary shear viscosity, e. g., for N_2 the relevant numbers are 22.5 vs 35 $\mathring{A}^2$, and for CF_4, 61 vs 63 $\mathring{A}^2$.[4] To some extent, the first factor can be considered to be an attempt (because of the limitations of the mean-free-path approach) to correct for the second factor. Interpreted in this perhaps crude fashion, the quantity Q can be given some physical justification. However, in this interpretation, Q will be only approximately constant since the ratio of the two cross sections is not fixed.

This paper is concerned with giving a more refined procedure to be employed in extracting g_{rot}

values from *static-field* SB measurements. The procedure developed here is mainly concerned with diatomic and linear molecules since it is for this class of molecules that the most work on collision theory has been carried out to date. In principle, similar procedures could be carried out for nonlinear polyatomic molecules and, considering that molecular collision theory is presently advancing rapidly, such work should be promising. As the present procedure involves a number of approximations which are difficult to overcome short of *ab initio* calculations, it seems highly unlikely that any procedure used to obtain g values from static SB measurements will ever have the accuracy to be found in the molecular-beam magnetic-resonance measurements. It is possible, however, to obtain agreement to within 15% of the g values found by other methods.

It should be mentioned that it is also possible to perform SB measurements with a combination of a static and an alternating magnetic field. Both cross[14] and collinear[9,15] static and alternating fields have been employed. Of these two possibilities, the collinear fields allow the simpler determination of rotational g values. The theoretical expressions for the "time-dependent" transport coefficients and torque involve infinite series of Bessel functions[16,17] and are hence quite complicated. However, in an experiment for which the alternating field frequency matches the static-field-induced molecular precession frequency, a resonance is observed, and it is possible thereby to determine the molecular precession frequency and hence the gyromagnetic ratio of the molecule concerned. This procedure promises to be almost as accurate as the molecular-beam magnetic-resonance method.

II. CALCULATION OF g_{rot} FROM SB DATA AND FIELD-FREE TRANSPORT COEFFICIENTS

The experimental quantities necessary for the determination of g_{rot} in the present paper are: λ_0 and η_0, the field-free thermal-conductivity and shear-viscosity coefficients, the ratio of the positions on the H/p axis (magnetic field strength and pressure) of the thermal-conductivity and shear-viscosity SB effects[3] $\Delta\lambda_\parallel/\lambda_0$ and $\Delta\eta_3/\eta_0$ and, finally, the position on the H/p axis and the saturation value for the shear-viscosity effect. With these data, together with certain approximate and exact relations among the various collision cross sections occurring in the theoretical expressions for these quantities, reasonable values of g_{rot} can be obtained.

Expressed in terms of collision cross sections defined recently,[18] the relevant transport coefficients are as follows. The field-free thermal conducitivity λ_0 is given by[19]

$$\lambda_0 = \frac{5}{2}\frac{k^2T}{m}\frac{1}{\Delta'}\left[\sigma\binom{1001}{1001} + 2r^{-1}\sigma\binom{1010}{1001} + r^{-2}\sigma\binom{1010}{1010}\right], \quad (1)$$

where k, T, and m have their usual meanings of Boltzmann's constant, temperature, and molecular mass, respectively; r^2 is the ratio $5k/2c_{int}$ with c_{int} being the heat capacity per molecule associated with internal states; the σ's are collision cross sections; and Δ' is given by

$$\Delta' = \langle v_{rel}\rangle_0\left[\sigma\binom{1010}{1010}\sigma\binom{1001}{1001} - \sigma^2\binom{1010}{1001}\right], \quad (2)$$

with $\langle v_{rel}\rangle_0$ being an average relative velocity

$$\langle v_{rel}\rangle_0 = (8kT/\pi\mu)^{1/2}, \quad (3)$$

μ being the reduced mass of the pair of colliding molecules. The field-free shear viscosity η_0 is given by

$$\eta_0 = kT[\langle v_{rel}\rangle_0\sigma\binom{2000}{2000}]^{-1}, \quad (4)$$

while the SB quantities required are given by[20]

$$\mu = \frac{(H/p)^{12}_{1/2,\lambda_\parallel}}{(H/p)^{02}_{1/2,\eta_3}} = \frac{\sigma_0\binom{1\,200}{1\,200}}{\sigma\binom{0\,200}{0\,200}}, \quad (5)$$

$$\left(\frac{H}{P}\right)^{02}_{1/2,\eta_3} = \frac{\hbar\langle v_{rel}\rangle_0\sigma\binom{0200}{0200}}{\mu_N kTg_{rot}}, \quad (6)$$

$$\left(\frac{\Delta\eta_3}{\eta_0}\right)^{02}_{sat} = \frac{-\sigma^2\binom{2000}{0200}}{\sigma\binom{2000}{2000}\sigma\binom{0200}{0200}} \quad (7)$$

($\hbar$ and μ_N have their standard meanings).

Upon first examination, it would appear that the task of obtaining values of g_{rot} is a quite formidable one since, in addition to g_{rot}, these five experimental quantities contain seven collision cross sections. The saving grace is provided by recent advances which have been made in collision theory for molecular gases.[21,22] In particular, for gases in which the anisotropic part of the intermolecular potential can be described by a simple P_2-type interaction,[21-23] there are a number of useful approximate relations[24] which can be employed. These relations make possible the calculation of g_{rot} from the quantities given above. The specific relations employed can be found in Table I. Using Table I, the following results are obtained:

$$\sigma\binom{1010}{1010} \simeq \frac{2}{3}\sigma\binom{2000}{2000} + \frac{5}{9}(\sqrt{30})\sigma\binom{2000}{0200}, \quad (8)$$

TABLE I. Relations between generalized cross sections (see Ref. 24).

$\sigma\binom{1010}{1200} = -\frac{1}{5}(\sqrt{5})\sigma\binom{2000}{0200}$	$\sigma\binom{1010}{1001} \simeq \frac{5}{3}\sqrt{3}\,\sigma\binom{2000}{0200}$
$\sigma\binom{1010}{1010} = \frac{2}{3}\sigma\binom{2000}{2000} + \frac{5}{6}\sigma\binom{0010}{0010}$	$\sigma_0\binom{1200}{1200} \simeq \sigma_0^{(0)}\binom{1200}{1200} + \frac{7}{6}\sigma\binom{0200}{0200}$
$\sigma\binom{0010}{0010} \simeq \frac{2}{3}(\sqrt{30})\,\sigma\binom{2000}{0200}$	$\sigma\binom{1001}{1001} \simeq \sigma_0^{(0)}\binom{1200}{1200} + \frac{7}{6}\sqrt{30}\,\sigma\binom{2000}{0200}$

TABLE II. Relevant data for N_2 and CO.

Gas	$10^4 \eta_0$ (P)	$\sigma\binom{2000}{2000}$ (Å^2)	$\left(\frac{H}{P}\right)^{02}_{1/2,\eta_3}$ (kOe/mm Hg)	$10^3\left(\frac{\Delta\eta_3}{\eta_0}\right)^{02}_{sat}$	$\left(\frac{H}{P}\right)^{12}_{1/2,\lambda_{\parallel}}$ (kOe/mm Hg)	$10^{-3}\lambda_0$ (cgs)
N_2	1.76	35[a]	3.5[b]	2.70[b]	7.0[c]	2.680[c]
CO	1.75	35[a]	4.2[d]	3.65[b]	7.7[c]	2.600[c]

[a]From the η_0 values listed in the *Handbook of Physics and Chemistry* (Chemical Rubber Publishing Co., Cleveland, 1964).
[b]H. Hulsman, E. J. van Waasdijk, A. L. J. Burgmans, H. F. P. Knaap, and J. J. M. Beenakker, Ref. 4.
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[d]Reference 6.

$$\sigma\binom{1010}{1001} \simeq \tfrac{5}{3}\sqrt{3}\,\sigma\binom{2000}{0200} , \tag{9}$$

$$\sigma\binom{1001}{1001} \simeq \sigma_0^{(0)}\binom{1200}{1200} + \tfrac{7}{6}(\sqrt{30})\sigma\binom{2000}{0200} , \tag{10}$$

$$\sigma_0^{(0)}\binom{1200}{1200} = (\mu - \tfrac{7}{6})\sigma\binom{0200}{0200} , \tag{11}$$

$$\sigma\binom{2000}{2000} = kT/(\eta_0\langle v_{rel}\rangle_0) , \tag{12}$$

$$\sigma\binom{2000}{0200} = [-(\Delta\eta_3/\eta_0)^{02}_{sat}\sigma\binom{2000}{2000}\sigma\binom{0200}{0200}]^{1/2} . \tag{13}$$

Substitution of the results given in Eqs. (8)–(13) into Eq. (1) leads to a cubic equation in $x = [\sigma\binom{0200}{0200}]^{1/2}$,

$$\alpha x^3 + \beta x^2 + \gamma x + \delta = 0 , \tag{14}$$

in which

$$\alpha = \tfrac{2}{9}(\sqrt{30})(\mu - \tfrac{7}{6})m\lambda_0\langle v_{rel}\rangle_0\xi/k^2 T , \tag{15}$$

$$\beta = \tfrac{2}{3}(\mu - \tfrac{7}{6})e - \tfrac{100}{9}e(\Delta\eta_3/\eta_0)^{02}_{sat} - (\mu - \tfrac{7}{6}) , \tag{16}$$

$$\gamma = \tfrac{7}{9}(\sqrt{30})[e - \tfrac{3}{2} - \tfrac{3}{7}(\sqrt{10})r^{-1} - \tfrac{5}{7}r^{-2}]\xi , \tag{17}$$

$$\delta = -\tfrac{2}{3}r^{-2}\sigma\binom{2000}{2000} , \tag{18}$$

with e the Eucken factor given by

$$e = \tfrac{2}{5}m\lambda_0/k\eta_0 \tag{19}$$

and ξ given by

$$\xi = [-(\Delta\eta_3/\eta_0)^{02}_{sat}\sigma\binom{2000}{2000}]^{1/2} . \tag{20}$$

As Takayanagi has shown,[23] the P_2-type potential can be considered to be probably the dominant part of the intermolecular potential for simple homonuclear diatomic molecules such as H_2, D_2, and N_2. For the moment it is not advisable to use this procedure for the hydrogen isotopes until it is certain whether or not the approximations inherent in the derivation of the relations of Table I are correct for these molecules. Since CO is only a very weakly polar gas it should also be reasonably well approximated by a P_2-type potential. For diatomic molecules, the value $(\tfrac{2}{5})^{1/2}$ can be used for r^{-1}. This, together with the data of Table II, when substituted into the expressions for the coefficients of Eq. (14), leads to the values tabulated

in Table III. The solutions of Eq. (14) for N_2 and CO then give $\sigma\binom{0200}{0200} = 22.5$ Å^2 and $\sigma\binom{0200}{0200} = 28.0$ Å^2, respectively. The value of g_{rot} can now be obtained from Eq. (6), expressible as

$$|g_{rot}| = 0.04515\sigma\binom{0200}{0200}/(H/p)^{02}_{1/2,\eta_3} , \tag{21}$$

where $\sigma\binom{0200}{0200}$ is expressed in Å^2 and $(H/p)^{02}_{1/2,\eta_3}$ is expressed in kOe/mm Hg. A comparison of the results obtained in this work with those given previously in the literature is also contained in Table IV.

III. DISCUSSION

As can be seen from examination of Table IV, it is possible to obtain values of g_{rot} to within 10–15% accuracy purely from the measurement of transport coefficients. The procedure outlined above requires a set of relations among the various collision cross sections which occur in the expressions for the transport coefficients. So far, it has been possible to obtain theoretically a set of such approximate relations for simple homonuclear diatomic molecules.[24] Before this procedure can be utilized for more complex molecules such as spherical or symmetric top molecules, a similar set of relations will be needed. In view of the reasonable success obtained for diatomic molecules, research in this direction promises to be fruitful. Of course, other procedures can be applied to the calculation of rotational g factors. In particular, for certain gases such as N_2, D_2, and other molecules carrying nuclear spins of magnitude 1, the dominant mechanism in nuclear spin relaxation in the gas phase is the quadrupolar relaxation. As is well known,[25] the quadrupolar term is related to the collision cross section

TABLE III. Values of the coefficients entering into Eq. (14).

Gas	e	μ	ξ	α (Å^{-1})	β	γ (Å)	δ (Å^2)
N_2	2.05	2.00	0.307	0.0458	0.374	-0.786	-9.33
CO	2.00	1.83	0.357	0.0411	0.302	-0.980	-9.33

TABLE IV. Cross section $\sigma\binom{0200}{0200}$ and g_{rot} values.

Gas	This work	$|g_{rot}|^a$ Mol. beam	Ref. 6	$\sigma\binom{0200}{0200}$ (Å^2)
N_2	0.285	0.2593^b	0.39	22.5
CO	0.301	0.2691^c	0.32	28.0

[a] Sign of g factor for both N_2 and CO is negative; see, e.g., Ref. 4.

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$\sigma\binom{0200}{0200}$ entering into the shear-viscosity SB effect. For such gases, therefore, it is possible to take the value of the cross section determined from NMR gas-phase measurements and make use of Eq. (6), thereby obtaining a value for g_{rot}. Moreover, the depolarized component of the scattered Rayleigh line contains a cross section closely related[26] to $\sigma\binom{0200}{0200}$. This means that in the near future, depolarized Rayleigh light-scattering measurements in gases can be utilized as a source for $\sigma\binom{0200}{0200}$ and, again in conjunction with SB effect measurements on the shear viscosity, values of g_{rot} can be calculated using Eq. (6). Depolarized Rayleigh light-scattering measurements do have one drawback in that it has been very difficult to remove the instrumental broadening from the experimental linewidths obtained. Modern techniques of computer folding and unfolding have now overcome this

problem. However, even early measurements[27] in which approximate procedures have been used for removal of instrumental broadening on such gases as H_2 seem promising: The cross section given by Cooper et al.[27] for (what must be assumed to be) n-H_2 is 0.77 Å^2 and this value, in conjunction with the reported $(H/p)_{1/2}$ value of 0.145 kOe/mm Hg found by Korving et al.[28] for n-H_2 gives a g_{rot} value of 0.67, which is only about 25% off from the accurately known value[5] of 0.88. One important point which must be stressed is that any expression which involves explicitly the rotational g value in a transport measurement need be associated with an inelastic collision cross section: Indeed, there is no way in which a purely elastic-collision cross section can arise in such a case.

In concluding, it may be fairly stated that, in principle, it is possible to obtain g_{rot} values purely from measurements of transport coefficients as long as both the field-free coefficients and their changes in an external magnetic field (SB effects) can be measured. However, there seems to be little likelihood that the method can compete in accuracy with the determination of g_{rot} from molecular-beam measurements. What is a useful aspect of the procedure outlined in the present work is its employment as a useful check on the internal consistency of all of the measurements made and on the theoretical relationships among collision cross sections which go into such a calculation.

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S and P States of the Helium Isoelectronic Sequence up to Z = 10

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Calculations have been made of the energy levels and other properties of the states $n\,^1S$, $n\,^3S$, $n\,^1P$, and $n\,^3P$, $n = 2$ to 5, for atoms belonging to the helium isoelectronic sequence up to $Z = 10$, and also for the higher excited S states of helium. The theoretical term values, including the contributions from the mass-polarization correction and the relativistic effects of order α^2 are listed. A detailed comparison with the experimentally determined energy differences between S and P states for He I up to F VIII shows a satisfactory agreement in almost every case, provided that we include an estimate of the Lamb-shift correction to the S-state energy level when considering transitions involving the $1\,^1S$, $2\,^1S$, or $2\,^3S$ states.

I. INTRODUCTION

In this paper, we shall present the results of a systematic calculation of the energy levels and other properties of the low-lying S and P states for two-electron atoms up to $Z = 10$. We have also calculated f values for transitions between these states, and the results will be presented in a forthcoming paper.[1]

On the experimental side, high-precision measurements of the energy difference between S and P levels in two-electron atoms were made as long as three decades ago.[2–4] Since that time, the accuracy of the experiments has been further improved, and many more lines have been measured.[5–12] Laser-produced plasmas have recently proved to be a fruitful source of heliumlike ions.[13–14] The advent of extraterrestrial spectroscopy has also led to quite a number of observations of two-electron spectra,[15–18] and the accuracy of measurements from this source will no doubt improve in the future. The observations on two-electron spectra now extend from the infrared to the x-ray region around 15 Å.

The method used in our calculations is basically the same as that employed for helium, the wavefunction being expanded in a triple series of La-guerre polynomials of the *perimetric* coordinates.[19–24] The expansion includes the interelectronic distance explicitly, and is thus particularly appropriate for the low-lying states, where the correlation effects are important. The effectiveness of the method decreases as the order of the excited state is increased. We have therefore carried out the calculation by this method for the 16 lowest excited states $n\,^3S$, $n\,^3S$, $n\,^1P$, and $n\,^3P$, $n = 2$, 3, 4, 5. In the case of He, we have carried our calculation up to the $15\,^1S$ and $17\,^3S$ states, which cover all of the observations.[25] However, the determination of the higher excited states by the present method necessitates the use of very large expansions (containing up to about 2000 terms), and these calculations were therefore not repeated for other atoms. The results presented here, and in a paper in preparation, represent therefore the maximum which we think could be achieved by the present method using the current generation of computers.

In Sec. II, we describe the method used in the calculations, and the numerical results obtained are listed in Tables III–XXII of Sec. III. In Sec. IV, we list our final theoretical term values and compare the results with experiment. Our comparison underlines the need for a calculation of the