Electron Energy Distribution in Slightly Ionized Air under the Influence of Electric and Magnetic Fields

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We obtain numerically computed solutions to the Boltzmann equation giving the electron energy distribution in weakly ionized air under the following assumptions: (1) that there are present a static magnetic field and an electric field of constant direction (perpendicular to the magnetic field) and a constant rms value; (2) that the gas is homogeneous and the fields uniform in space; (3) that the degree of ionization is weak enough so that electron-electron and electron-ion collisions are negligible; (4) that the fields are such that the average electron energy is much larger than the thermal energy of the gas molecules, and that the heating of the gas by the electrons is negligible; (5) that processes of creation and removal of free electrons are negligible; and (6) that electrons may lose energy in elastic collisions and may also excite rotational, vibrational, and electronic degrees of freedom. To describe these energy-loss processes we use experimental cross sections. We take the constituents of the air to be N_2, O_2, and O, the later being included for upper atmosphere applications. We give distribution functions for a number of limiting cases and compare our solutions to others which may be obtained by less extensive calculations. We demonstrate that while the ratio of electric field to pressure is a good scaling factor for dc excitation this is not the case if either the excitation frequency or the gyro frequency is large compared to the collision frequency.

1. INTRODUCTION

SUPPOSE that in a weakly ionized gas an electric field is established whose orientation and rms value are constant in time. If this field is weak, then it is possible that a quasi-steady state may result in which the gas temperature T_g is hardly increased, but in which the average electron energy is much greater than kT_g. In such a state the electrons are transferring energy to the translational and internal degrees of freedom of the molecules, but this energy is small enough to be removed easily by conduction and radiation from the region where the field exists.

We have become interested in situations of this sort through considering what may happen in the ionosphere when electric fields are applied. Such fields may occur naturally, as when the neutral gas moves across the geomagnetic field, or may be artificially produced, as by radio-frequency probing beams. The actual energy distribution of electrons which may result from the existence of such fields is not easy to predict because the electrons excite rotational, vibrational, and electronic degrees of freedom. Nevertheless, it is very interesting to know the exact form of this distribution in order to predict accurately certain properties. For instance, one would particularly like to know the average number of electrons in the high energy tail of the distribution above the threshold of electronic excitation. This would make possible the prediction of conditions under which excitation by electron impact might be significant in the production of the airglow, and of conditions under which radio-frequency beams might excite an artificial airglow. Also, the collision frequency of electrons in air depends strongly upon

their energy. Hence, a prediction of average collision frequencies in the ionosphere, which is very important for studies of wave propagation, can hardly be made unless the electron energy distribution is known.

Moved by these considerations, we have constructed a form of the Boltzmann equation in which we make certain fairly general assumptions and approximations which include the problems of interest to us. In doing this, we are fortunately able to draw upon the work of several authors[1-4] who have attacked similar problems. Our work adds to theirs chiefly in that we consider the presence of a molecular gas with rotational and vibrational degrees of freedom and in that we consider the discrete effects of several electron energy levels. The solution of our equation, incorporating known experimental data on electron collisions with nitrogen and oxygen, must be made numerically, but the use of a large computer has enabled us to obtain numerical approximations to the electron energy distribution for a wide range of parameters. In the present paper we give our analysis of the Boltzmann equation and discuss some typical properties of our numerical solutions. We leave to a separate paper detailed discussion of our solutions and of their application to our geophysical problems.

2. PARTICULAR EXPRESSION OF THE BOLTZMANN EQUATION

The general expression for the rate of change at a point v of the distribution function $f(v,t)$ of our electron

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[1] P. M. Morse, W. P. Allis, and E. S. Lamar, Phys. Rev. 48, 412 (1935).
[2] S. Chapman and T. G. Cowling, *Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1953), 2nd edition, Chap. 18.
[3] T. Holstein, Phys. Rev. 70, 367 (1946).
[4] C. S. Wu, California Institute of Technology Technical Report No. 32–14, 1960 (unpublished).

gas is

$$\partial f(\mathbf{v},t)/\partial t = -(e/m)(\mathbf{E}+\mathbf{v}\times\mathbf{B})\cdot\nabla_v f(\mathbf{v},t)$$
$$+(\partial f(\mathbf{v},t)/\partial t)_{\text{coll}} \quad (1)$$

where $\mathbf{E}$ is the electric field, $\mathbf{v}$ the velocity, and $\mathbf{B}$ the magnetic field; e and m represent the charge and mass of the electron, respectively. Here we have assumed that we have a homogeneous gas subject to spatially uniform electric and magnetic fields, so that the distribution function is independent of the spatial coordinates. We shall eventually be interested in quasi-steady conditions, in which we set $\partial f/\partial t = 0$, or in which it is meaningful to set equal to zero the average of $\partial f/\partial t$ over many cycles of a time-dependent electric field. For the present we shall keep all terms, however, so as not to lose generality.

Let us now discuss the last term of Eq. (1), which is the rate of change of the distribution function due to collisions made by electrons. We shall restrict ourselves to dealing with a weakly ionized gas, such that electron-electron and electron-ion collisions may be neglected. Furthermore, we shall assume that the electric field is large enough that the average energy of the electrons is much greater than kT_g. Under these conditions we may consider the neutral molecules to be essentially stationary, even though they absorb a small amount of translational kinetic energy from the electrons.

We consider four types of collision; (1) elastic collisions, (2) collisions exciting rotation, (3) collisions exciting vibration, and (4) collisions exciting electronic energy levels. We thereby neglect all processes which create or remove free electrons within the region of interest. For the ionosphere this means first of all that we deal with nighttime conditions only, so that there is no photoelectric production. Then in the ionospheric E region (95 to 120 km altitude) there is an equilibrium between downward diffusion of electrons and recombination plus attachment of electrons to electronegative molecules. The lifetime of an electron in the E region is very long, however, compared to any other characteristic time, so that these processes represent negligible sources and sinks. Neglect of attachment means, in general, that we restrict ourselves to regions of low enough pressure so that three-body attachment by reactions such as

$$O_2+e+M \rightarrow O_2^-+M \quad (2)$$
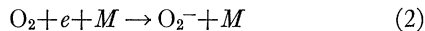
is negligible.[5] Also, we must restrict ourselves to electron energies less than 4 ev, so that dissociative attachment,

$$O_2+e \rightarrow O+O^-, \quad (3)$$
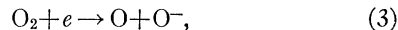
is impossible.[5] We also must assume that the concentration of negative ions is small enough so that detachment by electron impact is a negligible source of new electrons. Finally, we assume that our electrons never

[5] L. M. Chanin, A. V. Phelps, and M. A. Biondi, Phys. Rev. Letters **2**, 344 (1959).

reach energies high enough to ionize. If we consider pure N_2, the limitations concerning negative ions do not enter. In the general case, we can extend our region of validity by considering these effects as small perturbations.

For each specific process that we do consider, there will be a certain energy loss per collision and a certain cross section. We shall express the cross section in terms of the differential cross section $q(v,\psi)$ for scattering an electron through an angle ψ with the appropriate energy loss, which we in turn express as a relation between the magnitude of the electron velocity before and after collision (v' and v, respectively) and the scattering angle ψ: $v'=v'(v,\psi)$. Thus we can write that collisions of a given type will depopulate the velocity space in the neighborhood of a point $\mathbf{v}$ at a rate $-Nvf(\mathbf{v},t)\int_{\omega'}q(v,\psi)d\omega'$, where N is the number density of the neutral particles with which the collision is made. The space about this same point is also being populated by scattering of electrons whose velocities v' have magnitudes given by $v'=v(v,\psi)$. Holstein[3] has given a careful derivation of this term, showing that the net value of the rate of change of population about $\mathbf{v}$ is

$$(\partial f(\mathbf{v},t)/\partial t)_{\text{coll}}$$
$$=\sum_{i,j} N_i v \int_{\omega'}\left[f_i(\mathbf{v}_{ij}',t)\left(\frac{v_{ij}'}{v}\right)^3\frac{\partial v_{ij}}{\partial v}q_{ij}(v_{ij}',\psi)\right.$$
$$\left.-f(\mathbf{v},t)q_{ij}(v,\psi)\right]d\omega', \quad (4)$$

where the index i refers to the particle type and the index j to the process involved in the collision.

Equation (4) completes the analytical expression for $\partial f/\partial t$, but the differential equation obtained by setting $\partial f/\partial t = 0$ is completely intractable, since the distribution function depends on the direction as well as the magnitude of the velocity. One could proceed rigorously with a solution by expanding the function in spherical harmonics. We have chosen instead, following other authors,[2,4] to make an approximation to the function which is of first order in the field quantities $\mathbf{E}$ and $\mathbf{B}$. If we restrict ourselves to the case in which $\mathbf{E}$ is perpendicular to $\mathbf{B}$, then as Wu has shown,[4] the most general such approximation may be written

$$f(\mathbf{v},t) = f_0(v,t)+(\mathbf{v}\cdot\mathbf{E})f_1(v,t)+[\mathbf{v}\cdot(\mathbf{B}\times\mathbf{E})]f_2(v,t). \quad (5)$$

The functions f_0, f_1, and f_2 depend only upon the magnitude of $\mathbf{v}$ (and upon t) and we assume that the second and third terms of the expansion are much smaller than the term $f_0(v,t)$. The physical meaning of this expansion is straightforward: the functions f_1 and f_2 provide bulges on the distribution in the directions parallel to the electric field and to the Hall drift, respectively. The assumption that $f_0(v,t)$ is greater than the other terms corresponds to the experimental fact that the drift velocities of electrons in fields of the magnitude which we consider are very small compared

to the average velocities. We might note in passing that in normalizing the function $f(\mathbf{v},t)$, only the term $f_0(v,t)$ contributes, while in computing the conductivity parallel to $\mathbf{E}$ or the Hall conductivity, only the terms involving $f_1(v,t)$ or $f_2(v,t)$, respectively, enter.

When we substitute this expression for $f(\mathbf{v},t)$ into all but the collision term in Eq. (1), we get

$$\left(\frac{\partial f(\mathbf{v},t)}{\partial t}\right)_{\mathrm{coll}} = \frac{\partial}{\partial t}\{f_0(v,t)+(\mathbf{v}\cdot\mathbf{E})f_1(v,t)$$

$$+(\mathbf{v}\cdot[\mathbf{B}\times\mathbf{E}])f_2(v,t)\}+\frac{e}{m}\left\{\frac{\mathbf{v}\cdot\mathbf{E}}{v}\left[\frac{\partial f_0(v,t)}{\partial v}\right.\right.$$

$$+\mathbf{v}\cdot\mathbf{E}\frac{\partial f_1(v,t)}{\partial v}+\mathbf{v}\cdot[\mathbf{B}\times\mathbf{E}]\frac{\partial f_2(v,t)}{dv}\left.\right]+E^2 f_1(v,t)$$

$$+\mathbf{E}\cdot(\mathbf{v}\times\mathbf{B})f_1(v,t)-B^2(\mathbf{v}\cdot\mathbf{E})f_2(v,t)\Bigg\}. \quad (6)$$

The substitution of the same expression into the collision terms will permit the integration indicated in Eq. (4) and hence remove the problems of the dependence of $f(\mathbf{v},t)$ upon the direction of $\mathbf{v}$. It still gives us, however, a differential equation which depends upon the values of the functions f_0, f_1, and f_2 at two points, v and v'. To see how we may deal with this problem, let us now stop to consider in detail each type of collision which may occur.

3. COLLISION PROCESSES

Elastic Collisions

In an elastic collision, the conservation of kinetic energy and of momentum provides that $\Delta u/u \approx 2(m/M) \times (1-\cos\psi)$ is a good approximation to the fractional energy loss which an electron suffers in a collision (u is the electron energy, m/M the ratio of electronic and molecular masses). Now, since $\Delta u/u \approx 2\Delta v/v = 2(v'-v)/v$, we have that $v' \approx v[1+(m/M)(1-\cos\psi)]$ and that $\partial v'/\partial v = v'/v$. Because $\mathbf{v}'$ differs so little in magnitude from $\mathbf{v}$, we can here expand about the value v the functions of v' which appear in our collision expression and discard the terms of order higher than one in $(v'-v)$. If we denote by $q_c(v,\psi)$ the differential cross section for elastic scattering, then we have for the collision term involving $f_0(v,t)$ and $q_c(v,\psi)$

$$Nv\int_{\omega'}\left\{f_0(v',t)(v'/v)^3\frac{\partial v'}{\partial v}q_c(v',\psi)-f_0(v,t)q_c(v,\psi)\right\}d\omega'$$

$$\approx Nv\int_{\omega'}\left\{f_0(v,t)q_c(v,\psi)+v(m/M)(1-\cos\psi)v^{-4}\right.$$

$$\times\frac{\partial}{\partial v}[v^4 f_0(v,t)q_c(v,\psi)]-f_0(v,t)q_c(v,\psi)\right\}d\omega'$$

$$=Nv^{-2}(m/M)\frac{\partial}{\partial v}\left[v^4 f_0(v,t)\int_{\omega'}(1-\cos\psi)q_c(v,\psi)d\omega'\right]. \quad (7)$$

One such term will arise for each constituent.

The terms in f_1 and f_2 are more complicated, since they lack the spherical symmetry of f_0. In writing these terms let us establish a spherical coordinate system whose polar angle θ is measured from the direction of $\mathbf{E}$ and whose azimuthal angle ϕ is measured from the direction of $\mathbf{B}\times\mathbf{E}$. Thus, if (v,θ,ϕ) are the coordinates of $\mathbf{v}$, we have: $\mathbf{v}\cdot\mathbf{E}=vE\cos\theta$ and $\mathbf{v}\cdot(\mathbf{B}\times\mathbf{E})=vBE\sin\theta\cos\phi$. The term involving $f_1(v,t)$ and $q_c(v,\psi)$ for one constituent now becomes

$$Nv^2 E f_1(v,t)\int_{\omega'}(\cos\theta'-\cos\theta)q_c(v,\psi)d\omega'+Nv^{-2}E(m/M)$$

$$\times\frac{\partial}{\partial v}\left[v^5 f_1(v,t)\int_{\omega'}\cos\theta'(1-\cos\psi)q_c(v,\psi)d\omega'\right]. \quad (8)$$

In these integrals $\cos\theta$ is a constant, since the vector $\mathbf{v}$ is fixed; $\cos\theta'$, however, depends upon the angle ψ between $\mathbf{v}$ and $\mathbf{v}'$ and also upon θ. Holstein[3] has shown that $\cos\theta'=\cos\theta\cos\psi+\sin\theta\sin\psi\cos\gamma$, where γ is an azimuthal angle measured around the polar direction of the vector v, from an arbitrary origin. When this expression is substituted into our integrals the term involving $\cos\gamma$ integrates to zero, since the rest of the integral is independent of γ (i.e., the differential cross section is cylindrically symmetrical about the direction of $\mathbf{v}$). The leading term of Eq. (8) does not vanish altogether, however, as it did for f_0, but becomes for one constituent

$$-Nv^2 E f_1(v,t)\cos\theta\int_{\omega'}(1-\cos\psi)q_c(v,\psi)d\omega'. \quad (9)$$

We may neglect the second term of Eq. (8).[6]

Similarly, the collision term involving $f_2(v,t)$ and $q_c(v,\psi)$ will give an approximate expression

$$-Nv^2 EB f_2(v,t)\sin\theta\cos\phi\int_{\omega'}(1-\cos\psi)q_c(v,\psi)d\omega'. \quad (10)$$

This result follows directly when one considers that the expression $\sin\theta\cos\phi$ merely represents the cosine of an angle between $\mathbf{v}$ and a fixed direction, as $\cos\theta$ did in the development of Eq. (9).

Now, if we define $\sigma_c(v)=\int_{\omega'}(1-\cos\psi)q_c(v,\psi)d\omega'$ which is the usual "diffusion cross section" or "momentum transfer cross section," we can express for any constituent of the gas the contribution to $(\partial f/\partial t)_{\mathrm{coll}}$ due to elastic collisions as

$$Nv^{-2}(m/M)\frac{\partial}{\partial v}[v^4\sigma_c(v)f_0(v,t)]-Nv^2 E\sigma_c(v)f_1(v,t)\cos\theta$$

$$-Nv^2 EB\sigma_c(v)f_2(v,t)\sin\theta\cos\phi. \quad (11)$$

It remains to determine the value of $\sigma_c(v)$ for the

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[6] The propriety of neglecting this term is most easily seen at a later stage in the argument. This term, if retained, would appear in Eq. (20) where it is clearly compared only with terms of lower order.
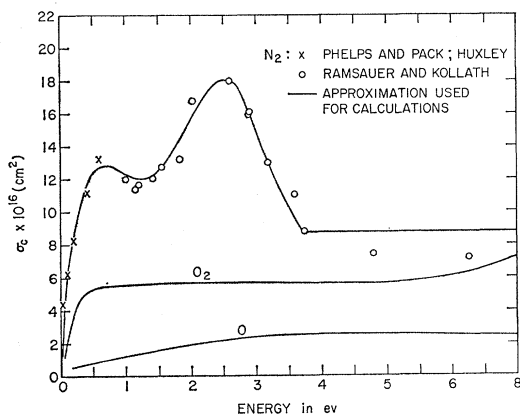
FIG. 1. Diffusion cross sections for N_2, O_2, and O.

gases of interest. Ramsauer and Kollath[7] have measured the total scattering cross section for N_2 and O_2, and the differential cross section for three values of ψ in N_2. They have also measured[8] the differential cross section for 11 values of ψ from $15°$ to $165°$ for several gases which unfortunately did not include N_2, but did include CO, which is isoelectronic with N_2 and which showed a very close resemblance to N_2 in the earlier sequence of measurements covering only three values of ψ. In order to obtain the cross section for elastic scattering from these measurements, we must subtract the contribution of inelastic scattering. The only inelastic process which is significant is vibrational excitation, which is discussed below.

Having subtracted the inelastic cross section from the total cross section we take the ψ dependence of $q_c(v,\psi)$ for N_2 to be the same as that for CO, but normalize the individual values so that their integral (or, more accurately, the sum of the 11 measured values) is equal to the total elastic cross section for N_2. Then we proceed to calculate $\sigma_c(v)$ for N_2 from its definition.

At low electron energies (<1 ev) Phelps and Pack[9] and also Huxley[10] have measured $\sigma_c(v)$ for N_2 directly by diffusion and mobility experiments, and agree very well with each other. Their values, together with the values we have calculated from Ramsauer and Kollath for higher energies, are shown in Fig. 1. Considering the great difference in technique between the two types of experiment, the agreement is very pleasing. There is even some evidence from the theoretical work of Fisk[11] that the secondary maximum of $\sigma_c(v)$ near the junction of the two measurements is real, so we have not attempted to smooth it out.

Crompton and Huxley[12] have measured $\sigma_c(v)$ for O_2 in the range 0.05 ev to 2 ev; the results are shown in Fig. 1. Their cross section has about the same value from 1 to 2 ev as Ramsauer and Kollath's total scattering cross section, suggesting that the scattering is nearly spherically symmetrical. We have thus simply used Ramsauer and Kollath's cross section at higher energies. Below 0.2 ev there is a decided discrepancy between the work of Ramsauer and Kollath and the results of Crompton and Huxley which at the moment we have left unresolved.

Neynaber et al.[13] have measured the total scattering cross section for elastic scattering of electrons from atomic oxygen from 2 to 12 ev. They further show that if one takes the theoretical prediction for s-wave scattering made by Bates and Massey[14] and adds the p-wave contribution calculated by Klein and Brueckner,[15] then one obtains good agreement with experiment. If we thus take the relative contributions of s- and p-wave scattering to be known, we can compute the angular dependence of the scattering and thus the momentum transfer cross section $\sigma_c(v)$. Our results are shown in Fig. 1.

Excitation of Rotation

The exchange of energy between electrons and the rotational motion of N_2 has been discussed theoretically by Gerjuoy and Stein,[16] who consider the interaction of the electron with the quadrupole moment of the molecule. They give simple closed expressions for cross sections for an electron to produce a change of rotational quantum number $\Delta J = \pm 2$. These cross sections are functions of J and of the ratio of initial and final electron momenta. Thus, if the distribution of molecules amongst rotational levels is known, we have a complete description. At any reasonable temperature, however, a large number of rotational levels is populated, which provides a computational difficulty. We have chosen to say, therefore, consistent with our earlier assumption that the average electron energy is much greater than kT_g, that we can regard the fractional energy loss per collision as small compared to unity for the great majority of our electrons. Under these conditions one can calculate from the results of Gerjuoy and Stein an average cross section for a collision producing a change in rotation. This average is (assuming the electron

[7] C. Ramsauer and R. Kollath, Ann. Physik 10, 143 (1931); ibid. 4, 91 (1930); ibid. 9, 756 (1931).

[8] C. Ramsauer and R. Kollath, Ann. Physik 12, 529 (1932).

[9] A. V. Phelps and J. L. Pack, Phys. Rev. Letters 3, 340 (1959).

[10] L. G. H. Huxley, J. Atmospheric and Terrest. Phys. 16, 46 (1959).

[11] See H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena (Clarendon Press, Oxford, England, 1952), pp. 205–217.

[12] These results are quoted as a private communication by I. P. Shkarofsky, M. P. Bachynski, and T. W. Johnson, RCA Victor Co., Ltd. Research Laboratories, Montreal, Canada, Research Report No. 7–801, 1960 (unpublished).

[13] R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, paper read at the Second International Conference on Electronic and Atomic Collisions, Boulder, Colorado, June 1961 (unpublished).

[14] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) A192, 1 (1947).

[15] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 1115 (1958).

[16] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).

momentum to be hardly changed in the collision):

$$\sigma_r = \frac{8\pi Q^2 a_0^2}{15} \sum_{J=0}^{\infty} N_J$$

$$\times \frac{(J+2)(J+1)(2J-1)+J(J-1)(2J+3)}{(2J+1)(2J-1)(2J+3)}, \quad (12)$$

where a_0 is the first Bohr radius, Q is the molecular quadrupole moment in units of ea_0^2, and N_J is the probability of a molecule's being in rotational level J. Fortunately, the factor involving J tends quickly to the value $\frac{1}{2}$ as J increases so that if N_J is small when J is small we have

$$\sigma_r = (4\pi Q^2 a_0^2/15), \quad (13)$$

independent of the distribution of N_J, since $\sum_{J=0}^{\infty} N_J = 1$. Taking the value $Q = 0.96$ adopted by Gerjuoy and Stein, we obtain $\sigma_r = 2.16 \times 10^{-17}$ cm². This σ_r, as well as being independent of electron energy, is also spherically symmetrical, since the authors show that each individual cross section is spherically symmetrical. In addition, the authors themselves show that the expression for the average rate of energy loss of electrons is similarly independent of the distribution of N_J and is

$$\langle du/dt \rangle_{av} = (32\pi Q^2 a_0^2 NvW/15) \quad (14)$$

for an electron of velocity **v**. N is the total density of molecules and W the rotational constant of the molecule, such that the energy of the Jth level is $WJ(J+1)$. We can now construct an average energy loss per collision for an electron of velocity v by dividing $\langle du/dt \rangle_{av}$ by the average collision frequency $vN\sigma_r$. This result gives $\langle \Delta u \rangle_{av} = 8W$, and since for nitrogen $W = 0.249 \times 10^{-3}$ ev ($\ll kT_g$) it is clear that our assumptions are valid over a range of energy including almost all of our electrons. Thus, we shall use these simple approximations for σ_r and $\langle \Delta u \rangle_{av}$ to put into our collision terms. Now, since $\Delta u = mv\Delta v$, the velocity change during a collision is $\Delta v = v' - v = 8W/mv$. These approximations are invalid for energies near the threshold of excitation. Thus we shall arbitrarily put in a cutoff, letting $\sigma_r = 0$ below a certain electron energy. This cutoff can be chosen (say at $u = 0.02$ ev) so that it does not exclude a large energy range but still insures that $\Delta v \ll v$. Then we can do again as we did for the elastic collisions and expand functions of v' about the neighboring value v.

The term in $(\partial f/\partial t)_{coll}$ involving f_0 and σ_r is now (since $\partial v'/\partial v = v/v'$, and σ_r is spherically symmetric):

$$(8WN\sigma_r/mv^2)(\partial/\partial v)[v^2 f_0(v,t)]. \quad (15)$$

The lead term involving f_1 is

$$Nv^2 E f_1(v,t) \int_{\omega'} (\cos\theta' - \cos\theta)(\sigma_r/4\pi)d\omega'$$

$$= -Nv^2 E\sigma_r f_1(v,t) \cos\theta. \quad (16)$$

Similarly, the lead term involving f_2 is

$$-Nv^2 EB\sigma_r f_2(v,t) \sin\theta \cos\phi. \quad (17)$$

As before[6] the terms involving the derivatives of f_1 and f_2 can be neglected.

Huxley[10] has tentatively concluded from experimental work that rotational excitation of O_2 in air is negligible compared to that of N_2. Therefore we shall not consider this process in our calculations.

Excitation of Electronic Levels

In considering excitation of electronic levels we can make little essential simplification of the basic expression, Eq. (4). We may note to begin with that the relation between v' and v, when a level of energy u_j is excited, is $v' = (v^2 + 2u_j/m)^{\frac{1}{2}}$ and hence that $\partial v'/\partial v = v/v'$. If we assume that all cross sections for electronic excitation are spherically symmetrical, then we obtain (letting $\sigma_{ij}(v)$ be the cross section for exciting a particular level j in constituent i) the following contribution to $(\partial f/\partial t)_{coll}$:

$$\sum_{i,j} N_i v\{[f_0(v_{ij}',t)(v_{ij}'/v)^2 \sigma_{ij}(v_{ij}') - f_0(v,t)\sigma_{ij}(v)]$$

$$-Ev\sigma_{ij}(v)f_1(v,t)\cos\theta$$

$$-EBv\sigma_{ij}(v)f_2(v,t)\sin\theta\cos\phi\}. \quad (18)$$

The term involving $f_1(v',t)\cos\theta'$ is zero because of the assumption of spherical symmetry, as is the corresponding term involving $f_2(v',t)$. Note that we have labeled inelastic cross sections with the indices i and j, with i referring to the constituent and j referring to the particular level in the molecule or atom. Since there will be only one elastic collision cross section per constituent and under the approximation being used at most one rotational cross section, we will label these as σ_{ic} and σ_{ir}, respectively. Each of these terms requires different treatment and for that reason this distinction is most convenient.

The energy levels in which we shall be interested for our ionospheric problem are the low-lying levels of O and O_2 shown in Figs. 2 and 3, the lowest level of N_2
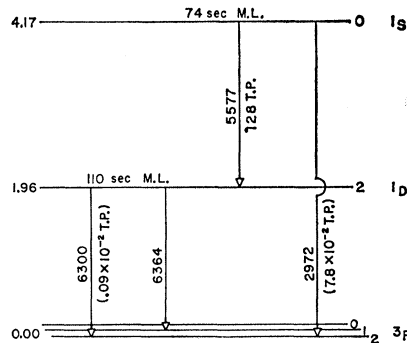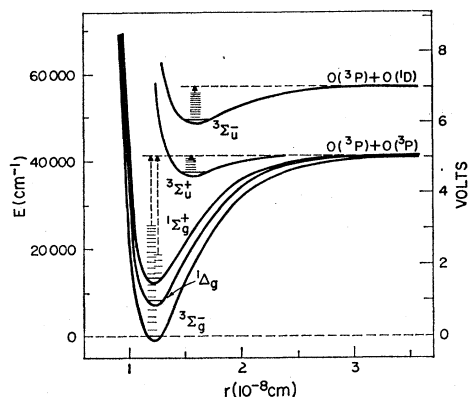

FIG. 2. Low-lying energy levels of atomic oxygen.

FIG. 3. Low-lying energy levels of O_2.

being at about 6.5 ev. Seaton[17] has calculated excitation cross sections for the atomic levels and these are shown in Fig. 4. Also shown are provisional estimates which we made of cross sections for excitation of the lowest O_2 levels, about which nothing was known when we began our calculations. Very recently, however, G. J. Schulz has made a study of these excitation processes and has been kind enough to give us preliminary information on his work, which suggests that our estimates may be as much as three orders of magnitude too large. We discuss below in Sec. 5 the manner in which the size of these cross sections influences our results.

Excitation of Vibration

The excitation of vibration must be treated by essentially the same technique as excitation of electronic levels, since even one vibrational quantum (0.29 ev in N_2) represents a substantial energy loss. Haas[18] and
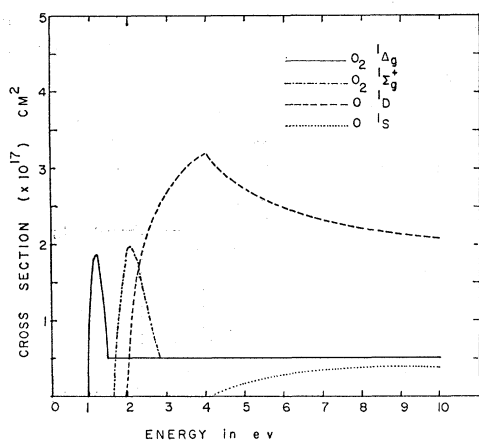
FIG. 4. Cross sections for excitation of the two lowest lying levels of atomic oxygen and assumed values for the two lowest levels in O_2.

[17] M. J. Seaton, Phil. Trans. Roy. Soc. (London) A245, 469 (1953).
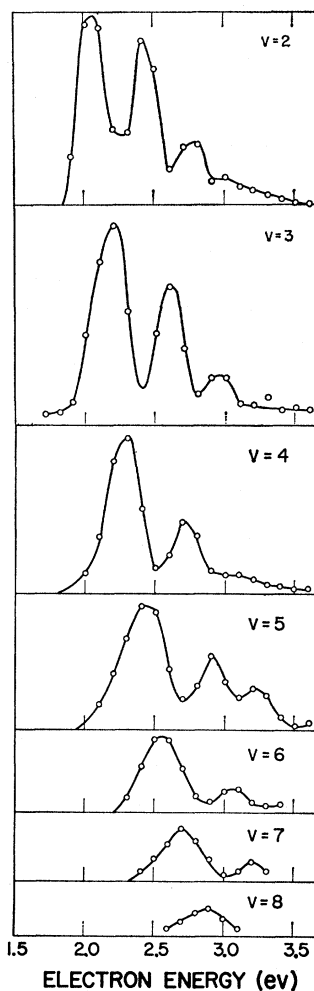[18] R. Haas, Z. Physik 148, 177 (1957).

FIG. 5. Cross sections for excitation of the various vibrational levels of N_2. These data have been kindly supplied to us in advance of publication by Dr. G. J. Schulz of the Westinghouse Laboratories. We have, on the advice of Dr. Schulz, used as a cross section for excitation to the $v=1$ state the cross section for $v=2$ shifted 0.1 ev to lower energy.

Schulz[19] have shown that there is a strong probability for electrons with energies between 1.7 and 3.5 ev to lose energy equal to one or more vibrational quanta in N_2. Both authors interpret this process as the formation of an unstable N_2^- ion which can decay into various vibrational levels of N_2.

Haas' experiment was of the swarm type and showed that the maximum of the cross section for this energy loss process occurs at 2.3 ev and is about 3×10^{-16} cm^2 in magnitude. Schulz first made measurements by the trapped-electron method and then extended these with a high-resolution electron gun and analyzer. In this latter experiment he was able to measure relative cross sections for exciting individual vibrational levels in N_2. These cross sections are shown in Fig. 5, in arbitrary units. For our calculation we normalize them so that their sum agrees with Haas' measurement at 2.3 ev. For the time being we shall assume that these cross sections are spherically symmetrical, so that these excitations appear in our equations in just the same

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

manner as electronic excitations. In further discussion we shall lump all these processes together as discrete excitation.

There is some evidence that electrons also excite vibration in O_2 at energies of a few tenths of an electron volt. Since the study of this process by mobility and diffusion experiments is complicated by attachment, it is difficult to assign cross sections to specific reactions. At present we shall simply ignore this process, since O_2 does not make up more than 10% of the total gas density in the region of the atmosphere in which we are principally interested.

4. SOLUTION OF THE BOLTZMANN EQUATION

If we now collect all the collision terms and substitute them into Eq. (6) this yields a lengthy expression which may be separated into three expressions for $\partial f_0/\partial t$, $\partial f_1/\partial t$, and $\partial f_2/\partial t$ by multiplying successively by $1/4\pi$, $(3/4\pi) \cos\theta$ and $(2/\pi) \cos\phi$ and integrating over the total solid angle. This process yields the following equations:

$$\frac{\partial}{\partial t}[f_0(v,t)] = -\frac{1}{3}\frac{eE^2}{mv}\frac{\partial}{\partial v}[v^3 f_1(v,t)]$$

$$+ \sum N_i \left\{ \frac{8W_i\sigma_{ir}}{mv^2}\frac{\partial}{\partial v}[v^2 f_0(v,t)] \right.$$

$$+ \frac{m}{M_i v^2}\frac{\partial}{\partial v}[\sigma_{ic}(v)v^4 f_0(v,t)]$$

$$\sum_j v[\sigma_{ij}(v_{ij}')f_0(v_{ij}',t)(v_{ij}'/v)^2$$

$$\left. -\sigma_{ij}(v)f_0(v,t)] \right\}, \quad (19)$$

$$\frac{\partial}{\partial t}[Evf_1(v,t)] = \frac{-eE}{m}\frac{\partial}{\partial v}[f_0(v,t)] + \frac{e}{m}B^2Evf_2(v,t)$$

$$- Ev^2 f_1(v,t)\sum_{i,j} N_i[\sigma_{ic}(v)$$

$$+ \sigma_{ir}(v) + \sigma_{ij}(v)], \quad (20)$$

and

$$\frac{\partial}{\partial t}[BEvf_2(v,t)] = -\frac{e}{m}BEvf_1(v,t)$$

$$- EBv^2 f_2(v,t)\sum_{i,j} N_i[\sigma_{ic}(v) + \sigma_{ir}(v) + \sigma_{ij}(v)]. \quad (21)$$

We now express the time dependence of the electric field as $E = E_0 \cos\beta t$, and assume that β is large enough so that f_0 and $\partial f_0/\partial v$ do not vary appreciably during one cycle of the exciting field. We thus consider the quasi-steady condition of constant E_0 in which f_0 and $\partial f_0/\partial v$ are essentially constant in time. Under these conditions we can solve Eqs. (20) and (21). We shall carry out only the solution for f_1, since it is the only

one which enters into Eq. (19). A solution of Eqs. (20) and (21) is

$$f_1(v,t) = -\frac{e}{mv}\frac{df_0(v)}{dv}(\alpha + \alpha' \tan\beta t), \quad (22)$$

where

$$\alpha = \frac{\nu(\beta^2 + \omega^2 + \nu^2)}{(\beta^2 - \omega^2)^2 + \nu^4 + 2\nu^2(\beta^2 + \omega^2)}.$$

Here $\omega \ (=eB/m)$ is the electron gyro frequency and $\nu \ (=\sum_{ij} N_i[\sigma_{ic}(v) + \sigma_{ir}(v) + \sigma_{ij}(v)])$ is the electron collision frequency. The form of α' is similar, but will not contribute to the final expression.

We may now, using Eq. (22), express Eq. (19) in terms of f_0 and its derivatives only. We then integrate over a cycle of the exciting field. Only the first term on the right-hand side of Eq. (19) is now considered to be time dependent. One portion of this term involves α' and integrates to zero, while the other portion involves $E_0^2 \cos^2\beta t$, which integrates to $E_0^2/2$. If we now use E to denote the rms value of the field we obtain:

$$\frac{1}{3}\left(\frac{eE}{mv}\right)^2\frac{d}{dv}\left[v^2\alpha(v)\frac{df_0(v)}{dv}\right] + \sum_i N_i \left\{ \frac{8W_i\sigma_{ir}}{mv^2}\frac{d}{dv}[v^2 f_0(v)] \right.$$

$$+ \frac{m}{M_i v^2}\frac{d}{dv}[v^4\sigma_{ic}(v)f_0(v)]$$

$$+ \sum_j v[\sigma_{ij}(v_{ij}')(v_{ij}'/v)^2 f_0(v_{ij}')$$

$$\left. - \sigma_{ij}(v)f_0(v)] \right\} = 0. \quad (23)$$

To obtain the steady-state solution for a dc field, we set $\beta = 0$ and all time derivatives equal to zero in Eqs. (19), (20), and (21). Mutual solution of these equations then gives Eq. (25) again, with E denoting the value of the dc field. It is not possible, however, to let β vary continuously from high frequencies to zero, because the assumptions involved in integrating over a cycle of the exciting field break down when $1/\beta$ is comparable to or greater than the relaxation time of the electrons. We define the relaxation time with the relation

$$\tau_r = -\int_{u_{av}}^{0.4u_{av}} \frac{du}{\eta(u)u\nu(u)},$$

where $\eta(u)$ is the average fractional energy loss of the electron per collision. In a case in which only elastic collisions are considered $\eta(u)$ is $2m/M$. In a molecular gas the average must be taken over all loss processes.

For our purposes it is convenient to have as the independent variable the energy u rather than the velocity. We therefore let $u = kv^2$, where k is such that u is expressed in electron volts; we also let $g(u) \equiv f(v)$,

but for simplicity we still use $\sigma(u)$ to denote cross sections as functions of u. Our equation then becomes

$$\frac{4}{3}\left(\frac{eE}{m}\right)^2 k\frac{d}{du}\left[u^{\frac{3}{2}}\alpha(u)\frac{dg(u)}{du}\right]$$

$$+\sum_i N_i k^{-\frac{1}{2}}\left\{\frac{2m}{M_i}\frac{d}{du}[u^2\sigma_{ic}(u)g(u)]\right.$$

$$+\frac{16W_i}{m}k^{\frac{1}{2}}\sigma_{ir}\frac{d}{du}[ug(u)]$$

$$+k^{\frac{1}{2}}\sum_j[(u+u_{ij})\sigma_{ij}(u+u_{ij})g(u+u_{ij})$$

$$\left.-u\sigma_{ij}(u)g(u)]\right\}=0. \quad (24)$$

The u_{ij} are defined from the equation $v_{ij}'=[v^2+(u_{ij}/k)]^{\frac{1}{2}}$. We may obtain as a first integral of Eq. (24) the following:

$$\frac{dg}{du}=-\sum_i\frac{m^2N_i}{(eE)^2\alpha(u)k}\left\{\frac{3}{2}\frac{m}{M_i}\frac{u^{\frac{1}{2}}}{k^{\frac{1}{2}}}\sigma_{ic}(u)g(u)\right.$$

$$+12\frac{W_ik}{m}\sigma_{ir}u^{-\frac{1}{2}}g(u)$$

$$+\tfrac{3}{4}k^{-\frac{1}{2}}u^{-\frac{1}{2}}\sum_j\int_0^u[(u+u_{ij})\sigma_{ij}(u+u_{ij})g(u+u_{ij})$$

$$\left.-u\sigma_{ij}(u)g(u)]du\right\}. \quad (25)$$

The constant of integration has been chosen to satisfy the condition that the first derivative must go to zero as u increases without limit.[20]

The solution of this equation, using experimental and theoretical data for the various cross sections, requires numerical procedures. The integral involving the inelastic cross sections in Eq. (25) requires knowledge of the function at energy values $u+u_{ij}$ for all i and j when the function is being evaluated at energy u. For this reason it is necessary, if one starts the solution at the origin, to use an iterative procedure in the solution. We have found that this procedure results in excessive use of computer time, principally because of the difficulty involved in determining good interpolation formulas.

We may, however, simplify the integral term in Eq. (25) if we note that $\sigma_{ij}(u)=0$ for $u<u_{ij}$ and if we assume that there exists some value u_m such that for $u>u_m$, $g(u)$ is so small that the integrand in this term may be considered to be zero. Under this assumption

[20] B. Sherman, J. Math. Anal. Appl. 1, 342 (1960).

we may write the integral as follows:

$$\int_0^u[(u+u_i)g(u+u_i)\sigma(u+u_i)-ug(u)\sigma(u)]du$$

$$=\int_0^{m-u_iu}(u+u_i)g(u+u_i)\sigma(u+u_i)du$$

$$-\int_{u_i}^{u_m}ug(u)\sigma(u)du+\int_{u_m-x}^{u_m}ug(u)du$$

$$-\int_{u_m-(x+u_i)}^{u_m-u_i}(u+u_i)g(u+u_i)\sigma(u+u_i)du,$$

where we have set the integral limit u equal to u_m-x. Since

$$\int_0^{u_m-u_i}(u+u_i)g(u+u_i)\sigma(u+u_i)du$$

$$-\int_{u_i}^{u_m}ug(u)\sigma(u)du=0,$$

we can solve Eq. (25) by starting at $u=u_m$ and integrating toward the origin. To obtain starting values for $g(u)$ we set $\sigma_{ic}(u)$ and $\sigma_{ir}(u)$ constant for $u>u_m$, whereupon we obtain an analytical solution to Eq. (25) in the region $u>u_m$.

After obtaining values of $g(u)$ for a particular case we construct the function $G(u)=Au^{\frac{1}{2}}g(u)$ such that $\int_0^{u_m}G(u)du=1$. This function $G(u)$ gives the fractional number of electrons per unit energy interval.

5. RESULTS

To classify the results which we will obtain let us first note that, as stated above, our solution is valid in two different frequency regions: zero frequency and frequencies such that $\beta\gg1/\tau_r$. We can further divide these regions by looking at the dependence of the function $\alpha=\nu(\beta^2+\omega^2+\nu^2)/[(\beta^2-\omega^2)^2+\nu^4+2\nu^2(\beta+\omega^2)]$ upon the relative magnitudes of the three frequencies involved. We shall now discuss several particular cases which are distinguished by this means.

Case I: $\nu\gg\beta$, ω: This limiting case may occur when $\beta=0$ (dc) or when β is at the lower end of the allowed ac range. This latter condition is possible because $\nu\gg1/\tau_r$ so that one may have $\nu\gg\beta\gg1/\tau_r$. In this limit α approaches the value $1/\nu$. If we substitute this asymptotic value into Eq. (25), we obtain

$$\frac{dg}{du}=-\{\sum_{ij}N_i[\sigma_{ij}(u)+\sigma_{ir}(u)+\sigma_{ic}(u)]\}\sum\frac{N_im^2}{(eE)^2k}$$

$$\times\left\{\frac{3m}{2M_i}\frac{u}{k^{\frac{1}{2}}}\sigma_{ic}(u)g(u)+\frac{12W_i}{m}k^{\frac{1}{2}}\sigma_{ir}g(u)\right.$$

$$+\frac{3}{4}\frac{u^{-1}}{k^{\frac{1}{2}}}\sum_j\int[(u+u_{ij})\sigma_{ij}(u+u_{ij})g(u+u_{ij})$$

$$\left.-u\sigma_{ij}(u)g(u)]du\right\}. \quad (26)$$

Now, if we express each N_i as $N_i = h_i N$, where N is the total density, we see that the solution of Eq. (26) will depend upon the ratio E/N and upon the relative composition of the gas. The magnetic field is negligible so long as $\omega \ll \nu$.

This general result is well known. We can present here, however, the entire distribution function for a set of parameters satisfying the above conditions. This is shown in Fig. 6(a) and 6(b) for the values: $E = 0.02$ v/m; $N = 6.7 \times 10^{12}$ cm^{-3}; $h(N_2) = 0.60$; $h(O_2) = 0.13$; $h(O) = 0.27$. For comparison we include a Maxwell distribution and a Druyvesteyn distribution each with the same average energy as the real distribution.

These latter functions can arise out of a crude analysis of this type of problem, as we may see by neglecting the inelastic collision terms in Eq. (26) and considering a gas of only one constituent, whereupon we get

$$dg/du = -[N\sigma_c(u)/keE]^2(3m^3/2M)ug(u). \quad (27)$$
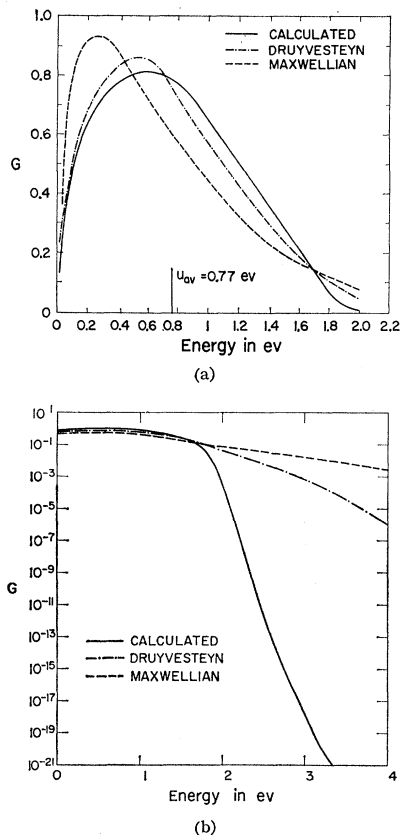
If we further assume that $\sigma_c(u)$ is a constant, the

(a)

(b)

FIG. 6. This figure, (a) and (b), shows the calculated electron energy distribution in air with a number density of 6.7×10^{12} cm^{-3}, of which 60% is N$_2$, 13% is O$_2$, and 27% is O. A dc electric field of 0.02 v/m is applied. The magnetic field is zero. The equivalent value of E/p is 1.07 (v/cm)/mm Hg. Maxwell and Druyvesteyn curves with the same average energy are drawn in for comparison. Fig. 6(b) is on a log plot in order to show the effect of the inelastic collisions on the high energy tail of the distribution function.
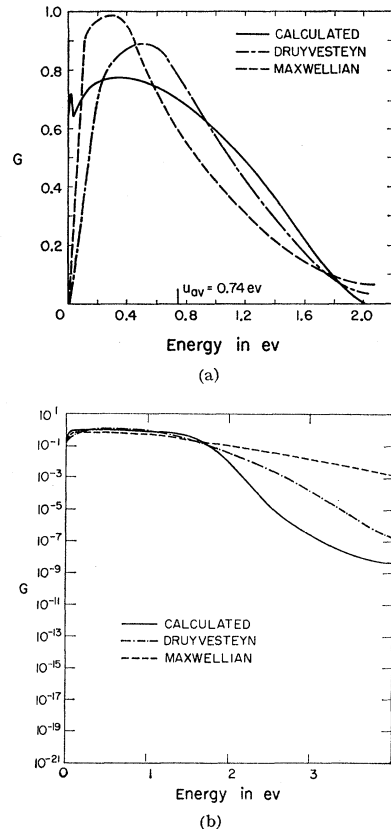

(a)

(b)

FIG. 7. This figure, (a) and (b), shows the calculated electron energy distribution compared to the distributions of Maxwell and Druyvesteyn for the same parameters as in Fig. 6(a) and 6(b) with the exception that the exciting field is 15 v/m at 50 Mc/sec. This is equivalent to a magnetic field of 5×10^{-5} webers/m^2 and an electric field of 0.425 v/m. Note that with this magnetic field the electric field required to obtain the same average energy is 20 times greater than that required without the magnetic field.

solution of Eq. (27) is the Druyvesteyn function $g_D(u)$ $= A_D \exp[-0.548(u/u_{av})^2]$. If we choose instead to let $u^{\frac{1}{2}}\sigma_c(u)$ be constant (constant collision frequency), then the solution of Eq. (27) has the form of a Maxwell distribution $g_m(u) = A_M \exp[-\frac{3}{2}(u/u_{av})]$. This is essentially a coincidence and does not mean that the electrons reach a thermal equilibrium. In strongly ionized gases the tendency is for the electrons to "thermalize" independent of the neutral gas because the effects of electron-electron collisions dominate those of electron-neutral collisions.[21] Extension of the temperature concept to slightly ionized gases, however, must be undertaken with caution. Either of the functions $G_M(u) = u^{\frac{1}{2}}g_M(u)$ or $G_D(u) = u^{\frac{1}{2}}g_D(u)$ may be a useful solution for gases in which inelastic collisions are unimportant, such as the rare-gases. Which one is the better approximation depends on the variation of $\sigma_c(u)$ with u. For the particular case we present in Fig. 6, however, the neglect of inelastic collisions will result in

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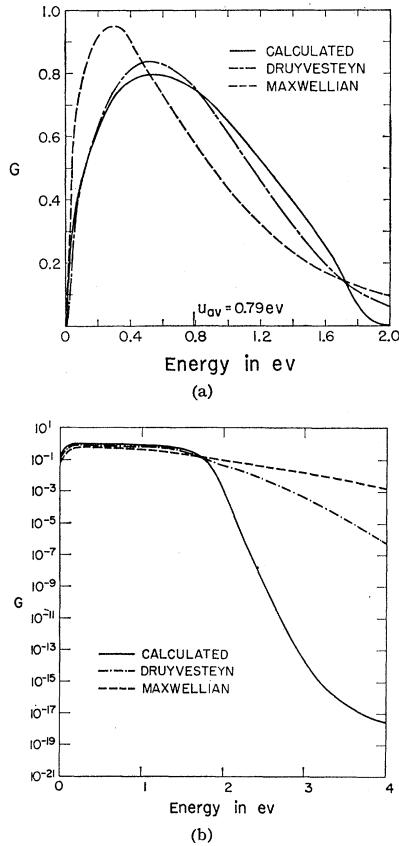[21] J. H. Cahn, Phys. Rev. **75**, 293 (1949).

(a)

(b)

FIG. 8. This figure, (a) and (b), shows the same types of comparison as do Figs. 6(a) and 6(b) and 7(a) and 7(b) with the exception that $\nu_{av} \approx \omega = \beta = 4.4 \times 10^5$ sec^{-1} and the electric field is 0.025 v/m.

an average energy of 25–30 ev instead of the 0.77 ev which results where these processes are included. One may on some occasions, however, assume one of the two above forms and normalize to an average energy determined by other means (e.g., by experiment). The difficulties inherent in even this process, however, are apparent in Fig. 6(b) if one is attempting to obtain results which depend upon the number density in the high energy tail of the distribution function.

Case II: $\beta \gg \nu$, ω: in this limiting case of very high exciting frequencies, α approaches the form ν/β^2. If we put this into Eq. (25) we obtain

$$\frac{dg}{du} = -\frac{\beta^2 m^2}{(eE)^2 k \sum_i N_i [\sigma_{ij}(u) + \sigma_{ir}(u) + \sigma_{ic}(u)]}$$

$$\times \sum_i N_i \left\{ \frac{3m}{2M_i} \sigma_{ic}(u) g(u) + \frac{12W_i}{m} k\sigma_{ir} u^{-1} g(u) \right.$$

$$+ \tfrac{3}{4} u^{-2} \sum_i \int_0^u \left[(u+u_{ij})\sigma_{ij}(u+u_{ij}) g(u+u_{ij}) \right.$$

$$\left. - u\sigma(u) g(u) \right] du \bigg\}. \quad (28)$$

If we again set $N_i = h_i N$, we note that Eq. (28), and hence its solution, are independent of N. Thus the distribution function depends only on the relative composition and not on the total density of the gas. The other parameters which one can control are β and E, occurring in the ratio E/β which is thus useful in scaling solutions. The effect of the magnetic field is negligible so long as $\omega \ll \beta$. The parameter E/N, which is used to scale dc results, has here no relevance whatever.

These results are also known (though perhaps not so widely as those for Case I) and are supported by experimental data of microwave discharges.[22] Our detailed results are here presented in Fig. 7 for $E=15$ v/m, $\beta = 3.14 \times 10^8$ sec^{-1}, and the same gas composition as Case I. They show a distribution function substantially different from that of Case I, in that there are
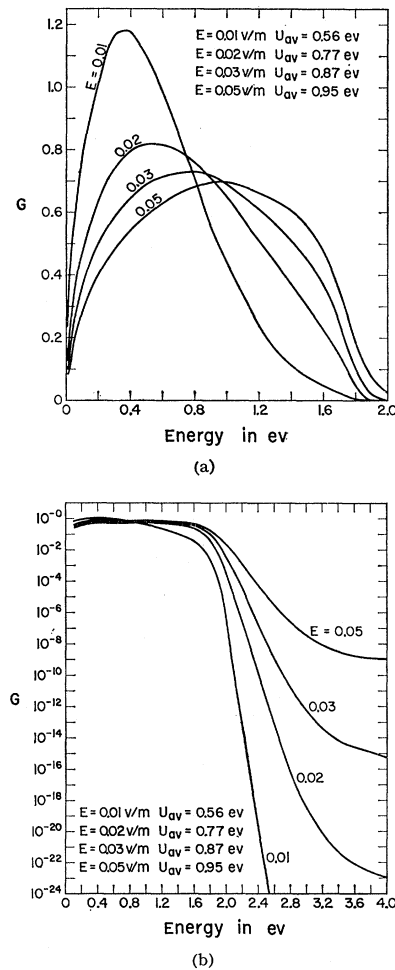

(a)

(b)

FIG. 9. This figure, (a) and (b), shows the change of the distribution with changing electric field. Other parameters are the same as for Fig. 6. Note in particular in Fig. 9(b) the large change in the tail of the distribution function even though the average energy changes but little.

[22] H. Margenau, Phys. Rev. 73, 297 (1948).

more electrons at very low and very high energies. The same comparison is made with the functions $G_D(u) = u^{\frac{1}{2}} g_D(u)$ and $G_M(u) = u^{\frac{1}{2}} g_M(u)$. In Fig. 7(a) the bump on the distribution function near the origin is evidence of our crude procedure in cutting off σ_r for nitrogen. This bump is imperceptible in Case I because the values of the function near the origin are so much smaller.

Case III: $\omega \gg \nu$, β: In this limit the form of α is ν/ω^2. This yields essentially the same results as those of Case II, with the scaling parameter now E/ω. In the present case the value of β is unimportant, so long as β is much less than ω (and so long as β falls within our basic limits). Thus the distribution functions of Case II and Case III are identical for equal values of the parameters E/β and E/ω. Thus the results in Fig. 7 may be taken, for example, to pertain to the conditions: $B = 5 \times 10^{-5}$ webers/m², $E = 0.425$ v/m. We may also compare this result to that of Case I and notice that to obtain the same average energy as that of Fig. 6, for which $B = 0$, one requires twenty times the electric field strength used in Case I.

In addition to the three limiting cases just discussed we have for comparison computed the distribution function for a case in which the average collision frequency ν_{av} is about equal to β which is in turn equal to ω. This case, shown in Fig. 8 is for the same gas parameters as for Figs. 6 and 7 and shows the same type of comparison. Here we have $\beta = \omega = 4.4 \times 10^5$ sec⁻¹ and $E = 0.025$ v/meter. These parameters result in an average energy of 0.787 ev with an average collision frequency of 3.92×10^5 sec⁻¹. This case has a shape very similar to that in Case I with the exception that the high energy tail is intermediate between the values for Case I and Case II. The electric field necessary for the excitation, however, is very little more than that required for strict dc excitation.

We show in addition the effect of increasing the electric field for a dc excitation as shown in Fig. 9. The gas parameters are the same as those used in the previous calculations. These calculations show the effect of the very large nitrogen vibrational cross sections in limiting the growth of the energy. The bulges which appear on the higher energy curves in the region from 1 to 2 ev are a reflection of the fact that in inelastic collisions with N_2 the energy at the threshold is usually considerably larger than the energy lost in the collision. Therefore, a collision of a 1.7- to 3.5-ev electron with a nitrogen molecule has a high probability
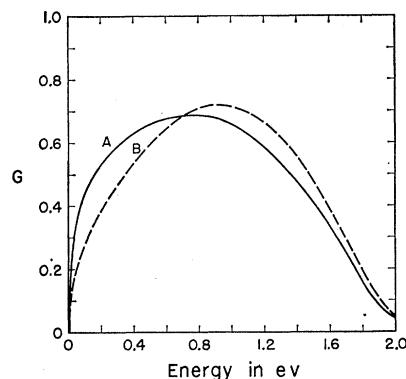

FIG. 10. This figure shows the effect of lowering the value of the assumed O_2 electronic cross sections by a factor of 10^4. Curve A gives the results for the smaller cross section, curve B the results for the larger.

of leaving the electron with energy between 1 and 2 ev, which results in a relatively higher population in this energy region. It is of interest to note that although the average energy changes only from 0.56 to 0.96 ev with a change in the electric field of from 0.01 to 0.05 v/m an experiment sensitive to the number of electrons with 2.4 ev energy, for example, would reflect a change of nearly 16 orders of magnitude.

In Sec. 3 it was stated that the effect of reducing the two molecular oxygen cross sections would be discussed. As an example we show in Fig. 10 two distributions with exactly the same parameters with the exception that in one case the O_2 cross sections are decreased by four orders of magnitude. The result is very slight, due principally to the fact that the original cross sections assumed for O_2 were small relative to the N_2 vibrational cross sections. All the cases presented here show the dominant role of the N_2 cross sections in controlling the energy of electrons in air.

ACKNOWLEDGMENTS