# Determination of Momentum Transfer and Inelastic Collision Cross Sections for Electrons in Nitrogen Using Transport Coefficients*

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Momentum transfer and inelastic collision cross sections for electrons in $N_2$ have been obtained from electron transport coefficients for values of the electron energy between about 0.003 and 30 eV. The recently proposed polarization correction to the rotational excitation cross sections of Gerjuoy and Stein leads to less satisfactory agreement between theory and experiment than do the unmodified cross sections. The cross sections for vibrational excitation are consistent with those of Schulz provided the total cross section is normalized to $5.5\times10^{-16}$ cm$^2$ at 2.2 eV. Furthermore, a tail extending down to the threshold of 0.29 eV is postulated for the $v=1$ vibrational level. Electronic excitation is approximated by a set of six effective cross sections which, for the most part, are consistent with previous results. The ionization cross section of Tate and Smith was used. The mean energy of electrons in $N_2$ subjected to high-frequency ac electric fields is found to be a single-valued function of the electric field $E$ divided by the ac radian frequency $\omega$, although there are regions of $E/\omega$ where the mean energy increases extremely rapidly with $E/\omega$.

## I. INTRODUCTION

THIS paper presents the results of an investigation to determine momentum transfer and inelastic collision cross sections for electrons in $N_2$ using transport coefficients. Previously, studies[1–3] have been made of $H_2$, $D_2$, and Ar, and in addition, Frost and Phelps[1] (hereafter called I) have reported some initial calculations for the rotational region of $N_2$. In this work we shall discuss the extension of the studies for $N_2$ in I to higher energies and present a somewhat more detailed analysis of the rotational region.

As in the analysis of $H_2$ by Engelhardt and Phelps[2] (hereafter called II), we consider three separate regions of the characteristic energy[4] $\epsilon_K$ given by

$$\epsilon_K = eD/\mu, \tag{1}$$

where $e$ is the electronic charge, $D$ is the diffusion coefficient, and $\mu$ is the mobility. The first region, designated as $A$, starts at thermal values of $\epsilon_K$; here elastic scattering and rotational excitation are the significant collision processes. Since the nitrogen is at 77°K, region $A$ is delineated by $\epsilon_K$ varying from approximately 0.007 to 0.08 eV. Our studies of region $A$ have investigated in detail the effect of the polarization correction suggested by Dalgarno and Moffett[5] and independently by Mjolsness and Sampson.[6] In region $B$ where $\epsilon_K$ varies from 0.08 to 1.3 eV, elastic scattering, and rotational and vibrational excitation are the dominant collision processes. In the case of vibrational excitation, we have relied heavily on the measurements by Schulz[7–9] for the determination of cross sections. For $\epsilon_K>1.3$ eV, i.e., region $C$ where electronic excitation is significant, we have constructed a set of equivalent excitation cross sections whose thresholds are based on Schulz' measurements.[7] The data of Tate and Smith[10] served as the basis for the ionization cross section used. Finally, over the entire region of interest,

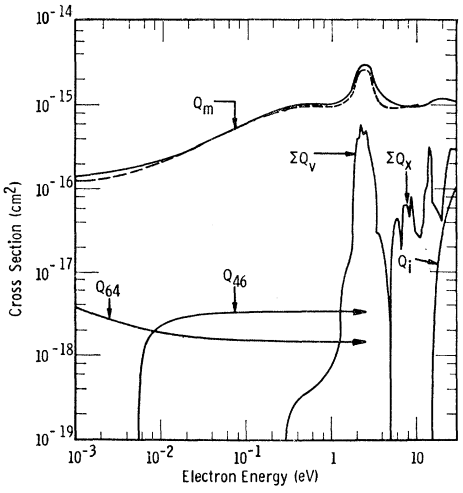


FIG. 1. Momentum transfer $Q_m$ and inelastic collision cross sections for electrons in $N_2$. The dashed $Q_m$ curve indicates the results reported previously by Frost and Phelps. To avoid confusion we show only the curves for rotational excitation at 77°K from $J=4$ to $J=6$ and de-excitation from $J=6$ to $J=4$ calculated for a quadrupole moment $\mathcal{Q}$ of 1.04 in atomic units using the theory of Gerjuoy and Stein. The curve labeled $\Sigma Q_v$ represents the total of all the vibrational cross sections from $v=1$ to 8, as the curve labeled $\Sigma Q_x$ represents the total of all six effective excitation cross sections with thresholds between 5.0 and 14.0 eV. The ionization cross section $Q_i$ represents the experimental results of Tate and Smith.

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[1] L. S. Frost and A. V. Phelps, Phys. Rev. **127**, 1621 (1962).

[2] A. G. Engelhardt and A. V. Phelps, Phys. Rev. **131**, 2115 (1963).

[3] A. G. Engelhardt and A. V. Phelps, Phys. Rev. **133**, A375 (1964).

[4] Equation II. (1) refers to Eq. (1) of II. Here we use precisely the same notation as in II.

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

[6] R. C. Mjolsness and D. H. Sampson, Bull. Am. Phys. Soc. **9**, 187 (1964).

[7] G. J. Schulz, Phys. Rev. **116**, 1141 (1959).

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

[9] G. J. Schulz, Phys. Rev. **135**, A988 (1964).

[10] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

i.e., electron energy $\epsilon \lesssim 30$ eV, we have determined a momentum transfer cross section which is consistent with most of the experimental data.

As in II, we have calculated distribution functions and transport coefficients for electrons subjected to high-frequency electric fields. In particular, we have been able to investigate the somewhat unusual behavior of the high-energy portion of the distribution function and of the average electron energy at high frequencies in $N_2$.

Our technique is virtually unchanged from that described in I and II, and consequently, a detailed description will be omitted. We solve numerically the time- and space-independent Boltzmann transport equation for the distribution function of electron energies in a neutral gas. Then, by suitable averages of appropriate cross sections over this distribution function, we are able to determine the various transport coefficients of interest. We then compare calculated and experimental values of these transport coefficients and make the appropriate adjustments in the momentum transfer and inelastic collision cross sections until a satisfactory fit is obtained.

## II. DETERMINATION OF CROSS SECTIONS

### Region A: Elastic Scattering and Rotational Excitation $[(kT/e) < \varepsilon_K < 0.08$ eV$]$

Shown in Fig. 1 are our best values for the momentum transfer cross section $Q_m$ and sample curves for rotational excitation between states with rotational quantum numbers $J=4$ and $J=6$, and for rotational de-excitation from $J=6$ to $J=4$. The dashed $Q_m$ curve indicates the results reported previously in I. The rotational curves shown were found using the theory of Gerjuoy and Stein.[11] As indicated below the application of the polarization correction proposed by Dalgarno and Moffett[5] and Mjolsness and Sampson[6] does not allow us to improve the agreement with experiment. For clarity, we have plotted only $Q_{46}$ and $Q_{64}$ as calculated using a quadrupole moment $\mathcal{Q}$ of 1.04 in units of $ea_0^2$ and no polarization correction.

In order to solve the Boltzmann transport equation accurately in region $A$, it is necessary to include inelastic collisions of the second kind, i.e., superelastic collisions. As discussed in I, the threshold energy for the lowest lying rotational level of $N_2$ is only $1.5\times10^{-3}$ eV, a value which is significantly less than the 77°K thermal value of $\epsilon_K = 0.00663$ eV, so that a large number of rotational excitation and de-excitation cross sections must be considered. For $\epsilon_K$ varying from $kT/e$ to approximately 3 $kT/e$ when $T=77$°K, the required number of rotational levels excited is manageable and we have used the exact expressions as given by Eqs. II. (18)–(24). For $\epsilon_K > 3kT/e$, it was necessary to replace the exact set of cross sections by an approximate set[1] whose thresholds had been increased by a factor of 2 and whose magnitudes were appropriately decreased. The correctness of this approximation was tested in the region around $\epsilon_K = 3\ kT/e$, where it was possible to use both methods; it was found that the results agreed to within a few percent. For $\epsilon_K \gtrsim 7\ kT/e$ (i.e., 0.046 eV) the continuous approximation for the rotational cross sections derived in I yields results accurate to within a few percent.

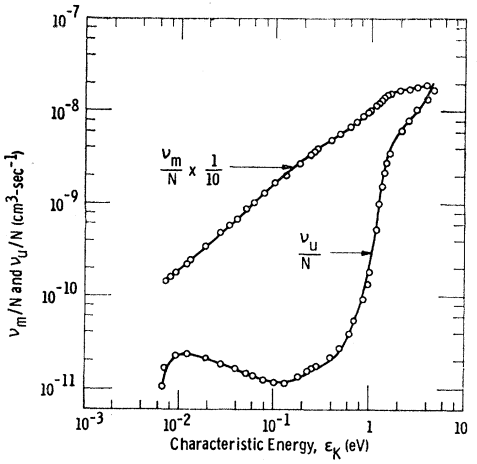


FIG. 2. Effective momentum transfer $\nu_m$ and energy exchange $\nu_u$ collision frequencies for electrons in $N_2$ at 77°K normalized to the neutral particle density $N$. The points represent our theoretical calculations using no polarization correction and $\mathcal{Q} = 1.04\ ea_0^2$, and the smooth curves represent an average of the best available experimental data.

Shown in Fig. 2 are plots displaying our calculated momentum transfer and energy exchange collision frequencies, i.e., $\nu_m$ and $\nu_u$, respectively, shown as points. Averages of the best available experimental data are shown as smooth curves. In the case of the $\nu_m/N$ curve, the satisfactory agreement vindicates our final choice of the $Q_m$ curve. As for the $\nu_u/N$ plot, the calculated points are for rotational cross sections computed using no polarization correction and $\mathcal{Q} = 1.04\ ea_0^2$. We consider the agreement to be reasonably good since the maximum discrepancy does not exceed 5% for $\epsilon_K > 0.01$ eV. As pointed out in I, the $\nu_m/N$ versus $\epsilon_K$ curve is very insensitive to the assumed values of the inelastic collision cross sections.

The effect of the theoretical polarization correction and of the sign and magnitude of the quadrupole moment is explored in greater detail in Fig. 3, where we show the experimental results as a smooth curve and the various calculations as points. The triangles are for a polarization correction[12] using a positive quadrupole moment of $\mathcal{Q} = +0.974\ ea_0^2$ [see Eqs. II. (23) and (24)]. This curve is fitted to experiment at $\epsilon_K \approx 0.012$ eV since the theory is most accurate near threshold

[11] E. Gerjuoy and S. Stein, Phys. Rev. **97**, 1671 (1955); **98**, 1848 (1955).

[12] The parallel and perpendicular polarizabilities used for $N_2$ are 16.1 and 9.8 in a.u. See J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

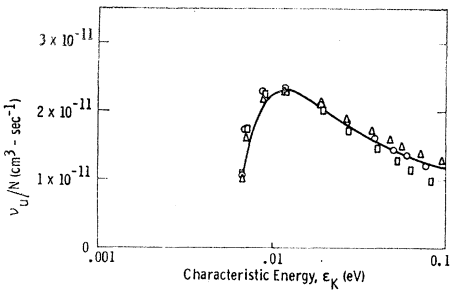


FIG. 3. Energy exchange collision frequency $\nu_u$ for electrons in $N_2$ at 77°K normalized to $N$. We show primarily the region where elastic scattering and rotational excitation are important. The smooth curve represents an average of the best available experimental data. The circles represent our calculated results for no polarization correction and $\mathcal{Q}=1.04\ ea_0^2$; the triangles represent calculations for a polarization correction and $\mathcal{Q}=+0.974\ ea_0^2$; and the squares represent those for a polarization correction and $\mathcal{Q}=-1.10\ ea_0^2$.

and since experiments should be reasonably accurate in this region. An acceptable fit to the $\nu_u/N$ data near $\epsilon_K=0.012$ eV for a polarization correction using a negative quadrupole moment of $\mathcal{Q}=-1.10\ ea_0^2$ is shown by the squares. The circles indicate that a value of $\mathcal{Q}=1.04\ ea_0^2$ produces good results when no polarization correction is used. A comparison of the three curves of Fig. 3 yields the conclusion that the use of a polarization correction, whether positive or negative, does not improve the agreement with experiment. A similar conclusion would have been reached had we used a least-squares fit for the same three cases for $\epsilon_K>0.01$ eV.

This conclusion supersedes that stated previously,[13] but is consistent with recent[14] theoretical investigations which indicate that the effect of the polarization correction using a negative[15] quadrupole moment is at least partially cancelled by other corrections. The magnitude of the quadrupole moment determined by our analysis appears to be in good agreement with most recent determinations as summarized by Poll[16] and Ketelaar and Rettschnick,[17] although the effect of averaging[1,2] over the internuclear separation does not appear to have been taken into account.

A direct comparison of the results of our calculations with experiment is furnished by Fig. 4 in terms of drift velocity and characteristic energy plots. Here the calculations for $\mathcal{Q}=1.04\ ea_0^2$ and $T=77$°K are shown as smooth curves, and the various experimental results[18–28] are shown as points. The agreement (in region $A$) with the $\epsilon_K$ data of Warren and Parker[25] and the $w$ data of Lowke[19] is excellent. A typical electron energy distribution function which is characteristic of this range of $\epsilon_K$ is shown in Fig. 12. This energy distribution is intermediate between Maxwellian and Druyvesteyn.[1]

### Region B: Elastic Scattering, Rotational Excitation and Vibrational Excitation [$0.08\leqslant\epsilon_K\leqslant1.4$ eV]

Above $\epsilon_K\approx0.1$ eV, a significant number of electrons possess energy in excess of the excitation energy[29] (0.29 eV) of the $v=1$ vibrational level, and vibrational excitation must be taken into account. For energies above 1.7 eV, the relative magnitudes and shapes of the eight vibrational cross sections, i.e., from $v=1$ to $v=8$, are the same as those given by Schulz.[8,9] We show the sum of these as $\sum Q_v$ in Fig. 1. Of particular significance is the tail of the $v=1$ cross section. We have found it necessary to add this tail to the $v=1$ cross section in order to obtain agreement with the experimental data.

The tail we have added is shown in greater detail in Fig. 5 as the solid line labeled $Q_{01}$. The dashed line indicates the result calculated by Chen.[30] Below 1.2 eV we have chosen his values since they give a good fit. Above 1.2 eV we have found it necessary to use a cross section significantly larger than his. This discrepancy cannot be accounted for by the uncertainty in the shape of the rotational excitation cross sections. The points shown in Fig. 5 represent the lowest energy data of Schulz.[9] Because of the low sensitivity of his apparatus, Schulz could not study this threshold region accurately, and, therefore, the disagreement is not considered to be significant. Also shown is the cross section $Q_{10}$ for vibrational de-excitation calculated using detailed balancing.[31] The excellent results using this tail with a quadrupole moment of $1.04\ ea_0^2$ are shown in

[13] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Bull. Am. Phys. Soc. 9, 187 (1964).
[14] D. H. Sampson and R. C. Mjolsness (private communication, 1964).
[15] C. W. Scherr, J. Chem. Phys. 23, 569 (1955). The negative sign has been recently confirmed theoretically by P. Cade, K. D. Sales, and A. C. Wahl (private communication); Bull. Am. Phys. Soc. 9, 102 (1964).
[16] J. D. Poll, Phys. Letters 7, 32 (1963).
[17] J. A. Ketelaar and R. P. H. Rettschnick, Mol. Phys. 7, 191 (1963–64).
[18] J. L. Pack and A. V. Phelps, Phys. Rev. 121, 798 (1961).
[19] J. J. Lowke, Australian J. Phys. 16, 115 (1963). Because the results of Bortner *et al.* [T. E. Bortner, G. S. Hurst, and W. G. Stone, Rev. Sci. Instr. 28, 103 (1957)] and J. C. Bowe [Phys. Rev. 117, 1411 (1960)] are consistently lower than those of Lowke, we have not plotted the former in Fig. 4.
[20] N. E. Bradbury and R. A. Nielsen, Phys. Rev. 49, 388 (1936).
[21] D. Errett, Ph.D. thesis, Purdue University, 1951 (unpublished).
[22] K. H. Wagner and H. Raether, Z. Physik 170, 540 (1962).
[23] W. Riemann, Z. Physik 122, 216 (1944).
[24] L. Frommhold, Z. Physik 160, 554 (1960).
[25] R. W. Warren and J. H. Parker, Phys. Rev. 128, 2661 (1962).
[26] J. S. Townsend and V. A. Bailey, Phil. Mag. 42, 873 (1921).
[27] R. W. Crompton and M. T. Elford, *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases* (Paris, 1963).
[28] L. W. Cochran and D. W. Forester, Phys. Rev. 126, 1785 (1962). Only data for $\epsilon_K>0.2$ eV is shown since the experiments were carried out at 298°K rather than 77°K.
[29] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).
[30] J. C. Y. Chen (private communication, 1963).
[31] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1934).

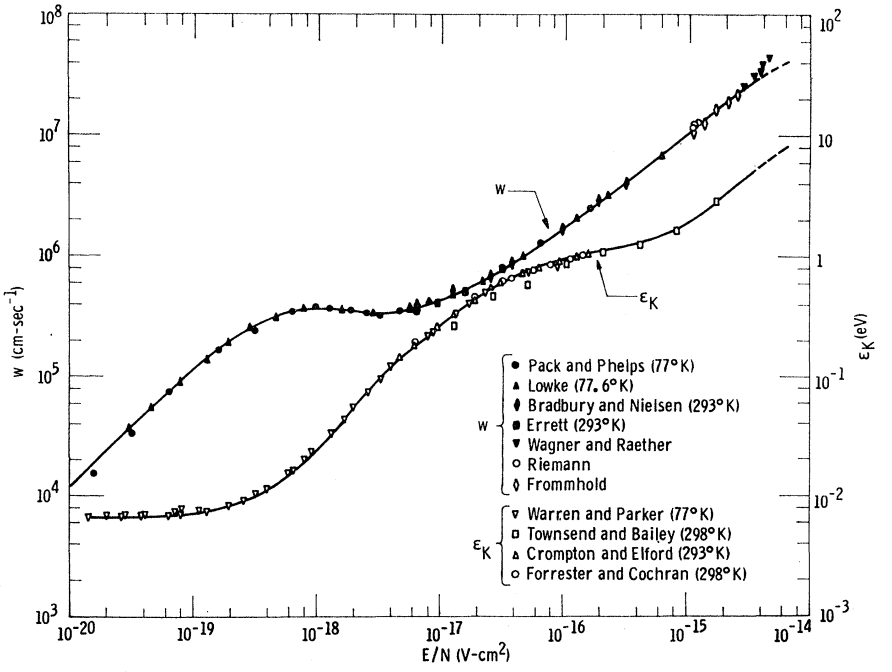


FIG. 4. Drift velocity $w$ and characteristic energy $\epsilon_K$ for electrons in $N_2$ at 77°K. The points represent the various experimental results and the smooth curves our computations for no polarization correction and $\mathcal{Q}=1.04\ ea_0^2$.

Fig. 2. The parameter $\nu_u/N$ is quite sensitive to variations in the tail for $0.1\leqslant\epsilon_K\lesssim 0.5$ eV. If the tail is deleted our calculated points fall well below the experimental line. Increasing the magnitude of higher energy portions of the vibrational cross sections has little effect on $\nu_u/N$ for $\epsilon_K\lesssim 0.5$ eV.

For $0.5\leqslant\epsilon_K\leqslant 1.3$ eV, the higher energy portion of the $v=1$ cross section, and the $v=2$ to 8 processes are the significant vibrational cross sections. In order to obtain the acceptably good agreement with the experimental $\nu_u/N$ data shown in Fig. 2, it was necessary to normalize $\sum Q_v$ to $5.5\times10^{-16}$ cm$^2$ at 2.2 eV. This is to be compared with a value of $3.8\times10^{-16}$ cm$^2$ obtained by Haas[32] and a value ranging from 3.3 to $5.8\times10^{-16}$ cm$^2$, depending on scattering angle, given by Schulz.[9]

Our final $Q_m$ curve applicable to this region of $\epsilon_K$ is confirmed by the good agreement for the $\nu_m/N$ plot. In terms of a comparison of calculated and experimental values of $w$ and $\epsilon_K$, we see from Fig. 4 that the agreement is quite good with all but one set of experimental data. The disagreement with the Townsend and Bailey[26] $\epsilon_K$ data is reminescent of previous discrepancies[2,3] in $H_2$ and in Ar.

### Region C: Elastic Scattering, Rotational, Vibrational, and Electronic Excitation, and Ionization [$\epsilon_K>1.3$ eV]

For $\epsilon_K>1.3$ eV the complexity of the analysis is increased by the growing importance of excitation processes whose thresholds and energy losses are equal to or are in excess of 5.0 eV. To simplify the analysis as much as possible, we have chosen to ascribe energy loss in this region to a small number of inelastic processes; namely, seven excitation and ionization cross sections as shown in Fig. 6. We rely heavily on the measurements by Schulz[7] who used the trapped elec-

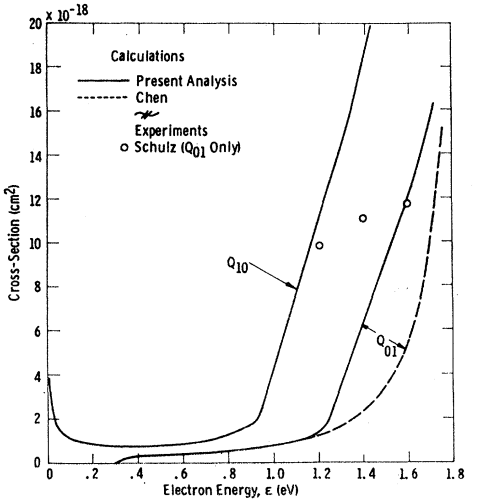


FIG. 5. Low-energy portion or "tail" of the $v=1$ vibrational cross section in the region where the electron energy $\epsilon\leqslant 1.7$ eV. The derived cross section $Q_{01}$ for vibrational excitation, and the cross section $Q_{10}$ for vibrational de-excitation calculated using detailed balancing are shown as solid curves. The curve derived by Chen for $Q_{10}$ is shown as a dashed line. Below 1.2 eV his results and ours are identical. The points represent the experimental results of Schulz for $Q_{01}$ when normalized to our value for the sum of the vibrational excitation cross sections of 5.5 $\times10^{-16}$ cm$^2$ at 2.2 eV.

[32] R. Haas, Z. Physik 148, 177 (1957).

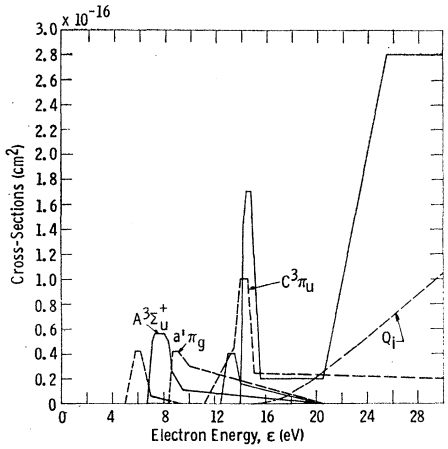


FIG. 6. Effective excitation cross sections with thresholds between 5.0 and 14.0 eV and the ionization cross section $Q_i$. The three excitation processes which have been clearly identified are the $A^3\Sigma_u^+$, the $a^1\pi_g$, and the $C^3\pi_u$. These three levels have thresholds at 6.7, 8.4, and 11.2 eV, respectively. The other three whose exact nature is as yet undetermined have thresholds at 5.0, 12.5, and 14.0 eV. The solid and dashed curves have been used solely for the purpose of clarity in presentation.

tron method to deduce the behavior of excitation cross sections near threshold. Schulz observed three excitation processes which he was able to identify as the $A^3\Sigma_u^+$ state with a threshold at 6.7 eV, the $a^1\pi_g$ state with a threshold at 8.4 eV and the $C^3\pi_u$ state with a threshold at 11.2 eV. In addition to the three processes just discussed Schulz' data also suggest the presence of three unidentified processes with thresholds in the vicinity of 5 eV (presumably vibrational excitation), 12.5 and 14 eV. We have found it desirable to include cross sections for these six processes and have used the threshold energy as suggested by the peaks in Schulz' data. It should be noted that with $N_2$ significant errors result from the use of effective excitation cross sections which are too widely spaced. This is because the large vibrational excitation cross section beginning at 1.7 eV acts as a barrier to the gain of energy by electrons which re-enter the distribution at energies below 1.7 eV after an inelastic collision. Electrons re-entering above 2.9 eV do not experience this barrier. Figure 6 displays the effective vibrational and electronic excitation cross sections we have used to obtain the best fit with experimental data.

As in I and II, it must be emphasized that our derived cross sections are a reasonably realistic set but that they are not unique. The "$C$" state excitation cross section which we have used is in reasonable agreement with recent results of Schulz,[7,33] of Stewart and Gabathuler,[34] and of Legler,[35] but peaks at a significantly lower energy than that obtained by Kishko.[36] However, the additional large cross sections at energies near 14.5 eV, which were found in this analysis to be necessary in order to fit the $\delta/N$ data discussed below, have not been observed to date in any direct experimental measurement of cross sections. Similarly, direct experimental evidence has not been obtained for the rapidly rising cross section at energies above 20 eV. In our analysis this cross section was assigned to the 14-eV level for convenience. The energy loss associated with this cross section may well correspond to some process in which most of the excitation energy is dissipated in radiation or dissociation rather than ionization. Evidence for this type of process has been obtained by Przybylski,[37] although his analysis yields an excitation coefficient which is too small to account for the energy losses. If this excitation process does have an energy loss near 20 eV, then the total cross section required will be significantly smaller than that shown in Fig. 1. Note that except for the $C$ state, the cross sections given in Fig. 6 may not give accurate excitation rates for the individual states when $E/N$ is high enough so that cross sections significantly above threshold are important.

For the ionization cross section $Q_i$ we have used the results of Tate and Smith[10] as shown in Figs. 1 and 6. Sample calculations were performed using three ionization cross sections with different thresholds as given by Fox[38] rather than the single one beginning at 15.6 eV. As long as the sum of the three ionization cross sections was normalized to the same value as the single one, no significant differences were found to exist in the transport coefficients.

In region $C$ in addition to the $\nu_u/N$ and $\nu_m/N$ data,

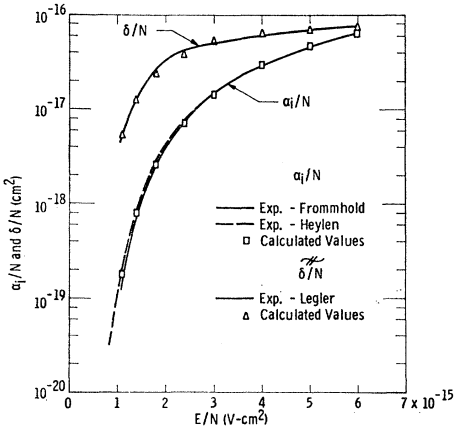


FIG. 7. Ionization coefficient $\alpha_i$ and photon excitation coefficient $\delta$ for electrons in $N_2$ normalized to $N$. $\delta$ is associated with the $C^3\pi_u$ state. Our calculations are shown as points and the various experimental results as smooth curves.

[33] G. J. Schulz (private communication, 1963).
[34] D. T. Stewart and E. Gabathuler, Proc. Phys. Soc. (London) 72, 287 (1958). We have assumed that the apparent threshold found in these measurements can be shifted to 11.2 eV.
[35] W. Legler, Z. Physik 173, 169 (1963).
[36] S. M. Kishko, Opt. i Spektroskopiya 8, 160 (1960) [English transl.: Opt. Spectry. (USSR) 8, 84 (1960)].
[37] A. Przybylski, Z. Physik 168, 504 (1962).
[38] R. E. Fox, J. Chem. Phys. 35, 1379 (1961).

we have recourse to two other experimentally determined transport coefficients—the photon excitation coefficient for the $C$ state $\delta$ and the ionization coefficient $\alpha_i$. Both of these coefficients were calculated using Eqs. II. (10) and (10a). Our procedure in determining excitation cross sections for this region has been first to base our initial estimates primarily on the results of Schulz.[7] A comparison (with experimental results) of calculated values of $\nu_u$, $\delta$, and $\alpha_i$ resulting from the cross sections so obtained led to subsequent revision until acceptable agreement was obtained for all three coefficients.

Figure 7 shows plots of $\delta$ and $\alpha_i$ both normalized to the neutral particle density $N$. The experimental results of Frommhold,[24] Heylen,[39] and Legler[35] are shown as smooth curves and our calculated results as points. In the case of $\alpha_i/N$ the agreement is essentially perfect, but it should be noted that this agreement was obtained for the higher values of $E/N$ by postulating the somewhat unusual shape for the 14-eV process above 20 eV. We were unable to reduce the residual errors of the order of 10% which remain in the $\delta/N$ plot in the region $1.5\times10^{-15}\leqslant E/N\leqslant 2.5\times10^{-15}$ V-cm$^2$. The $\nu_u/N$ results shown in Fig. 2 for region $C$ are considered acceptable.

An additional point to be emphasized in connection with the $\delta/N$ and $\alpha_i/N$ plots is that above $E/N=3.5\times10^{-15}$ V-cm$^2$ over 10% of the total energy input from the field to the electrons is being consumed in the ionization process. Since we have neglected the presence of the extra electron produced in the ionization process, the accuracy of the results above this value of $E/N$ is open to question, and they are shown as dashed lines in Fig. 4.

The momentum transfer cross section derived for region $C$ and shown in Fig. 1 is about 20% smaller than that given by Frost and Phelps for energies above about 2 eV. Our $Q_m(\epsilon)$ curve is therefore about 20% lower than the total cross section given by Brode,[40] but is found to be consistent with mobility and $\epsilon_K$ data by Heylen.[41] The difference between the total cross section and our $Q_m$ curve is typical of the behavior found in the rare gases.[42]

The behavior of the distribution function $f(\epsilon)$ in regions $B$ and $C$ is illustrated[43] by Fig. 8 where we show $f(\epsilon)$ plotted against $\epsilon$ in eV for three values of $\epsilon_K$. At the lowest value of $\epsilon_K$, i.e., 1.0 eV, vibrational excitation is by far the dominant process. The precipitous decrease in $f(\epsilon)$ near 2.0 eV indicates there

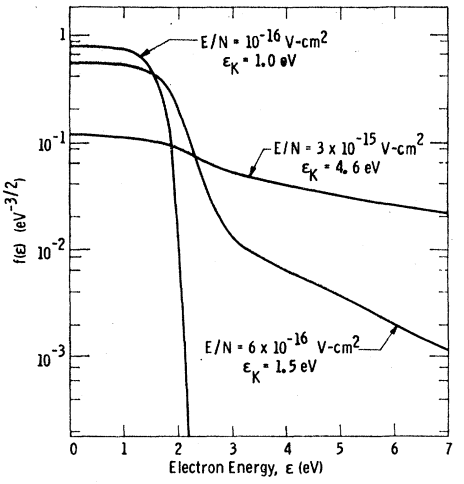


FIG. 8. Energy distribution functions $f(\epsilon)$ for electrons in $N_2$ for three values of $E/N$ and corresponding values of $\epsilon_K$. $f(\epsilon)$ is defined such that $\int_0^\infty \epsilon^{1/2}f(\epsilon)d\epsilon=1$.

are few electrons able to pass the peak of the total vibrational cross section which, therefore, acts almost as an impenetrable barrier. In addition, at low energies the behavior of $f(\epsilon)$ is highly non-Maxwellian as is the case for the other two cases shown, viz., $\epsilon_K=1.5$ and 4.6 eV. For $\epsilon_K=1.5$ eV a substantial number of electrons have energies in excess of 2.2 eV and a high-energy tail is clearly in evidence. In the case of $\epsilon_K=4.6$ eV, the highest value shown, the tail is quite pronounced and extends well into the region of the high-energy electronic excitation processes. Similar plots of $f(\epsilon)$ for air have been reported by Carleton and Megill.[44]

## III. ADDITIONAL CALCULATIONS

In this section we use the results of the previous section to examine the fraction of the input energy dissipated in each of the collision processes. We also use these results to predict the variation of the ratio of the "magnetic drift velocity"[1,3] to the time-of-flight drift velocity with $E/N$, and of the mean electron energy with the strength of a very-high-frequency electric field.

### A. Fractional Energy Loss

We examine the power input from the electrons to the various elastic and inelastic processes as a means of delineating the different regions of dominance and scrutinizing to some extent the sensitivity of the analysis. Figure 9 shows plots of the fractional power input to elastic and inelastic collisions versus $E/N$; an $\epsilon_K$ scale has been added for convenience. Because the continuous approximation to rotation has been used for $E/N>3.0\times10^{-18}$ V-cm$^2$ we have not separated the power input to elastic collisions from that to rotational excitation. The dashed lines indicate the region

[39] A. E. D. Heylen, Nature **183**, 1545 (1959).
[40] R. B. Brode, Rev. Mod. Phys. **5**, 257 (1933).
[41] A. E. D. Heylen, Proc. Phys. Soc. (London) **79**, 284 (1962).
[42] H. S. W. Massey and E. H. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 15.
[43] The curves of Figs. 8, 11, and 12 were obtained from preliminary calculations performed using a polarization correction with a positive quadrupole moment of $+0.96\ ea_0^2$. However, within the context of the discussion of these figures, the results shown do not differ significantly from those obtained using $\mathcal{Q}=1.04\ ea_0^2$ and no polarization correction.
[44] N. P. Carleton and L. R. Megill, Phys. Rev. **126**, 2089 (1962).

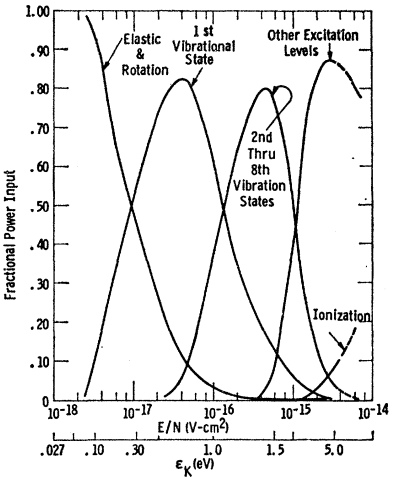


FIG. 9. Fractional power input to elastic and inelastic collisions for electrons in $N_2$ at 77°K as a function of $E/N$. An $\epsilon_K$ scale has been inserted under the $E/N$ scale for convenience. Because the continuous approximation to rotational excitation was used in the energy balance calculations we show combined the power input to elastic collisions and rotational excitation. As shown in I, the contribution of elastic collisions to the rate of energy loss is less than 10% of that for rotational excitation for $\epsilon_K<0.1$ eV. In the interests of simplicity we have also summed the power input to all of the vibrational levels except the first and that to all other excitation levels with the exception of ionization. The fractional power inputs above $E/N=3.5\times10^{-15}$ V-cm² are shown as dashed lines to indicate that in excess of 10% of the total power input is being consumed in ionization and that our results may be in error.

where the fractional power input to ionization is in excess of 10%, since as discussed previously the results in this region may be in error. A number of significant points emerge from a scrutiny of this figure. Up to $E/N=9.0\times10^{-18}$ V-cm² most of the power is consumed in elastic collisions and rotational excitation. However, starting at $E/N=3\times10^{-18}$ V-cm², corresponding to $\epsilon_K=0.10$, the power input to the first vibrational state (primarily the tail) rises rapidly until at $E/N=4.0\times10^{-17}$ V-cm² over 80% of the power input is to this state. A similar situation exists for the 2nd through 8th vibrational states and the electronic excitation levels at higher $E/N$. As a result of this fairly good separation, we have been able to determine with quite acceptable accuracy the shape and magnitude of the tail of the $v=1$ state, the peak value of the total vibrational cross section and the effective electronic excitation cross sections.

## B. Magnetic Deflection Data

Frost and Phelps[1] showed that the ratio of the "magnetic drift velocity" $w_M$ to the time-of-flight drift velocity $w$ is a moderately sensitive indication of the variation of the frequency of momentum transfer collisions with electron energy. The magnetic drift velocity is determined from measurements of the deflection of an electron swarm in a weak magnetic field.[26] With the increasing precision of measurements of electron transport coefficients,[19] we expect that studies of this quantity will yield valuable information regarding the energy dependence of the momentum transfer collision frequency $\nu(\epsilon)$. Here $\nu(\epsilon)=(2e\epsilon/m)^{1/2}Q_m(\epsilon)$ is characteristic of monoenergetic electrons and is to be distinguished from $\nu_m/N$ shown in Fig. 2 which is a function of $\epsilon_K$ and is an effective value for all of the electrons. Now the "magnetic drift velocity" has been calculated by Townsend and Bailey[26] by the relation $w_M=(E/B)\tan\theta$, where $\theta$ is the angle through which a stream of electrons is deflected in a magnetic field $B$ perpendicular to the electric field $E$. The value of $w_M$ can be calculated from the electron energy distribution using the relation[2,3]

$$w_M=(E/B)(\mu_\perp/\mu_T). \tag{2}$$

Since the time-of-flight drift velocity $w$ is given by $w=\mu_{11}E$,

$$w_M/w=\mu_\perp/\mu_T\mu_{11}B. \tag{3}$$

In the limit of small magnetic fields this ratio[45] becomes

$$w_M/w=\mu_\perp/\mu^2B, \tag{4}$$

and has previously[1] been called the "magnetic deflection coefficient." In the case of a momentum transfer collision frequency $\nu(\epsilon)$ which is independent of electron energy $w_M/w=1$ for all $E/N$ and $B/N$.

Calculated values of the low-magnetic field limit of $w_M/w$ for $N_2$ at 77 and 300°K are shown by the smooth curves of Fig. 10. The only experimental measurements of $w_M$ are those of Townsend and Bailey[26] and when these are combined with the experimental time-of-flight data of Lowke[19] one obtains the points shown in Fig. 10. The agreement between the calculated and experimental value is satisfactory over the limited range of $E/N$ for which data are available. Two

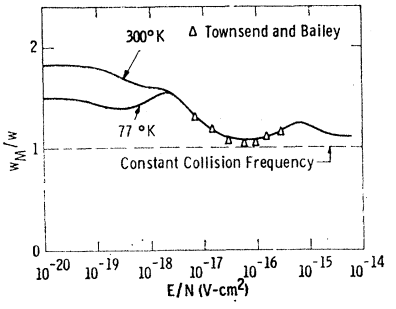


FIG. 10. Magnetic deflection coefficient $w_M/w$ for electrons in $N_2$ at 77 and 300°K in the low magnetic field limit. Our calculations are shown by the smooth curve and the experimental results of Townsend and Bailey by triangles. The dashed curve which represents $w_M/w=1$ is the limiting value for a constant collision frequency, i.e., $Q_m\propto\epsilon^{-1/2}$.

[45] Two values of this ratio are plotted incorrectly in Fig. 4 of I. The correct value for the Maxwellian distribution and $Q_m$ constant is 1.177 and that for a generalized Druyvesteyn distribution and $Q_m\propto\epsilon^{1/2}$ is 1.163.

regions of especial interest which have not been studied experimentally are the region near $E/N=6\times10^{-16}$ V-cm$^2$ and the thermal region below $E/N=10^{-19}$ V-cm$^2$. The calculations for $E/N$ near $6\times10^{-16}$ V-cm$^2$ or $\epsilon_K=1.5$ eV show a peak in the value of $w_M/w$ and indicate a greater energy dependence of the frequency of momentum transfer collisions for electrons in this energy range than for electrons with energies above or below this range. Such a behavior for $\nu(\epsilon)$ or $\epsilon^{1/2}Q_m(\epsilon)$ can be deduced from Fig. 1 for electrons with energies between 1.5 and 2 eV.

The curves of Fig. 10 for the thermal region, $E/N<10^{-19}$ V-cm$^2$, show that $w_M/w$ is calculated to be significantly larger at 300°K than at 77°K. We ascribe this to a more rapid variation[46] of the frequency of momentum transfer collisions for electrons with energies near 0.026 eV than for electrons near 0.0066 eV. This behavior can be deduced from the curve of $Q_m(\epsilon)$ in Fig. 1 which shows that $Q_m(\epsilon)$ approaches a finite value as $\epsilon\rightarrow0$ such that $\nu(\epsilon)$ varies as $\epsilon^{1/2}$ rather than $\epsilon$ as is the case at higher electron energies. Also, the slight minimum in $w_M/w$ near $E/N=3\times10^{-19}$ V-cm$^2$ for 77°K is due to the fact that as $E/N$ increases, there is a decrease in $w_M/w$ resulting from a change in the energy distribution from Maxwellian to the generalized Druyesteyn[41] for a given energy variation of the collision frequency (see I). Subsequently, $w_M/w$ increases due to the increasing collision frequency.

These results show that measurements of the magnetic deflection coefficient and of the shape of cyclotron resonance peaks show a similar sensitivity[47] to energy variation of $\nu(\epsilon)$. This similarity is expected since, as was pointed out in I and II, the conductivity integrals used in the evaluation of ac experiments differ only by numerical coefficients from the mobility integrals applicable to dc measurements in the presence of crossed magnetic and electric fields. In particular, it is easily shown that if $\omega$ and $\omega_b=eB/m$ are numerically equal, then

$$\frac{w_M}{w}=\frac{\mu_\perp}{\mu_T\mu_\parallel B}=\frac{\sigma_i}{\sigma_r}\frac{ne^2}{m\omega\sigma_r(\omega=0)}, \tag{5}$$

where $\sigma_r$ and $\sigma_i$ are the real and imaginary components of the ac conductivity parallel to the ac electric field when no magnetic field is present. In the presence of a magnetic field and in the usual experimental conditions,[48] the integral expressions for $\sigma_r$ and $\sigma_i$ are unchanged except for the substitution of $\omega-\omega_b$ for $\omega$. Thus, for thermal electrons the right-hand side of Eq. (5) has the same value at cyclotron resonance ($\omega=\omega_b$) as $w_M/w$ in Fig. 10 for $E/N\rightarrow0$ and $B\rightarrow0$.

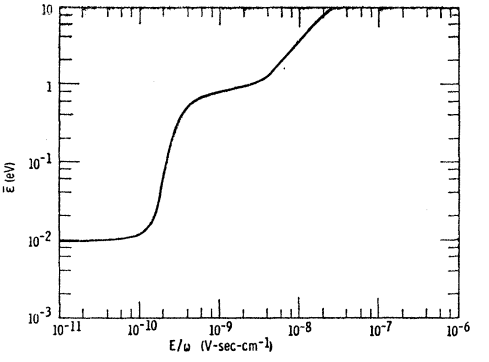


FIG. 11. Mean electron energy $\bar{\epsilon}$ of electrons in $N_2$ at 77°K as a function of $E/\omega$ at high frequencies. The calculations were performed for $\omega/N=6\times10^{-7}$ cm$^3$-sec$^{-1}$ when $E/\omega<3.33\times10^{-9}$ V-sec-cm$^{-1}$ and for $\omega/N=6\times10^{-6}$ cm$^3$-sec$^{-1}$ when $E/\omega>3.33\times10^{-9}$ V-sec-cm$^{-1}$.

### C. AC Calculations

Most previous calculations of the behavior of electrons in $N_2$ subjected to high frequency, ac electric fields have made use of approximate forms for $Q_m$ and $f(\epsilon)$. In particular, Altshuler[49] has derived expressions for the mean electron energy $\bar{\epsilon}$ based on the following three assumptions:

(i) The electrons lose energy to nitrogen molecules only by rotational excitation,

(ii) the effective electron collision frequency is a linear function of $\bar{\epsilon}$, and

(iii) the electron energy distribution function $f(\epsilon)$ is Maxwellian. Perhaps the most startling result of Altshuler's investigation is the prediction of a "hysteresis" effect in the curve of $\bar{\epsilon}$ as a function $E/\omega$, where $\omega$ is the ac radian frequency. As may be inferred from the discussion in Sec. II the accuracy of all three assumptions is open to serious question. We have therefore made use of the cross sections determined in Sec. II to calculate the mean electron energy and the various measurable transport coefficients.

Plotted versus $E/\omega$ in Fig. 11 are our calculated[43] values of $\bar{\epsilon}$ found by computing the distribution function using the Boltzmann equation appropriate to the ac electric field[2] and the cross sections shown in Fig. 1. Perhaps the most important point to be noted is that $\bar{\epsilon}$ is a single-valued function of $E/\omega$. The curve does not exhibit "hysteresis" or double-valued effects described by Altshuler although $\bar{\epsilon}$ does rise steeply in the regions where $10^{-10}\leqslant E/\omega\leqslant4\times10^{-10}$ V-sec-cm$^{-1}$ and $E/\omega\gtrsim2\times10^{-9}$ V-sec-cm$^{-1}$. The explanation for the rather unusual behavior[50] of $\bar{\epsilon}$ with increasing $E/\omega$ is

[46] For a Maxwellian distribution and $\nu(\epsilon)=a\epsilon^j$,

$$w_M/w=[\Gamma(\tfrac{5}{2}-j)\Gamma(\tfrac{5}{2})]/[\Gamma(\tfrac{5}{2}-j/2)]^2 \quad \text{when} \quad j<\tfrac{5}{2}.$$

This expression is valid only for $\omega_b\ll\nu(\epsilon)$, where $\omega_b$ is the electron cyclotron frequency.

[47] L. R. Megill, F. C. Fehsenfeld, and L. K. Droppleman, Bull. Am. Phys. Soc. 9, 186 (1964).

[48] See, for example, F. C. Fehsenfeld, J. Chem. Phys. 39, 1653 (1963).

[49] S. Altshuler, J. Geophys. Res. 68, 4707 (1963).

[50] A. V. Phelps, Natl. Bur. Std. Tech. Note No. 211, Vol. 5 (1964).

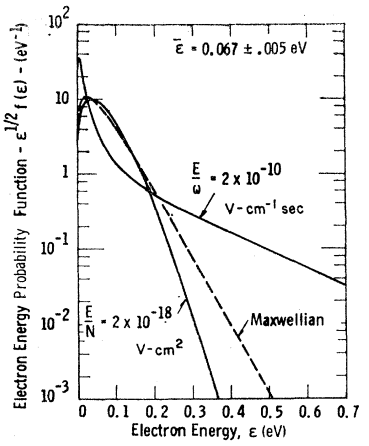


FIG. 12. ac and dc energy probability functions, $\epsilon^{1/2}f(\epsilon)$, for electrons in $N_2$ at 77°K when $\bar{\epsilon}=0.067\pm0.005$ eV. $\epsilon^{1/2}f(\epsilon)d\epsilon$ is the probability of an electron having an energy between $\epsilon$ and $\epsilon+d\epsilon$. The dc case shown represents our calculated results when $E/N=2.0\times10^{-18}$ V-cm$^2$ and $\omega=0$. For comparison purposes we display the Maxwellian given by

$$\epsilon^{1/2}f(\epsilon)=[(27\epsilon/2\pi)(\bar{\epsilon})^{-3}]^{1/2}\exp(-3\epsilon/2\bar{\epsilon}).$$

found in Fig. 12 where we show[43] $\epsilon^{1/2}f(\epsilon)$ versus $\epsilon$ for a dc case $E/N=1.2\times10^{-18}$ V-cm$^2$, and for a very-high-frequency ac case, $E/\omega=2\times10^{-10}$ V-sec-cm$^{-1}$ and $\omega/N=6\times10^{-7}$ cm$^3$-sec$^{-1}$. In addition, a Maxwellian energy probability function is also plotted. For all three cases, $\bar{\epsilon}=0.067\pm0.005$ eV. Although the energy probability function in the dc case is intermediate between the Maxwellian and Druyvesteyn forms,[1] $\epsilon^{1/2}f(\epsilon)$ in the ac case peaks at very low energies and has a long tail at high energies. Since the energy loss processes are the same in both cases, the differences are due to the energy dependence of the energy gain term.[2,49] At the highest $\bar{\epsilon}$ of Fig. 11, the electron energy probability functions for a given $\bar{\epsilon}$ are much more nearly independent of frequency because of the less rapid variation of the electron collision frequency with energy.

## IV. CONCLUSIONS

By means of a numerical solution of the Boltzmann transport equation and subsequent comparison of calculated and experimental values of transport coefficients,[51] we have derived a set of momentum transfer and inelastic collision cross sections for electrons in nitrogen. The gas temperature was taken to be 77°K corresponding to a thermal value of 0.00663 eV for the characteristic energy. From 0.003 to 30 eV a momentum transfer cross section has been found which is consistent with the experimental data. For rotational excitation we find that the theory of Gerjuoy and Stein gives a good fit to experiment using values of the quadrupole moment which are in agreement with most other recent determinations. The use of the polarization correction leads to less satisfactory agreement with experiment. Our cross sections for vibrational excitation are consistent with those of Schulz provided the total cross section is normalized to 5.5 $\times10^{-16}$ cm$^2$ at 2.2 eV. In addition we have found it necessary to add to the $v=1$ vibrational cross section a tail extending down to the threshold of 0.29 eV. We have approximated electronic excitation by a set of six cross sections. The three of these which can be identified unambiguously are the $A^3\Sigma_u^+$, $a^1\pi_g$, and $C^3\pi_u$ states with thresholds at 6.7, 8.4, and 11.2 eV, respectively. The other three whose exact identity is unknown at present have thresholds at 5.0, 12.5, and 14.0 eV. The cross sections we have found for all six of these processes are consistent with Schulz' data. It was determined that a single-energy-loss ionization cross section beginning at 15.6 eV gives almost the same results as three ionization cross sections with different thresholds, provided that the sum of the three ionization cross sections is normalized to the same value as the single one. Finally, using the derived elastic and inelastic cross sections we conclude that the mean electron energy, $\bar{\epsilon}$, is a single-valued function of the electric field $E$ divided by the ac radian frequency $\omega$. However, there is a region of $E/\omega$ where $\bar{\epsilon}$ does increase very rapidly with increasing $E/\omega$—so much in fact that if the distribution function is erroneously assumed to be Maxwellian and energy losses due to vibrational excitation are neglected, then $\bar{\epsilon}$ becomes a multivalued function of $E/\omega$.

[51] A tabulation of the final values of the cross sections and calculated transport coefficients is available on request.

## ACKNOWLEDGMENTS

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