Rotational Excitation and Momentum Transfer Cross Sections for Electrons in H₂ and N₂ from Transport Coefficients*

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Rotational excitation and momentum transfer cross sections for low-energy electrons in hydrogen and nitrogen are obtained from a comparison of theoretical and experimental values for the mobility and the diffusion coefficient. The theoretical values of the transport coefficients were obtained by calculating accurate electron energy distribution functions using an assumed set of elastic and inelastic cross sections. The discrete nature of the energy loss occurring in a rotational or vibrational excitation collision was included in the theory, as were collisions of the second kind with thermally excited molecules. The resulting values of drift velocity and characteristic energy D/μ were compared with experimental data and adjustments made in the assumed cross sections until good agreement was obtained. The momentum transfer cross sections found in this manner agree well with several recent analyses valid in restricted energy ranges. The final values of the rotational excitation cross sections are about twice the values computed using the theory of Gerjuoy and Stein and the latest available value for the molecular electric quadrupole moments. In hydrogen, the analysis has been extended to energies for which vibrational excitation is important. A vibrational cross section with a maximum of roughly 5×10^{-17} cm² at 3 eV is consistent with the measurements.

I. INTRODUCTION

FOR many years it has been realized that the energy lost by low-energy electrons in collisions with molecular gases is much greater than that expected from the recoil of the molecule in an elastic collision. The primary source of experimental data has been the measurements of the electron mobility μ and of the characteristic energy D/μ, where D is the electron diffusion coefficient. The available data have been summarized by Healy and Reed,[1] Massey and Burhop,[2] Loeb,[3] and Craggs and Massey.[4] These authors also summarize the efforts which have been made to analyze these experiments in terms of the cross sections for elastic and inelastic scattering of the electrons. Because of the complexities of accurate solutions of the Boltzmann equation applicable to these problems and a lack of knowledge as to the energy loss processes, it has been customary to assume that the distribution of electron energies in the experimental drift tube is either Maxwellian or Druyvesteyn[3] and that the elastic scattering cross section and the product of the energy loss and the rotational and vibrational cross sections are either independent of energy[1–5] or vary slowly with the energy.[6,7]

The assumption of slowly varying rotational and vibrational cross sections seemed reasonable for homonuclear molecules such as H₂ and N₂ on the basis of classical and some quantum mechanical calculations.[8] Huxley[9] has used the room temperature data to evaluate a classically derived formula with adjustable coefficients for a rotational excitation cross section which increases linearly with electron energy near threshold. However, Gerjuoy and Stein[10] had pointed out that these molecules possess an electric quadrupole moment and have calculated a cross section for rotational excitation which increases very rapidly close to threshold and for which the magnitude can be calculated from measured electric quadrupole moments. Attempts by Gerjuoy and Stein to compare their results with experiment, using the usual simplified treatments of the experimental data, indicated only approximate agreement with experiment. We, therefore, have compared theory and experiment using a considerably more exact analysis than that used for this problem to date.[11] In the present work we have solved the appropriate Boltzmann equation for dc electric fields including the effects of energy dependent cross sections and the important discrete energy loss processes for electrons with average energies below about 2 eV. The role of inelastic collisions in the energy range above about

[1] R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless Limited, Sydney, 1941).

[2] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), Chap. I and p. 278.

[3] L. B. Loeb *Basic Processes in Gaseous Electronics* (University of California Press, Berkeley, California, 1955), Chaps. III and IV.

[4] J. D. Craggs and H. S. W. Massey, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, pp. 344–357.

[5] L. G. Huxley and A. A. Zaazou, Proc. Roy. Soc. (London) A196, 402 (1949).

[6] T. Kihara, Revs. Modern Phys. 24, 45 (1952); J. C. Bowe, Phys. Rev. 117, 1416 (1960); and M. A. Uman and G. Warfield, *ibid.* 120, 1542 (1960).

[7] G. Bekefi and S. C. Brown, Phys. Rev. 112, 159 (1958).

[8] P. M. Morse, Phys. Rev. 90, 51 (1953) and T. R. Carson, Proc. Phys. Soc. (London) A67, 908 (1954).

[9] L. G. H. Huxley, Australian J. Phys. 9, 44 (1956) and J. Atmospheric and Terrest. Phys. 16, 46 (1959). In the case of H₂, the fit of this theory to the room temperature data yields a threshold of at least 0.12 eV. This value is much too high to explain the 77°K data presented in our Figs. 1 and 3.

[10] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955); 98, 1848 (1955). See also H. S. W. Massey, Phil. Mag. 4, 336 (1959). Apparently, the importance of rotational excitation was first recognized by W. H. Bennett and L. H. Thomas, Phys. Rev. 62, 41 (1942).

[11] For a partial report of this work see L. S. Frost and A. V. Phelps, *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 192.

0.5 eV has been considered most recently by Heylen and Lewis.[12] A comparison of our method of analysis with some features of previous methods is given in Appendix I. We have not attempted to apply our technique to the related problem in which the dc field is replaced by a high-frequency ac electric field[7] or is accompanied by a strong magnetic field.

Since the measured electron mobility and ratio of the diffusion coefficient to the mobility are averages over a broad range of electron energies the best we can hope for in our analysis is to find a set of energy-dependent momentum transfer and inelastic cross-section curves which are consistent with the measurements. Our procedure for determining a consistent set of cross sections is to (a) assume elastic and inelastic cross sections based on previous experiment and theory, (b) use a digital computer to solve the appropriate Boltzmann transport equation and evaluate the mobility and diffusion coefficients for the assumed input cross sections and a range of experimental parameters, (c) compare appropriate combinations of the computed values of D and μ with the experimental values over a wide range of the experimental parameters, and (d) readjust the input cross sections so as to obtain good fit between the theoretical and experimental combinations of D and μ. If our procedure has been successful, we shall then have good agreement between the computed and measured values of μ and of D/μ as a function of the experimental parameters. Since it is the basis of all of our analysis, we shall discuss the Boltzmann transport equation appropriate to this problem in Sec. II. In Sec. III, we shall apply our procedure first to the determination of a set of elastic and inelastic cross sections for hydrogen using experimental data obtained at 300°K. These will then be used to predict values of μ and D/μ at 77°K. Finally, the procedure is applied to the determination of elastic and rotational excitation cross sections in nitrogen.

II. SOLUTION OF BOLTZMANN TRANSPORT EQUATION

Consider a swarm of electrons drifting through a gas at temperature T under the influence of a uniform dc electric field E, in V/cm. Let N be the number of gas molecules per cc, $Q_m(u)$ be the momentum transfer cross section for electron-molecule collisions as a function of electron energy u, and $Q_j(u)$ be a rotational, vibrational, or electronic excitation cross section with an energy loss of u_j. The steady-state distribution function $f(u)$ is then given by the solution of the Boltzmann equation. Upon extending the results of Holstein[13] and Margenau[14] to include collisions of the second kind, the Boltzmann equation is

$$\frac{E^2}{3}\frac{d}{du}\left(\frac{u}{NQ_m}\frac{df}{du}\right)+\frac{2m}{M}\frac{d}{du}(u^2NQ_mf)+\frac{2mkT}{Me}\frac{d}{du}\left(u^2NQ_m\frac{df}{du}\right)+\sum_j (u+u_j)f(u+u_j)NQ_j(u+u_j)-uf(u)N_j\sum_j Q_j(u)$$

$$+\sum_j (u-u_j)f(u-u_j)NQ_{-j}(u-u_j)-uf(u)N\sum_j Q_{-j}(u)=0. \quad (1)$$

Here e and m are the electronic charge and mass, M is the molecular mass, k is the Boltzmann constant, and u is the electron energy in electron volts. Thus $u=mv^2/2e$, where v is the electron speed. The last two terms express the effect of collisions of the second kind, in which thermally excited molecules impart excitation energy to the electron. $Q_{-j}(u)$ is defined as the cross section for a collision in which the electron gains the energy u_j. Both $Q_j(u)$ and $Q_{-j}(u)$ include the fractional population and statistical weight factors of the initial molecular state, so that multiplication by the total molecule density N gives the reciprocal of the mean free path for the process. In Eq. (1) we have assumed that the gas density is high enough so that terms due to electron density gradients[15] may be neglected.

For computational purposes it is convenient to use normalized variables. Therefore, we make the substitutions

$$z=\frac{eu}{kT}, \quad \theta=\frac{Q_m(u)}{Q_0}, \quad \alpha=\frac{M}{6m}\left(\frac{eE}{NQ_0kT}\right)^2, \quad \eta_{\pm j}=\frac{MQ_{\pm j}}{2mQ_0}, \quad (2)$$

where Q_0 is the value of Q_m at some reference energy. Using the Klein-Rosseland[16] relation, i.e., detailed balancing between collisions of the first and second kind, we have

$$(z-z_j)\eta_{-j}(z-z_j)=\exp(-z_j)z\eta_j(z) \quad \text{for} \quad z\geq z_j.$$

Employing the Boltzmann relation for relative population of various excited states, we obtain the following

[12] A. E. D. Heylen and T. J. Lewis, *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), Vol. I, p. 156; and T. J. Lewis, Proc. Roy. Soc. (London) **A244**, 166 (1958). See also reference 34.

[15] W. P. Allis and H. W. Allen, Phys. Rev. **52**, 703 (1937).

[13] T. Holstein, Phys. Rev. **70**, 367 (1946). Except for the third and the last two terms, Eq. (1) is the same as Holstein's Eq. (54'). The third term is the same as the last term of Eq. (11) of reference 14. The last two terms of Eq. (1) are obtained from the fourth and fifth terms by noting that in collisions of the second kind electrons gain rather than lose an energy equal to u_j.

[14] H. Margenau, Phys. Rev. **69**, 508 (1946). See also reference 18 and S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1953).

[16] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1934), p. 57.

difference-differential equation:[17]

$$\left(\frac{\alpha}{\theta}+z\theta\right)z\frac{df}{dz}+z^2\theta f$$

$$+\sum_j \int_z^{z+z_j} z\eta_j(z)[f(z)-\exp(-z_j)f(z-z_j)]dz=0. \quad (3)$$

Before discussing the techniques for solving Eq. (3), it is convenient to discuss the experimentally determined quantities. We have chosen to consider only the most commonly measured transport coefficients: (a) the diffusion coefficient D; (b) the parallel mobility $\mu_{||}$, which is the dc mobility parallel to the electric and magnetic fields; and (c) the perpendicular mobility $\mu_\perp$, which is the mobility perpendicular to both the mutually orthogonal electric and magnetic fields. We shall limit our discussion to the low-magnetic-field limit of these coefficients. For convenience we shall omit the subscript from $\mu_{||}$ and, unless otherwise noted, use the term mobility to mean the parallel mobility. The relations used to calculate these coefficients are[18]

$$D=\frac{2(kT/m)^{1/2}}{3NQ_0}\int_0^\infty \frac{z}{\theta}f(z)dz, \quad (4)$$

$$\mu=\frac{e(2/kTm)^{1/2}}{3NQ_0}\int_0^\infty f(z)\frac{d}{dz}\left(\frac{z}{\theta}\right)dz$$

$$=-\frac{e(2/kTm)^{1/2}}{3NQ_0}\int_0^\infty \frac{z}{\theta}\frac{df}{dz}dz, \quad (5)$$

$$\mu_\perp=\frac{e^2B}{3mQ_0^2N^2kT}\int_0^\infty f\frac{d}{dz}\left(\frac{z^{1/2}}{\theta^2}\right)dz$$

$$=-\frac{e^2B}{3mQ_0^2N^2kT}\int_0^\infty \frac{z^{1/2}}{\theta^2}\frac{df}{dz}dz, \quad (6)$$

where

$$\int_0^\infty z^{1/2}f(z)dz=1.$$

The quantities customarily determined by experiment are μ, D/μ, and $\mu_\perp/\mu_T$. Here μ_T is the mobility in a direction parallel to the electric field when the electric and magnetic fields are perpendicular to each other. In the limit of low magnetic fields considered here $\mu_T=\mu$. The mobility μ is usually obtained from the time of flight of electrons between two electrodes of a drift tube,[3,19–21] i.e., the mobility equals the drift

velocity w divided by the electric field E. The quantity D/μ is usually determined using the Townsend method[1–5] in which one measures the ratio of the diffusive motion at right angles to the electric field to the motion in the electric field direction. D/μ has the dimensions of energy as can be seen from Eqs. (4) and (5) and in the case of a Maxwellian energy distribution is equal to the quantity kT_e/e, where T_e is the electron temperature. Thus, D/μ is an experimentally significant measure of the average energy of the electrons and we will call it the "characteristic energy." The quantity $\mu_\perp/\mu$ is equal to the tangent of the angle of deflection of a stream of electrons drifting along an electric field when a weak magnetic field is applied at right angles to the electric field.[1–5,22] As can be seen from Eqs. (5) and (6) the quantity $\mu_\perp(\mu B)^{-1}$ has the dimensions of a mobility and, for θ proportional to $z^{-1/2}$, is equal to μ. In general, this is not the case and the departure of $\mu_\perp(\mu^2B)^{-1}$, the "magnetic deflection coefficient," from unity is a measure of the departure of the product of the momentum transfer cross section and the electron speed, i.e., the collision frequency per molecule, from a constant independent of electron energy.[15] An additional transport coefficient of interest is the diffusion coefficient across a magnetic field.[1,3] Because of the scarcity of experimental data, we have not evaluated this quantity.

Because of the wide range of u_j values required to describe inelastic collisions in a molecular gas and the mathematical complexity of Eq. (3), we have been unable to solve it exactly for the whole range of electron energies as characterized by D/μ. Therefore, we will discuss the solutions used in various ranges of D/μ and u_j.

(a) Exact solution in thermal region: $D/\mu<10kT/e$ and $u_j<10kT/e$.

At sufficiently low electric fields the electron energies approach thermal $(D/\mu \to kT/e)$ and it is essential to take into account the energy gained by the electrons in collisions with the gas molecules. This means that in those gases for which $u_j<10kT/e$ and for $D/\mu<10kT/e$ we must solve Eq. (3) exactly instead of neglecting the second term inside the integral as is possible at higher fields and D/μ.[13,18,23] The procedure which we use has been developed for us by Boyer and Sherman[17] and is summarized in Appendix II. In

[17] B. Sherman, J. Math. Analysis and Application 1, 342 (1960) and R. Boyer and B. Sherman (private communication).

[18] W. P. Allis, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21.

[19] H. B. Wahlin, Phys. Rev. 27, 588 (1926); 23, 169 (1924).

[20] N. E. Bradbury and R. A. Nielsen, Phys. Rev. 49, 388 (1936); and R. A. Nielsen, *ibid.* 50, 950 (1936).

[21] The various measurements in lower E/p range have been

compared by J. L. Pack and A. V. Phelps, Phys. Rev. 121, 798 (1961). Note that the Q_m values for N₂ as determined from the microwave measurement are plotted incorrectly in Fig. 13 of this reference. They should be lowered by 10% and so are in much better agreement with the dc results than would appear in the figure. Footnote 19 of this reference should be corrected to indicate discrepancies of 5% and 50% rather than 15% and 40%. The same error appears in Fig. 1 of J. L. Pack and A. V. Phelps, Phys. Rev. Letters 3, 340 (1959).

[22] J. S. Townsend and V. A. Bailey, Phil. Mag. 42, 873 (1921).

[23] See for example, M. J. Druyvesteyn and F. M. Penning, Revs. Modern Phys. 12, 87 (1940); J. A. Smit, Physica 3, 543 (1936); I. Abdelnabi and H. S. W. Massey, Proc. Phys. Soc. (London) A66, 288 (1953); and reference 13.

general, it involves integrating Eq. (3), approximating the result as a system of linear equations, and solving the resulting system to obtain the distribution function $f(z)$.

The range of D/μ over which this procedure is useful can be estimated as follows. In order to obtain a good approximation to the excitation cross sections near the threshold it is necessary to limit the energy difference between grid points to something less than the u_j for the lowest state, i.e., less than u_1. Because of the limited memory capacity of the computer, the maximum energy range that can be handled with our IBM 7090 Computer program is less than about 160 u_1. A rough estimate of the maximum value of D/μ for which the solutions are expected to be accurate is $D/\mu < 160u_1/10$ or about $20u_1$. In the case of hydrogen $u_1 = 0.045$ eV, so that the exact method of solution could be used for D/μ values up to about 0.9 eV. However, the calculations described in Sec IIIA show that, for D/μ values greater than 0.15 eV in H_2 and temperatures of 300°K or below, the effects of rotational excitation in H_2 are independent of the temperature used in the calculation. This means that for $D/\mu > 0.15$ eV we can use the populations of rotational states characteristic of 77°K where the densities of excited states are low enough so that collisions of the second kind can be neglected. The approximation used in solving the Boltzmann equation when collisions of the second kind are negligible is discussed in (b) below.

Unfortunately, u_1 for the rotational excitation of nitrogen is 1.5×10^{-3} eV so that even for data obtained at 77°K the limiting value of D/μ for the exact solution is only about three times kT/e. A similar situation exists for nearly all gases of interest except H_2 and D_2. Two attempts to get around this difficulty have been successful in limited ranges of D/μ. First, the true Q_j have been replaced by an approximately equivalent set having values of u_j larger than the true values. Secondly, the terms of Eq. (1) due to discrete rotational energy losses have been approximated by the continuous function of energy derived in (c) below.

(b) Solution neglecting collisions of the second kind.

The equation to be solved in this case is

$$\left[\left(\frac{\alpha}{\theta}\right) + z\theta\right]z\frac{df}{dz} + z^2\theta f + \sum_j \int_z^{z+z_j} z\eta_j(z)f(z)dz = 0. \quad (7)$$

The mathematics of this equation have been discussed in detail by Sherman[17] and the procedure used for its solution is summarized in Appendix II. This approximation is valid when the density of excited molecular states is low enough so that the energy gain due to collisions of the second kind is negligible compared to the energy loss. In our calculations this occurs when the electron energy is high enough so that rotational excitation and de-excitation are negligible compared

to vibrational or electronic excitation or in the very special case of H_2 and D_2 at low temperatures, e.g., 77°K.

(c) Solution approximating rotational excitation as a continuous function: $D/\mu \gg kT/e$.

Here, the object is to approximate the effect of a large number of rotational levels in the Boltzmann equation by a continuous function of the electron energy. This is accomplished by approximating the difference terms of Eq. (1) by differentials. If we let the sum of the difference terms for the rotational states of Eq. (1) be Z and use the results of Gerjuoy and Stein[10] for the cross sections and selection rules, we have

$$\frac{Z}{N} = \sum_J \frac{p_J}{P_r} \exp\left(-\frac{eE_J}{kT}\right)$$

$$\times [(u+u_J)f(u+u_J)\sigma_{J,J+2}(u+u_J)$$

$$-uf(u)\sigma_{J,J+2}(u) + (u-u_J)f(u-u_J)\sigma_{J,J-2}$$

$$\times (u-u_J) - uf(u)\sigma_{J,J-2}(u)]. \quad (8)$$

Here the factor $(p_J/P_r)\exp(-eE_J/kT)$ is the fraction of the molecules in the Jth rotational level, where $p_J = (2t+1)(t+a)(2J+1)$, where t is the nuclear spin,[24] J is the rotational quantum number, and $P_r = \sum_J p_J \times \exp(-eE_J/kT)$. Note that $\sigma_{J,J+2}(u)$ is zero for $u < u_J$ and $\sigma_{J,J-2} \equiv 0$ for $J=0$ and 1. For hydrogen, $t=1/2$, $a=0$ for even J (parahydrogen) and $a=1$ for odd J (orthohydrogen).[24] For nitrogen, $t=1$, $a=0$ for odd J and $a=1$ for even J. The energy levels of the rotating molecule E_J are given to sufficient accuracy for our purposes by $E_J = J(J+1)B_0$, where B_0 is the rotational constant determined from spectroscopic data.[25] Using the selection rule $\Delta J = \pm 2$, the energy given up by an electron in excitation is $u_J = (4J+6)B_0$ while that gained in de-excitation is $u_{-J} = (4J-2)B_0$. According to Gerjuoy and Stein[10]

$$\sigma_{J,J+2}(u) = \frac{(J+2)(J+1)}{(2J+3)(2J+1)}\sigma_0\left[1 - \frac{(4J+6)B_0}{u}\right]^{1/2},$$

and

$$\sigma_{J,J-2}(u) = \frac{J(J-1)}{(2J-1)(2J+1)}\sigma_0\left[1 + \frac{(4J-2)B_0}{u}\right]^{1/2}, \quad (9)$$

where $\sigma_0 = 8\pi q^2 a_0^2/15$, q is the electric quadrupole moment, and a_0 is the Bohr radius. In our notation $Q_{J,J+2} = (p_J\sigma_{J,J+2}/P_r)\exp(-eE_J/kT)$, etc.

We now consider the conditions for which the energy losses in rotational excitation are small enough to allow us to expand $f(u+u_J)$ and $f(u-u_J)$ in Taylor series expansions. Because of the exponential popula-

[24] A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen* (Cambridge University Press, New York, 1935), pp. 110 and 158.
[25] G. Herzberg, *Spectra of Diatomic Molecules* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 532 and 553.

tion factor in Eq. (8) and the weak dependence of the cross sections in Eq. (9) on J, we need consider only levels for which $J < (5kT/eB_0)^{1/2}$ provided that $kT/eB_0 \gg 1$ as in nitrogen where $B_0 = 2.5 \times 10^{-4}$ eV. For the rotational levels with $J \leq (5kT/eB_0)^{1/2}$, the energy lost or gained is $u_J \leq 4(5kTB_0/e)^{1/2}$ so that our condition

of $u \sim D/\mu \gg kT/e$ means that $u/u_J \gg (kT/80eB_0)^{1/2}$ or $u/u_J \gg 1$ for temperatures of interest. This condition allows us to expand $f(u \pm u_{\pm J})$ in a Taylor's series. In addition the cross sections given by Eq. (9) become independent of u over the important range of energy. With these simplifications Eq. (8) becomes[26]

$$Z = \frac{N}{P_r} \sum_J p_J \exp\left(-\frac{eE_J}{kT}\right)[u_J\sigma_{J,J+2} - u_{-J}\sigma_{J,J-2}]\frac{d[uf(u)]}{du}$$

$$= \frac{4B_0\sigma_0 N}{P_r}\frac{d}{du}[uf(u)]\sum_J p_J \exp\left(-\frac{eE_J}{kT}\right) = 4B_0\sigma_0 N\frac{d}{du}[uf(u)]. \quad (10)$$

Here we have neglected terms in $u_{\pm J}^2$ or higher. If D/μ is low enough compared to the threshold for vibrational excitation or if the cross section for vibrational excitation near threshold is small enough, as is the case for nitrogen,[27] then the Boltzmann equation becomes

$$\frac{d}{du}\left(\frac{eu}{\theta}\frac{df}{du}\right) + \frac{d}{du}(u\theta + B_0\eta_r)uf = 0. \quad (11)$$

This result is essentially equivalent to that obtained by Gerjuoy and Stein.[10] Repeated integration of Eq. (11) gives

$$f(u) = A\exp\left[-\int_0^u \frac{\theta(u\theta + B_0\eta_r)du}{\epsilon}\right], \quad (12)$$

where A is a normalization constant, $\eta_r = 2M\sigma_0/mQ_0$, and $\epsilon = ME^2/6mN^2Q_0^2$. If D/μ is large enough so that vibrational or electronic excitation is important we can add the appropriate inelastic collision terms from Eq. (1) and solve for f using the same basic technique as for Eq. (7).

III. DETERMINATION OF CROSS SECTIONS

The determination of elastic and inelastic cross sections by comparing experimental and theoretical transport coefficients is considerably simplified by the introduction of two new combinations of transport coefficients which effectively separate the effects of momentum transfer collisions and inelastic collisions. The first of these is the effective frequency for momentum transfer or "elastic" collisions which is defined by the relation

$$\nu_m/N = e/m\mu N = (e/m)(1/w)E/N. \quad (13)$$

It will be noted from Eq. (5) that if the true frequency of momentum transfer collisions, i.e., the product of NQ_m and the electron speed, is independent of electron energy the collision frequency is given exactly by Eq. (13). Since in a real gas the true momentum transfer collision frequency is a function of the electron energy, it is convenient to plot our experimental and theoretical

values of ν_m/N as a function of an experimental quantity which measures the electron energy, i.e., D/μ.

A combination of transport coefficients characteristic of inelastic collisions can be deduced by writing the power balance for an average electron. Thus, the power input per electron due to the electric field, weE, is equal to the frequency of energy exchange collisions ν_u times the excess of the electron energy over its thermal equilibrium value. If we take D/μ as our measure of the electron energy, then

$$\frac{\nu_u}{N} = \frac{wE/N}{D/\mu - kT/e}. \quad (14)$$

Here again, it is convenient to plot energy exchange collision frequency as a function of the characteristic energy, D/μ, since ν_u/N is principally a measure of the frequency of inelastic collisions $\nu Q_j(u)$ times the fractional energy exchanged per inelastic collision.[28]

We are now ready to consider the determination of elastic and inelastic cross sections for H₂ and N₂.

A. Hydrogen

Figure 1 shows the measured values of drift velocity $w = \mu E$ and of D/μ on which we base our analysis of hydrogen. The points show the experimental data of various authors[20–22,29–30] while the smooth curves show

[27] G. J. Schulz, Phys. Rev. 125, 229 (1962).

[26] In a previous report of this work[11] the numerical coefficient in the final expression for Eq. (10) was erroneously given as 6 instead of 4. Also, in the earlier report terms in $u_{\pm J}^2$ were retained. The arguments presented in the above text show that the approximations made are valid only for $D/\mu \gg kT/e$ so that thermalization effects can be neglected.

[28] We believe that the energy exchange parameter defined by Eq. (14) offers several advantages over the energy loss per collision parameter used in previous analyses of swarm experiments. See references 1 to 12. First, its definition in terms of experimental and theoretical transport coefficients is independent of assumptions regarding the energy dependence of the distribution function. Secondly, the energy loss per collision parameter customarily used does not separate the elastic and inelastic effects but instead gives their ratio. The ratio of elastic and inelastic cross sections is seldom evaluated theoretically and generally has little significance in terms of atomic structure.

[29] R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) A215, 467 (1952). Recently, these data have been re-analyzed and the Q_m values obtained are in much better agreement with our
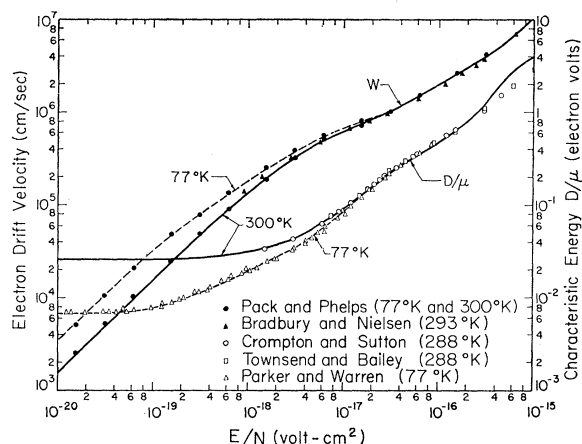
FIG. 1. Drift velocity and D/μ as a function of E/N for H_2 at 77°K and room temperature. The points are experimental data and the curves are the result of our theoretical calculations. The D/μ vs E/N data at 77°K were measured after the completion of the theoretical calculations.

the results of substituting the final set of assumed cross sections into the theoretical expressions discussed in Sec. II. Since at the time of our calculations D/μ data were available only at or near 300°K, the procedure was to choose our input cross sections to give a good fit to the 290 to 300°K data and then to predict values of w and D/μ at 77°K for comparison with experiment. A detailed discussion of the comparison is postponed until after the procedure is outlined and the significant processes are discussed.

The actual procedure which is used to arrive at the cross sections is to use the available data to construct a trial set of elastic and inelastic cross sections. Thus, the first momentum transfer cross-section estimate is a smooth curve through the data of Pack and Phelps,[21] Bekefi and Brown,[7] and Brode[31] and was similar to the final curve shown in Fig. 2. The first estimates of the rotational excitation cross sections were the cross sections predicted by Gerjuoy and Stein[10] and given by Eqs. (9) using an electric quadrupole moment of $0.393ea_0^2$, from measurements by Harrick and Ramsey.[32] Here a_0 is the Bohr radius. The first and final estimate of the vibrational excitation cross sections neglects excitation to states above the first and assumes that the cross section increased linearly with energy near the threshold and then passes through the values given by Ramien.[33] The assumed electronic excitation cross section has a threshold at 8.8 eV and is based on the data of Ramien.[33]

The assumed cross sections are used to compute $f(u)$, using the theory outlined in Sec. II(a) at low D/μ and in Sec. II(b) at high D/μ. The calculated electron energy distributions for the range of D/μ values covered in our calculations are intermediate between Maxwellian and Druyvesteyn, over the important range of u, i.e., $f(u)$ lies between

$$A \exp[-\mu(D/\mu)^{-1}] \quad \text{and} \quad B \exp[-u^2\pi^{-1}(D/\mu)^{-2}].$$

These results are then used to calculate μ, μ_1, D, ν_m/N, and ν_u/N for comparison with the experimental values. The comparison of measured and theoretical ν_m/N and ν_u/N values is shown in Fig. 3 where the solid and dashed curves are averages obtained from the experimental data of Fig. 1 for 300 and 77°K, respectively. The points are the results of our theoretical calculation using the final set of assumed cross sections. As will be shown below discrepancies between the computed and experimental values of ν_m/N are due primarily to errors in the assumed momentum transfer cross section and are minimized by appropriate trial and error adjustment of the elastic cross section. The final momentum transfer cross-section curve is in good agreement with the previous experimental data shown in Fig. 2 over the energy range analyzed, i.e., approximately 0.003 to 2 eV. Our cross section is also within 15% of that obtained by Heylen[34] in the energy range
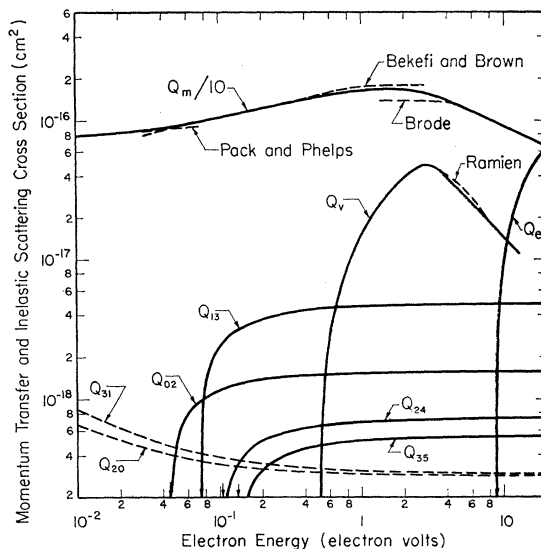

FIG. 2. Final assumed cross sections for H_2 as a function of electron energy. Q_m is the momentum transfer cross section. Q_{02}, Q_{13}, Q_{24}, Q_{35}, Q_{20}, and Q_{31} are the cross sections for electron collision induced transitions between the rotational states indicated by the subscripts times the fraction of the molecules in the initial state (first subscript) at 300°K. At 77°K only the Q_{02} and Q_{13} cross sections are important. The relative magnitudes and energy dependences are as given by Gerjuoy and Stein. Q_v and Q_e are the assumed cross sections for the excitation of the first vibrational state and the electronic states. As discussed in the text, Q_v is only a first approximation to the correct curve.

results. See I. P. Shkarofsky, T. W. Johnston, and M. P. Bachynski, Planetary and Space Science 6, 24 (1961).

[30] J. H. Parker and R. W. Warren, Bull. Am. Phys. Soc. 6, 387 (1961); and (private communication).

[31] The high-energy portion of our Q_m curves in Figs. 2 and 6 are taken to be equal to the total scattering cross section curves given in the review article by R. B. Brode, Revs. Modern Phys. 5, 257 (1933).

[32] N. J. Harrick and N. F. Ramsey, Phys. Rev. 88, 228 (1952).

[33] H. Ramien, Z. Physik 70, 353 (1931).

[34] A. E. D. Heylen, Proc. Phys. Soc. (London) 76, 779 (1960); 79, 284 (1962). We do not expect to agree with Heylen for energies

from 0.05 to 3 eV and is about 50% higher than the theoretical curve calculated by Massey and Ridley.[35]

Similarly, discrepancies between the computed and experimental values of ν_u/N are minimized by adjusting the assumed inelastic cross sections to give the fit shown in Fig. 3. Experience shows that errors in ν_u/N for D/μ values below about 0.15 eV are due to incorrect rotational excitation cross sections which we adjust by changing the assumed effective electric quadrupole moment keeping the relative magnitudes of the cross section for various states and their energy dependences fixed. By adjustment of the effective quadrupole moment to $(2.5)^{1/2}$ times the value from data by Harrick and Ramsey[32] we obtain the fit indicated in Fig. 3 for D/μ less than about 0.1 eV. Dalgarno and Moffett[36] state that the effective quadrupole moment should be increased by about 20% because of the vibrational motion of the molecule. In view of the large unexplained discrepancy remaining one may question the applicability of the theoretical energy dependence and the relative cross sections for various transitions. However, the assumed energy dependence and relative cross sections fit the experimental data to within the experimental accuracy for energies below about 0.15 eV. In addition, as predicted by Gerjuoy and Stein,[10] there is no evidence for an appreciable cross section for the $J=0$ to $J=1$ rotational excitation processes near its threshold.

Discrepancies at D/μ between 0.2 and 0.7 eV were then reduced by adjusting the shape of the assumed vibrational excitation cross section in the energy range between threshold and about 1.5 eV. In view of uncertainties in the number of vibrational levels of importance no attempt was made to remove the remaining discrepancy shown in Figs. 1 and 3 for D/μ values near 0.5 eV. We are unable to obtain a fit between the computed and experimental values of ν_u/N for $D/\mu>0.8$ eV without either increasing the vibrational excitation cross section at energies above 3 eV to several times Ramien's value or introducing a new excitation process at an energy of roughly 5 eV. Some indication of an energy loss process in this energy range has also been obtained by Schulz.[37] His later experiments using a double electrostatic analyzer[37] indicate that the vibrational excitation cross section proposed by Chen and Magee[38] is much too large. Further experiments and analyses in this energy range are required to settle this question.

below 0.05 eV in H₂, because of his neglect of thermalization effects in his empirical fit to the experimental values of D/μ.

[35] H. S. W. Massey and R. O. Ridley, Proc. Phys. Soc. (London) A69, 659 (1956). See also C. Carter, N. H. March, and D. Vincent, Proc. Phys. Soc. (London) 71, 2 (1958).

[36] A. Dalgarno and W. Moffett, Indian Academy of Sciences Symposium on Collision Processes, 1962 (unpublished).

[37] G. J. Schulz, Phys. Rev. 116, 1141 (1959); and (private communication).

[38] J. C. Y. Chen and J. L. Magee, *Proceedings of the International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 155.
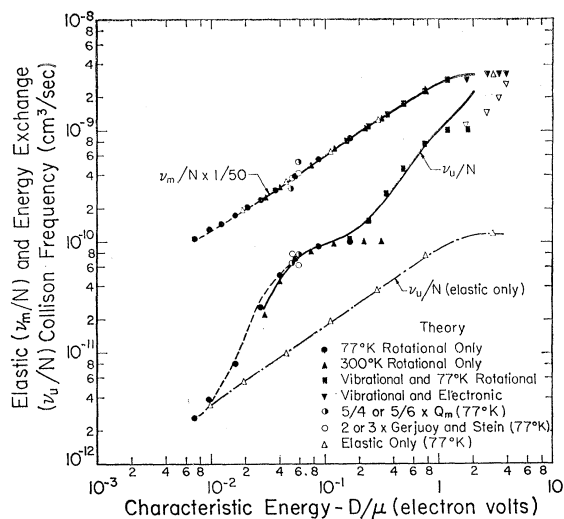

FIG. 3. Elastic and energy-exchange collision frequencies as a function of D/μ for H₂. The points are the results of our theoretical calculations. The solid and dashed curves are average values calculated from the experimental data shown in Fig. 1 for 300 and 77°K, respectively. The lowest curve gives the energy-exchange collision frequency calculated neglecting inelastic collisions. The energy exchange due to elastic collisions is included in all calculations.

The sensitivity of the present technique for determining cross sections and the usefulness of the quantities ν_m/N and ν_u/N as measures of the elastic and inelastic cross sections, respectively, can be seen by changing the final cross sections shown in Fig. 2 by $\sim 20\%$ and noting the effect on the computed values of ν_m/N and ν_u/N. Thus, in Fig. 3 we see that a small change in the magnitude of the assumed elastic cross section results in a proportional change in ν_m/N and that a change in the assumed rotational excitation cross sections causes a proportional change in ν_u/N when allowance is made for the effect of the contribution of elastic scattering to the energy loss. We can see the degree of separation of the elastic and inelastic effects by noting the changes in ν_m/N due to changes in inelastic cross section and the changes in ν_u/N due to changes in Q_m. Thus, the change in the assumed rotational excitation cross sections results in points which lie on the original ν_m/N vs D/μ curve. As a further indication that the theoretical ν_m/N is essentially independent of the assumed inelastic cross sections, we note that the values of the ν_m/N calculated assuming no inelastic collision, i.e., the open triangles of Fig. 3, are in excellent agreement with the other theoretical values and with experiment. We also note that the change in the elastic cross section produces only a small departure from the ν_u/N curve. Some departure is expected since the contribution of elastic recoil scattering to the loss of energy by electrons in H₂ is appreciable, i.e., about 1/5 of the inelastic contribution. The ν_u/N values calculated assuming no inelastic energy loss are shown in Fig. 3 by the lower broken line.

The predicted values of w and D/μ at 77°K shown in Fig. 1 are connected by the dashed curves. From Fig. 1 we see rather good agreement with the measured drift velocities and D/μ values. Note that for E/N values near 2×10^{-18} V-cm^2 at 77°K the predicted drift velocities are about 7% below the measured values. This is approximately the change in drift velocity that is predicted by theory if the ratio of orthohydrogen to parahydrogen were equal to the equilibrium value for 77°K instead of equal to the ratio characteristic of 300°K as assumed. However, a better measure of change in the inelastic scattering, such as would be caused by a change in the ortho-parahydrogen ratio, is ν_u/N. Figure 3 shows that the discrepancy between the measured values of ν_u/N and the points shown is only about one third of that expected for a change in the ortho-parahydrogen ratio from its equilibrium value at 300°K to its value at 77°K. In order for the ortho-parahydrogen ratio to reach its equilibrium value for 77°K the time required for ortho-para conversion[24] at 77°K at the metal parts, e.g., gold plated electrodes and Kovar walls, would have to be short compared to the duration of a series of runs, e.g., 5 h. Since the conversion process depends critically on the surface conditions, measurements of the ortho-para hydrogen ratio would be necessary to resolve this question. No drift was observed in the values of D/μ and w.

Figure 4 shows a comparison of our theoretical curve of the magnetic deflection coefficient $\mu_\perp(\mu^2 B)^{-1}$ with experimental points obtained from the magnetic deflection data, i.e., $(\mu_\perp/\mu)$, of Townsend and Bailey[22]

and of Hall[39] and from the drift velocity data of Fig. 1. The lowest arrow is the theoretical value computed by Allis and Allen[15] assuming that the momentum transfer cross section and the "energy loss per collision" were independent of energy, i.e., a Druyvesteyn energy distribution, while the third arrow gives the value expected for a Maxwellian distribution and a constant Q_m. The solid lines give the results of our theoretical calculations. These values are seen to be in satisfactory agreement with the experimental points calculated from the data of Townsend and Bailey[22] over the common range of D/μ. The relatively large departure from unity for D/μ values near 0.1 eV appears to be due to the increasing momentum transfer cross section with electron energy. The decrease in $\mu_\perp(\mu^2 B)^{-1}$ to approximately the theoretical value for a Druyvesteyn distribution near 1 eV corresponds to the energy

FIG. 5. Drift velocity and characteristic energy D/μ as a function of E/N for N_2 at 77°K and room temperature. The points are the experimental data and the solid curves are the results of our theoretical calculations.

independent portion of the Q_m curve. The further decrease in the theoretical value at higher D/μ corresponds to the approach of Q_m to a $u^{-1/2}$ dependence on electron energy. The relatively large values of $\mu_\perp(\mu^2 B)^{-1}$ near 0.1 eV should not be interpreted as indicating a distribution function varying more slowly with energy than a Maxwellian, since the computed distribution functions at energies near 0.1 eV are intermediate between Maxwellian and Druyvesteyn. On the other hand the increase in $\mu_\perp(\mu^2 B)^{-1}$ predicted as D/μ approaches kT/e presumably is due to the fact that the electron energy distribution function is becoming more Maxwellian[40] and that the momentum transfer cross section is increasing slowly with energy.
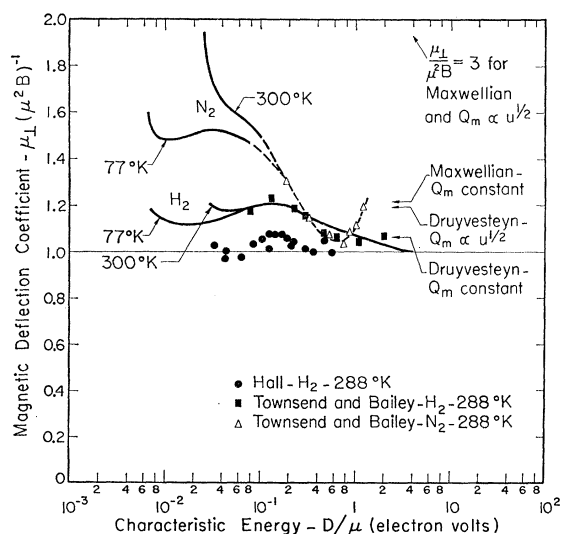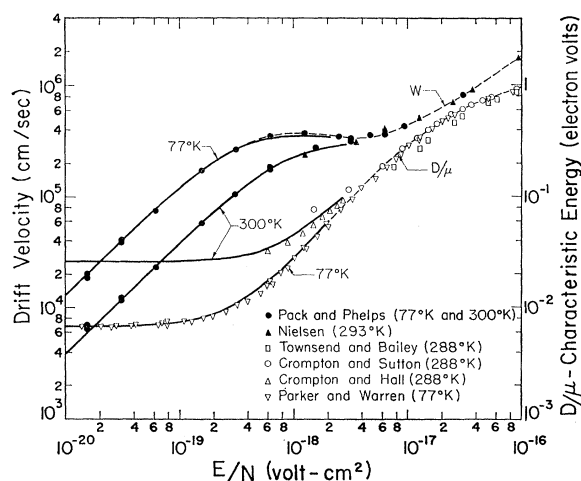

FIG. 4. Magnetic deflection coefficient $\mu_\perp(\mu^2 B)^{-1}$ for H_2 and N_2 as a function of the characteristic electron energy. The solid curves are the results of our theoretical calculations and the points are experimental data. The arrows at the right give the predicted values of $\mu_\perp(\mu^2 B)^{-1}$ for the electron energy distribution functions and energy dependences of Q_m indicated.

[39] B. I. H. Hall, Proc. Phys. Soc. (London) B68, 334 (1955). Although we know of no reason for the low values of $\mu_\perp/\mu$ obtained from this experiment, we note that the method of obtaining $\mu_\perp/\mu$ from measured currents is different than that of reference 22.

[40] It is of interest to note that the quantity $\mu_\perp(\mu^2 B)^{-1}$ represents the same average over the distribution function and Q_d as the

Finally, we wish to point out that when earlier types of analyses of swarm experiments are reformulated so as to be consistent with the Boltzmann equation their application to this problem yields results in reasonable agreement with those obtained above. Details of the theory and a numerical example are given in Appendix I.

B. Nitrogen

The determination of the rotational excitation cross sections for nitrogen proceeds in the same way as for hydrogen. The points of Fig. 5 show the experimental values for the drift velocity[20,21] and for D/μ.[9,22,29,30] The smooth curves show the values of w and D/μ computed using the momentum transfer cross section shown by the solid curve of Fig. 6 and rotational excitation cross sections as calculated from Eqs. (9) using an electric quadrupole moment of $1.01ea_0^2$. The smooth curves of Fig. 7 are averages of the experimental data at 300°K while the points are the theoretically computed values obtained using the final assumed
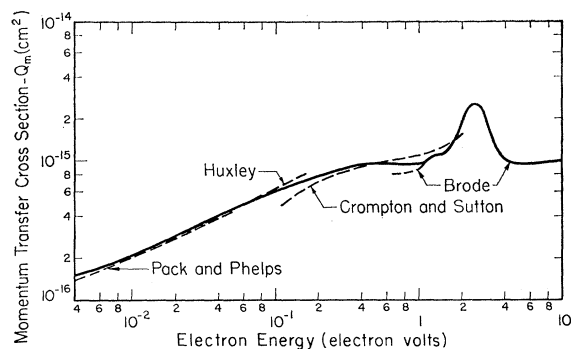

FIG. 6. Final assumed momentum transfer cross section Q_m for N₂ as a function of electron energy.

cross sections and the theory of Secs. II(a) and (c). Thus, the solid points of Fig. 7 at the lowest D/μ represent the results of an "exact" solution taking into account the discrete energy losses and gains in rotational excitation and de-excitation collisions. Because of the very low threshold energy for the excitation of the first rotational transition, i.e., 1.5×10^{-3} eV, for the $J=0$ to $J=2$ transition, we were able to use the

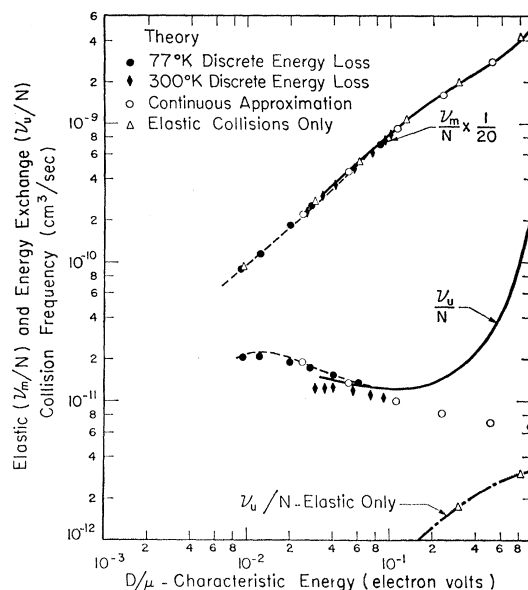

FIG. 7. Elastic and energy-exchange collision frequencies as a function of D/μ for N₂. The points are the result of our theoretical calculations. The solid and dashed curves are average values calculated from the experimental data of Fig. 1 for 300 and 77°K, respectively. The lowest broken curve gives the values of ν_u/N calculated neglecting inelastic collisions.

exact form of Eqs. (9) only for D/μ values below about 0.02 eV at 77°K.

At D/μ values above 0.02 eV and at 300°K it was necessary to replace the set of cross sections given by Eqs. (9) by an approximate set having the same functional forms but with the thresholds increased by factors of 2 to 5 and with the magnitudes adjusted to give the same value for the sum of the products of energy loss times cross section. Since these approximations are somewhat arbitrary several different approximations were tried at each E/N. The spread of the results is within the area of the points shown. Fortunately, the results of the calculations using the continuous approximation for the rotational excitation process, i.e., the open circles of Fig. 7, show that this approximation is good[40a] to better than 10% for D/μ values greater than about 3 times kT/e, i.e., $D/\mu > 0.02$ at 77°K and $D/\mu > 0.07$ at 300°K. As yet, no attempt has been made to include the effects of vibrational excitation of N₂ in our calculations although it could be done in a straightforward manner by using the continuous approximation for rotational excitation and by substituting the vibrational excitation cross sections found by Schulz[27] in the theory of Sec. II(b). This energy loss process has been included by Carleton and

high pressure limit of the quantity $\sigma_i ne^2(m\omega\sigma_r^2)^{-1}$, where σ_r and σ_i are the real and imaginary parts of the ac conductivity of a weakly ionized gas with no magnetic field. Here, ω is the applied angular frequency and n is the electron density. This quantity has been considered in some detail for Maxwellian distributions. See for example: P. Mulmud, Phys. Rev. 114, 29 (1959) and A. V. Phelps, J. Appl. Phys. 31, 1723 (1960). The evaluation of $\mu_\perp$ and μ for a Maxwellian distribution and various dependences of Q_m on u has been considered by M. S. Sodha, Phys. Rev. 116, 486 (1959). Phelps shows that for a rapidly varying Q_m with u, such as that found in N₂, one must go to very high pressures in order to obtain the limiting values of σ_r/σ_i (or $\mu_\perp/\mu_T$) and that small departures from the simple power law for Q_m lead to appreciable changes in the limit. We expect the limit to be more difficult to reach experimentally as the generalized coefficient $\mu_\perp(\mu_T\mu B)^{-1}$ departs further from unity.

[40a] *Note added in proof.* This remark applies only to the calculation of ν_u/N, which varies slowly with temperature. This approximation yields values of μ and D/μ correct to better than 10% only for D/μ greater than about 6 times kT/e.

Megill[41] at D/μ such that the continuous approximation is valid for rotational excitation.

From Fig. 6, we see that the final momentum transfer cross section is in good agreement with the results of Pack and Phelps[21], Huxley[9], Crompton and Sutton,[29] and Brode.[31] The final magnitude of the molecular electric quadrupole moment used in our calculations is in good agreement with the value of $0.96ea_0^2$ obtained by Smith and Howard[42] but is $(2.5)^{1/2}$ times larger than the more recent value of $0.60ea_0^2$ obtained by Feeny, Madigosky and Winters.[43]

Figures 5 and 7 show that there are residual discrepancies between our theory and the experiments. Thus, at E/N values near 10^{-18} V-cm² the calculated drift velocities at 77°K are too low by about 5%. According to Fig. 7 this is due to the assumption of values of Q_m which are too large by about 5% at energies near 0.02 eV. Figure 5 also shows that our calculated values of D/μ are too high by about 5% at 77°K and 300°K for D/μ values slightly above thermal although about half of the apparent discrepancy at 300°K is due to the fact that the data was taken at 288°K. According to Fig. 7, the assumed rotational cross sections are too small at these energies by about the same amount. The changes indicated by these considerations were not made in our calculations because the final D/μ data was not available at that time. The resultant errors in the "consistent" set of momentum transfer and rotational excitation cross sections are believed to be less than 10%.

Figure 4 shows the available values of $\mu_\perp(\mu^2 B)^{-1}$ for nitrogen. Unfortunately, there is no overlap between theory and experiment. Also, since the D/μ data obtained by Townsend and Bailey,[22] Fig. 5, do not agree with the more recent data we are inclined to distrust the $\mu_\perp/\mu$ values. The most striking feature of this plot is the very large values of $\mu_\perp(\mu^2 B)^{-1}$ found theoretically for nitrogen at near thermal energies. However, these values are well below the theoretical value of 3 for a Maxwellian distribution when the momentum transfer cross section is proportional to the square root of the electron energy and are a measure of the departure from this simple energy dependence.[40]

In the case of N_2 no attempt was made to prove the sensitivity of our calculated values of ν_m/N and ν_u/N to their respective cross sections. However, we expect a very nearly 1 to 1 correspondence as for H_2. Thus, the magnitude of the final set of assumed energy dependent cross sections is believed to be as accurate as the comparisons shown in Fig. 7 or to better than 10% for the momentum transfer and rotational excitation cross sections. The small error assigned to the excitation cross section is based on the agreement

with the D/μ data of Parker and Warren.[30] It must be remembered that our results for the energy dependence are not unique and that rapid oscillations in cross section with energy cannot be resolved in this analysis.

As in the case of hydrogen, we note the lack of dependence of the theoretical values of ν_m/N vs D/μ on the assumed energy loss process. Thus, the open circles of Fig. 7 show the results of calculations including rotational excitation while the open triangles show values computed assuming elastic collisions only. In these cases the ν_m/N values are within 5% of the experimental curve and within 2% of each other. Furthermore, the use of a Maxwellian energy distribution of energies leads to values of ν_m/N vs D/μ which are within 5% of the values calculated using the distribution functions obtained from the Boltzmann equation. A typical energy distribution obtained in our calculation for N_2 resembles a Druyvesteyn at energies above $u=D/\mu$ but is more like a Maxwellian at energies below $u=D/\mu$.

It is of interest to compare our values of ν_u/N with the values of the corresponding quantity, $G\nu/N$, used in ionospheric interaction theory.[9,29,44] In most analyses $G\nu/N$ is defined in terms of quantities measured in laboratory experiments as the value of $2\nu_u/3N$ from Eq. (14). Thus, Huxley's[9,44] formula gives a value of 1.02×10^{-11} cm³/sec for thermal electrons at 300°K, whereas, our theory for 300°K extrapolates to a value of 0.8×10^{-11} cm³/sec. The difference arises primarily from the use of different experimental data as a basis of adjusting the rotational cross section parameters. At present we do not know whether the slight decrease in our values of ν_u/N as $D/\mu \rightarrow kT/e$ is a real effect or due to systematic errors in our calculation of D/μ which may be of the order of 0.5%. Further investigations of this near thermal region are required.

IV. DISCUSSION

The preceding analyses of measured transport coefficients for electrons in hydrogen and nitrogen show that by using appropriate combinations of coefficients one can separate the effects of elastic and inelastic collisions. The elastic and inelastic collision frequencies can be used to obtain a set of energy dependent momentum transfer and inelastic collision cross sections which are reasonable and which when substituted into the Boltzmann equation yield transport coefficients in good agreement with experiments. The final set of cross sections is not unique and in general will disagree in detail with future high resolution experimental or theoretical data if the latter vary too rapidly with energy. A proper averaging over the true distribution function is especially important for inelastic collision processes near threshold, e.g., H_2 near $D/\mu = 0.3$ eV

[41] N. P. Carleton and L. R. Megill, Bull. Am. Phys. Soc., 7, 129 (1962), and Phys. Rev. 126, 2089 (1962).

[42] W. V. Smith and R. Howard, Phys. Rev. 79, 132 (1950).

[43] H. Feeny, W. Madigosky and B. Winters, J. Chem. Phys. 27, 898 (1957).

[44] A. Dalgarno, Ann. Geophys. 17, 16 (1961) and D. Formato and A. Gilardini, *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1961), p. 660.

and N_2 near $D/\mu=0.2$ eV. However, our calculation shows that for low D/μ, the distribution functions are intermediate between Maxwellian and Druyvesteyn, and that the use of approximate distribution functions is satisfactory for the determination of the momentum transfer cross section in H_2 and N_2 over the energy range considered in our analyses. This fact accounts for the success of Heylen,[34] who used a Maxwellian energy distribution function for the calculation of electron drift velocities in H_2 using an assumed momentum transfer cross section and experimental values of D/μ vs E/N. As yet we have no information as to whether the use of approximate distribution functions is sufficiently accurate to be useful for other gases.

An important conclusion of the analysis presented above is that certain features of the predictions of Gerjuoy and Stein concerning the process of rotational excitation in the homonuclear molecules H_2 and N_2 are consistent with experiment. In particular, the comparison of calculated and measured values of electron drift velocity and of D/μ in hydrogen at 77°K shows that the predicted energy dependence of the excitation cross sections and the selection rule against $J=0$ to $J=1$ transitions are in good agreement with experiment in the energy range from threshold to above 0.15 eV. In the case of N_2 the predicted energy dependence for the sum of the large number of significant rotational excitation transitions is in agreement with experiment at 77°K over the energy range from 0.01 to about 0.1 eV. At present our knowledge of the vibrational excitation cross sections is not good enough to allow us to say whether the predicted energy dependence for rotational excitations is valid near and above the threshold for vibrational excitation. Evidence of a significant departure from the theory of Gerjuoy and Stein, as modified by Dalgarno, is our assumption of an effective quadrupole moment 30% larger than the measured value in order to obtain agreement between theory and experiment in H_2. Since the quadrupole moment measured by Harrick and Ramsey is claimed to be accurate to $\pm10\%$ and we claim a $\pm5\%$ accuracy in the quadrupole moment derived from our experiments and analysis, it appears that the discrepancy is real. The same discrepancy occurs in the case of N_2 when one uses the most recent value for the quadrupole moment of N_2 as determined from microwave line broadening experiments. However, the accuracy of the quadrupole determination in the case of N_2 is probably considerably less than for H_2.

The technique of analyzing measured drift velocity and D/μ data to obtain momentum transfer and excitation cross sections described in this paper is capable of application to a number of interesting problems. The analysis of H_2 and N_2 is being extended to higher energies and to H_2-Ar mixtures so as to improve the accuracy of our estimate of the vibrational excitation cross sections. In addition, the technique

is being used to study other molecular gases, such as O_2 and CO_2.

V. ACKNOWLEDGMENTS

APPENDIX I. COMPARISON WITH EARLIER ANALYSES

In this Appendix we will show some relationships between the Boltzmann transport equation approach used in this paper and the earlier approximate methods of analyzing swarm experiments. The basis of our analysis will be an energy balance[45] obtained by multiplying Eq. (1) by $udu(2e/m)^{1/2}$ and integrating over all energies. Thus, we find that

$$wE=\left(\frac{2e}{m}\right)^{1/2}\frac{2m}{M}\int_0^\infty u^2NQ_m\left[f(u)+\frac{kT}{e}\frac{df(u)}{du}\right]du$$

$$+\left(\frac{2e}{m}\right)^{1/2}\sum_i u_j\int_0^\infty uf(u)$$

$$\times[NQ_j(u)-NQ_{-j}(u)]du, \quad (A1)$$

where

$$\int_0^\infty u^{1/2}f(u)du=1.$$

The left-hand side of Eq. (A1) is the power input per electron in eV/sec from the electric field while the first and second terms of the right-hand side give the net power loss to elastic and inelastic collisions, respectively. The second term is equal to the dW_e/dt term of Gerjuoy and Stein.[10] Note that according to Eq. (14), $wE=\nu_u(D/\mu-kT/e)$, so that Eq. (A1) could be used to compute the contributions of elastic and inelastic collisions to ν_u/N.

As an example of the application of this energy balance we will consider electrons in H_2 at an E/N which yields a value of D/μ in the range of maximum sensitivity of ν_u/N to the assumed rotational excitation cross sections but with negligible contribution from vibrational excitation, i.e., $E/N=7.5\times10^{-18}$ V-cm² so

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[45] This energy balance is an improved version of that used to analyze H_2 data by R. W. Lunt and C. A. Meek, Proc. Roy. Soc. (London) **A157**, 146 (1936); and R. W. Lunt (private communication).

that $D/\mu=0.076$ eV and $w=5.4\times10^5$ cm/sec at 300°K. For these conditions the results of our calculations are that the power input per electron is $4.1\times10^{-12}N$ eV/sec while the net energy lost to elastic collisions is 7.6 $\times10^{-13}N$ eV/sec and that lost to inelastic collisions is $3.5\times10^{-12}N$ eV/sec. The experimental value for the power input is $4.1\times10^{-12}N$ eV/sec. The source of 4% discrepancy between the calculated power input and calculated total power lost is as yet undetermined but may well be in the evaluation of the integrals on the right-hand side of Eq. (A1) since they were calculated by hand using fewer points than the other calculations given in this paper. If we had used the quadrupole moment used by Gerjuoy and Stein,[10] the energy lost to inelastic collisions would have been $1.4\times10^{-12}N$ eV/sec for a total loss of about half the observed value. Also, if we use a constant value of Q_m equal to the value at the peak of the distribution function, i.e., 10×10^{-16} cm², and a Maxwellian distribution of velocities with the same value of D/μ as was done by Gerjuoy and Stein,[10] we find a net elastic loss of $1\times10^{-13}N$ eV/sec and inelastic losses which are very nearly the same as that given above. Thus, in this approximation the rotational cross sections required are a factor of 2.2 times the value given by Gerjuoy and Stein as compared to a factor of 2.5 obtained using accurate distribution functions.

As a further point we note that the quantity most often used in analyses of energy losses in molecular gases is basically the ratio of the drift energy or "ordered" energy to an energy characteristic of the random motion of the electrons. Since we prefer to use experimentally measurable quantities and make no assumptions as to the form of the distribution function, we define this ratio by the relation,

$$\Lambda=\frac{mw^2}{e(D/\mu)}=\frac{\nu_u}{\nu_m}\frac{(D/\mu-kT/e)}{D/\mu}. \quad (A2)$$

Since the drift energy is dissipated when electrons of characteristic energy D/μ collide with the gas molecules, we can consider Λ as the fraction of the characteristic energy lost in such a collision. We note that Λ is within 4% of the "mean energy loss per collision, λ," calculated in previous analyses[1-10] assuming a Druyvesteyn distribution. We can obtain the value of w^2 needed in Eq. (A2) by multiplying both sides of Eq. (A1) by the electron mobility μ. Thus

$$\Lambda\equiv\left(\frac{2m}{e}\right)^{1/2}\frac{\mu N}{(D/\mu)}\left[\frac{2m}{M}\int_0^\infty u^2Q_m\left[f(u)+\frac{kT}{e}\frac{df(u)}{du}\right]du\right.$$
$$\left.+\sum_j u_j\int_0^\infty nf(u)[Q_j(u)-Q_{-j}(u)]du\right]. \quad (A3)$$

Using the results of our calculations for $E/N=7.5$ $\times10^{-18}$ V-cm², $\Lambda=2.2\times10^{-3}$ while the elastic and inelastic terms are 0.4×10^{-3} and 1.9×10^{-3}, respectively. In units of $2m/M$, $\Lambda'\equiv(M/2m)\Lambda=4.1$ while the elastic and inelastic terms are 0.8 and 3.5, respectively. Using a Maxwellian distribution and cross section as above the elastic and inelastic contributions to Λ' are 1 and 3.5, respectively. When these values are scaled by λ/Λ we see that some previous analyses[10,45] have considerably over-estimated the role of elastic collisions, i.e., at this D/μ they conclude that elastic and inelastic collisions make roughly equal contributions rather than in the ratio of about 1 to 4 as we find. A partial correction for this effect is given by Huxley,[9] who took the fractional energy loss per collision to be proportional to $(2m/M)[1-kT(eD/\mu)^{-1}]$ instead of $2m/M$ as did Gerjuoy and Stein. Unfortunately, the results of Sec. IIIA show that one cannot conduct these analyses of H_2 data at energies high enough to avoid the effects of elastic energy gain without taking into account the energy loss due to vibrational excitation. Similar analyses can be carried out for N_2, e.g., for D/μ near 0.1 eV where the analysis of Sec. IIIB indicates that the energy gain due to elastic collisions and vibrational excitation collisions can be neglected. Unfortunately, much of the earlier D/μ data for N_2 at low E/N appears to be significantly in error with a resultant poor fit between theory and experiment.[10,44]

APPENDIX II. SOLUTION OF EQUATIONS

The purpose of this section is to outline the procedures actually used to solve for the distribution function under the various approximations to Eq. (3).

(A) Exact Solution

Following Sherman[17] we make the following transformations: Let $f(z)=v(z)\gamma(z)$ where

$$\gamma(z)=\exp\left[-\int_0^z\frac{y\theta^2(y)dy}{\alpha+y\theta^2(y)}\right] \quad (A4)$$

so that Eq. (3) becomes

$$\frac{dv(z)}{dz}+\frac{1}{\gamma(z)h(z)}\sum_{k=1}^n\int_z^{z+z_k}x\eta_k(x)\gamma(x)v(x)dx-\frac{1}{\gamma(z)h(z)}\sum_{k=1}^n\exp(-z_k)\int_{z-z_k}^z(x+z_k)\eta_k(x+z_k)\gamma(x)v(x)dx=0, \quad (A5)$$

where $h(z)=z[\alpha+z\theta^2(z)][\theta(z)]^{-1}$ and z_k and η_k are the normalized energy loss and cross section for inelastic collisions.

Boyer has shown that if one integrates Eq. (A5) from z to δ and changes the order of integration the result is that

$$v(z)=v(\delta)+\sum_{k=1}^{n}\int_{z}^{\delta+z_k} x\eta_k(x)\gamma(x)\{G[\min(\delta,x)]-G[\max(z,\,x-z_k)]\}v(x)dx$$

$$-\sum_{k=1}^{n}\exp(-z_k)\int_{z-z_k}^{\delta}(x+z_k)\eta_k(x+z_k)\gamma(x)\left\{\begin{matrix}G[\min(\delta,\,x+z_k)]\\ -G[\max(z,x)]\end{matrix}\right\}v(x)dx, \quad (A6)$$

where

$$G(x)=\int_{0}^{x}\frac{dy}{h(y)\gamma(y)}$$

and where $G[\min(a,b)]$ means that the argument of G is taken as the lesser of the values a or b, and similarly for $G[\max(a,b)]$. Using an approximation similar to that justified by Sherman for the case of no collisions of the second kind, we assume $v(z)=1$ for $z\geq\delta$. Now let $\delta=Nh$, $Z_k=N_kh$, $x_i=ih$ and $v(x_i)=v_i$ so that we can approximate the integrals in Eq. (A6) by summations. Thus,

$$v_i=\sum_{j=1}^{N-1}b_{ij}v_j+a_i, \quad (A7)$$

where

$$b_{ij}=hE_{ij}\sum_{k=1}^{n}x_j\eta_k(x_j)\gamma(x_j)$$
$$\times\{G(x_j)-G[\max(x_i,\,x_j-z_k)]\}$$
$$-h\sum_{k=1}^{n}(x_j+z_k)E_{ij}{}^k\eta_k(x_j+z_k)\gamma(x_j)\exp(-z_k)$$
$$\times\{G[\min(\delta,\,x_j+z_k)-G[\max(x_i,x_j)]\}. \quad (A8)$$

Also

$$E_{ij}=0 \text{ for } j\leq i \quad E_{ij}{}^k=0 \text{ for } j\leq i-N_k$$
$$=1 \text{ for } j>i, \quad =1 \text{ for } j>i-N_k,$$

and

$$a_i=1+h\sum_{k=1}^{n}\sum_{j=N}^{N+N_k}x_j\eta_k(x_j)\gamma(x_j)$$
$$\times\{G(\delta)-G[\max(x_i,\,x_j-z_k)]\}. \quad (A9)$$

The computational steps are:

(a) Select a mesh size N subject to the computer limitations;

(b) assume $\theta(z_i)$ and a set of $\eta_k(z_i)$;

(c) calculate $\gamma(z_i)$ and $G(z_i)$ for $1\leq i\leq N+N_k(\max)$;

(d) compute the coefficients b_{ij} and a_i;

(e) solve the set of linear equations to find the v_i;

(f) compute the f_i; and

(g) evaluate the transport integrals in Eqs. (4) to (6).

(B) Solution without Collisions of the Second Kind

Here one proceeds as above to obtain the first two terms in Eq. (A6), i.e.,

$$\frac{dv(z)}{dz}+\sum_{k=1}^{n}\int_{z}^{z+z_k}\frac{x\eta_k(x)\gamma(x)v(x)dx}{h(z)\gamma(z)}=0. \quad (A10)$$

Using Simpson's three point numerical integration formula Eq. (A10) can be written in the form

$$v(z_{i-1})=v(z_{i+1})+\frac{h}{3}[s(z_{i-1})+4s(z_i)+s(z_{i+1})], \quad (A11)$$

where

$$s(z_i)=\sum_{k=1}^{n}\int_{z_i}^{z_i+z_k}\frac{v(x)x\eta_k(x)}{h(z_i)}\exp\left(-\int_{z_i}^{x}g(y)dy\right)dx.$$

The method of solution used by Sherman is to assume $v(z)=1$ for $z\geq\delta$ and prolong leftward from δ to zero. Here δ is much larger than $eD/\mu kT$ and is found by trial and error adjustment until the resultant change in the transport integrals is satisfactorily small.