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Measurements of the Attachment of Low-Energy Electrons to Oxygen Molecules*

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The attachment coefficients for low-energy electrons to oxygen are determined from the electron and negative-ion waveforms resulting when a pulse of photoelectrons traverses a drift tube. The pressure dependence of the attachment coefficient shows that for average electron energies below about 1 eV the electrons attach to oxygen in three-body collisions involving two oxygen molecules or an oxygen molecule and a foreign gas molecule. The three-body coefficient for pure oxygen increases with electron energy to a maximum of 5×10^{-30} cm^6/sec at an average energy of 0.09 eV and then decreases slowly. At gas temperatures of 370, 300, 195, and 77°K the three-body attachment coefficients for thermal electrons are, respectively, 3.1×10^{-30}, 2.8×10^{-30}, 2×10^{-30}, and less than 1×10^{-30} cm^6/sec. The efficiences of N_2 and He as third bodies are approximately 50 and 100 times lower than for O_2. These results predict attachment coefficients for the lower ionosphere which are one to two orders of magnitude lower than the previously accepted values. For average electron energies above about 1.5 eV the pressure dependence and the magnitude of the attachment coefficient are consistent with previous electron beam studies of the process of dissociative attachment.

I. INTRODUCTION

STUDIES of the attachment of electrons to oxygen molecules to form negative ions have been the subject of a number of investigations during the last several decades.[1–18] The present paper is concerned with the experimental determination of the rate of attachment to oxygen molecules by electrons with average energies between a few hundredths and a few electron volts.[10] In the earlier work it was concluded that, at pressures of the order of tens of mm Hg, the attachment process exhibited a *two*-body pressure dependence[1,6,7] over the entire energy range. In contrast, it will be shown that the low-energy (<1 eV) electron attachment involves a *three*-body process, thus removing some of the apparent contradictions of theoretical ideas concerning the nature of the attachment reaction.

The previously proposed attachment processes are reviewed in Sec. II. In Secs. III and IV we give the principle of the measurement and discuss the apparatus. The results are presented in Sec. V and their significance is discussed in Sec. VI. The implications of these results for ionospheric analyses are briefly summarized in Sec. VII.

II. ELECTRON ATTACHMENT PROCESSES

The capture of an electron by a neutral atom or molecule to form a stable negative ion involves the transition of an electron from a free (continuum) state to a bound state of the resulting negative ion, with an attendant release of energy. For the case of *radiative* attachment the electron makes a radiative transition from the free to the bound state, i.e.,

$$e+O_2\rightarrow O_2^-+h\nu, \tag{1}$$

where the emitted photon carries off the excess energy of the reaction. For the purposes of the present paper, the rate of radiative attachment is too small to be detected.[14]

There are two attachment processes involving radiationless electron capture of interest for oxygen. In these processes there is an intermediate, unstable negative-ion state formed. Thus, the attachment process may be considered to occur in two stages; first, the formation of an unstable state of the negative ion, which then may either re-emit the electron (auto-

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[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).

[2] R. H. Healey and C. B. Kirkpatrick as quoted in R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless Ltd., Sydney, Australia, 1941), p. 94.

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[15] W. W. Lozier, Phys. Rev. **46**, 268 (1934).

[16] J. D. Craggs, R. Thorburn and B. A. Tozer, Proc. Roy. Soc. (London) **A240**, 473 (1957); I. S. Buchelnikova, Zhur. Eksptl. i. Theoret. Fiz. **35**, 1119, (1953) [translation: Soviet Phys—JETP **35**, 783 (1959)]; and G. J. Schulz, this issue [Phys. Rev. **128**, 178 (1962)].

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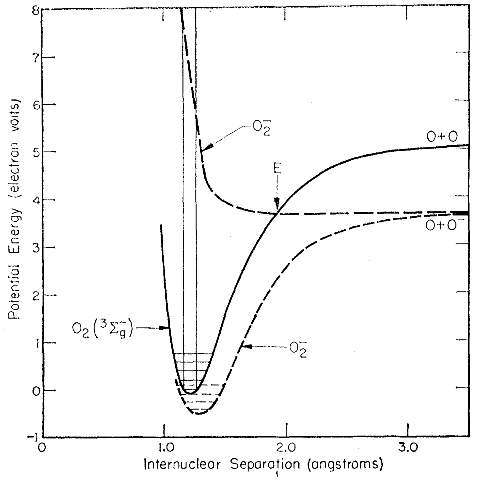

FIG. 1. Potential energy curves for O_2 and O_2^-. The curve for the $^3\Sigma_g^-$ state of O_2 is based on spectrographic observations. The curves for O_2^- are hypothetical curves drawn to be consistent with results presented in this paper insofar as the energies of oxygen negative ion formation are concerned.

detachment) or be stabilized by dissociation or by a collision with a third body.

Dissociative attachment of electrons to oxygen molecules has been shown to be important[15,16] at electron energies of several eV. This process may be expressed in reaction form as

$$O_2+e \rightarrow (O_2^-)_{\text{unstable}} \rightarrow O+O^-+\text{kinetic energy}. \quad (2)$$

Referring to Fig. 1, if an electron of several eV energy collides with an oxygen molecule initially in the $^3\Sigma_g^-$ ground state, a negative ion may be formed in the state with a repulsive potential-energy curve. The unstable molecular negative ion then begins to dissociate. If, before autodetachment of the electron occurs, the nuclei move apart a sufficient distance so that autodetachment is no longer energetically possible (point E) the dissociation continues, leading to the formation of a stable atomic negative ion and an atom. The difference in energy between the initial and final states appears as kinetic energy of motion of the dissociating fragments. Both the magnitude of the attachment rate and its dependence on incident electron energy are determined by the details of the potential curves of Fig. 1. For oxygen, the threshold for dissociative capture occurs at an electron energy of 4.5 eV.[15,16]

In addition to the dissociative process for diatomic molecules, there is the possibility of a similar process involving temporary molecular complexes such as O_4. This possibility is discussed in Sec. VI B.

In order to explain the appreciable electron attachment rate at lower (near-thermal) electron energies, Bloch and Bradbury[18] suggested a two-step process involving an electron and two oxygen molecules. They proposed that a low energy electron (~0.1 eV) collided with a neutral oxygen molecule in its ground ($v=0$) vibration state, leading to formation of a negative ion in an excited ($v=1$) vibration state. Thus,

$$(O_2)_{v=0}+e \rightleftharpoons (O_2^-)_{v=1}. \quad (3)$$

Unless this excited negative ion loses its energy of vibrational excitation, the reaction reverses by autodetachment of the electron. The second step in the attachment process involves the removal of the vibration energy by a third body, i.e.,

$$(O_2^-)_{v=1}+X \rightleftharpoons (O_2^-)_{v=0}+X+\text{energy}. \quad (4)$$

In pure O_2 the third body X is another oxygen molecule and the vibration excitation energy of the negative ion is transferred "by resonance" to the other molecule.[4,18] In the light of more recent information[19] concerning the electron affinity of the O_2 ions formed in swarm experiments, the Bloch-Bradbury picture of the attachment process must be modified to place the negative ion in a higher vibration state than $v=1$, as indicated by the potential curves of Fig. 1. In addition, it will be seen that other atoms and molecules may act as third bodies in stabilizing the attachment reaction given in Eq. (4). In over-all effect, the Bloch-Bradbury process is a three-body reaction, i.e.,

$$O_2+e+X \rightleftharpoons O_2^-+X+\text{energy}. \quad (5)$$

In order to discuss the rates of electron loss by the various attachment processes we introduce the appropriate rate coefficients. Thus, the time rate of change of electron density as a result of attachment may be represented by

$$\left.\frac{dn_e}{dt}\right|_a = -\nu_a n_e = -\beta n(O_2)n_e - K(X)n(X)n(O_2)n_e, \quad (6)$$

where n_e, $n(O_2)$, and $n(X)$ are, respectively, the densities of electrons, oxygen molecules, and "third body" atoms or molecules. The quantity ν_a is the over-all attachment frequency; β is the two-body and K the three-body attachment coefficient, representing processes of the types illustrated by Eqs. (1) and (2) and by Eq. (5), respectively.

In the case of a two-body reaction, it is possible to characterize the process by a cross section for attachment, σ, which is related to β by

$$\beta = \langle \sigma v \rangle, \quad (7)$$

where v is the velocity of relative motion of the colliding

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[19] A. V. Phelps and J. L. Pack, Phys. Rev. Letters **6**, 111 (1961). Evidence for a higher affinity for O_2^- formed from O_3 is given by R. K. Curran, J. Chem. Phys. **35**, 1849 (1961). However, Pack and Phelps, Bull. Amer. Phys. Soc., **7**, 131 (1962), show that the O_2^- ions formed via the three-body process require at least 5×10^8 momentum transfer collisions for de-excitation to any possible lower state. This means that for the purposes of this paper it is proper to use 0.44 eV for the affinity of O_2.

particles, and the averaging is carried over the energy distribution of the electrons.

The present experimental techniques do not provide a direct measurement of ν_a, β, or K. Instead, one is able to determine the quantity α, the attachment coefficient per unit drift distance of an electron drifting through the gas under the influence of an applied electric field.

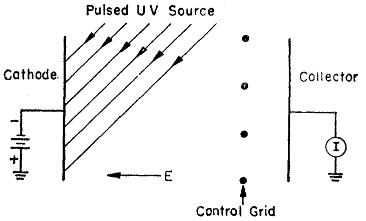

FIG. 2. Schematic diagram showing essential elements of the drift tube used to measure electron attachment in oxygen.

III. PRINCIPLE OF MEASUREMENT

The present measuring technique is an outgrowth of methods introduced many years ago by Loeb and his students.[3] It involves an extension of a method used by Doehring[6] which permits us to obtain measurements at very low applied electric fields. The principle of the measurement may be illustrated with the aid of Fig. 2. Electrons are released in a pulse of short time duration by means of an ultraviolet light pulse falling on the photocathode. They then drift through the gas-filled tube under the action of the applied electric field. Some of the electrons are captured by neutral molecules to form negative ions; the remainder reach the collector electrode after passing through a control grid. The negative ions then drift across the tube and the time dependence of the negative-ion current arriving at the control grid[20] is used to determine the attachment coefficient. The control grid is used to sample the ion current at some time, t, delayed relative to the short light pulse. This time sampling procedure allows much more accurate determinations of the ion current waveform than would be possible with oscillographic observation.

One may calculate the electron and ion densities present in the drift region as the result of the pulse of photoelectrons leaving the cathode. During the light pulse, the electron current density at the cathode is given by $w_e n_e(0)$, where w_e is the electron drift velocity. If we neglect diffusion effects, the variation of the electron density as a result of attachment and drift motion is given by the continuity relation,

$$\partial n_e/\partial t+w_e\partial n_e/\partial z=-\nu_a n_e. \tag{8}$$

Since the light pulse is long enough so that the electrons may be considered to have reached a steady-state distribution, the solution to Eq. (8) is

$$n_e=n_e(0)\exp(-\nu_a z/w_e)=n_e(0)\exp(-\alpha z). \tag{9}$$

Since the negative ion drift velocity is $\sim 10^{-3}$ times that of the electrons, we can make the light pulse short enough so that the ions do not move appreciably during the time electrons are present. The density of ions produced during the light pulse, δt, is therefore $n_i(z)=(\nu_a\delta t)n_e(z)$. Thus, we have

$$n_i(z)=\nu_a\delta t n_e(0)\exp(-\alpha z), \tag{10}$$

for $0\leq z\leq L$, where L is the distance between cathode and control grid.[20] This distribution moves toward the grid under the influence of the applied field with a drift velocity, w_i. Neglecting diffusion effects, the continuity equation for the ions during the period following the electron pulse is

$$\partial n_i/\partial t+w_i\partial n_i/\partial z=0. \tag{11}$$

The solution to this equation satisfying the initial conditions given by Eq. (10) is $n_i=\nu_a\delta t n_e(0)\exp[-\alpha(z-w_i t)]$, where δt is the duration of the light pulse. Thus, the current per unit area at the grid, $I(t)=ew_i n_i(t,L)$, is given by

$$\begin{aligned} I(t)=ew_i\nu_a\delta t n_e(0)&\exp[-\alpha(L-w_i t)]\\ &=I_0\exp(\alpha w_i t), \end{aligned} \tag{12}$$

for $0\leq t\leq L/w_i$, and $I(t)=0$ thereafter. The quantity $I_0=ew_i\nu_a\delta t n_e(0)\exp(-\alpha L)$ is the initial ion current reaching the collector.

Experimentally, the quantity w_i is determined from the observed transit time of the ions formed adjacent to the photocathode, i.e., the difference in the times of maximum electron current and a time intermediate between that of peak ion current and that at which the ion current has dropped to half its peak value. The exact point depends upon the effects of diffusion on the waveform.[6] The value of αw_i is determined from the slope of the $\ln I$ vs t curve using Eq. (12). Figure 3 shows an example of the measurements, in which the effects of diffusion broadening and of the finite photoelectron and grid pulse durations are present. However, the ion transit time and the slope of the growing ion current curve are still readily determined. Thus, the attachment coefficient α may be determined from observations of the time variation in the ion current arriving at the collector.

Alternatively, we have been able to check these values of α by comparing the total number of electrons reaching the collector with the number of negative ions formed in the drift space. If the only electron loss is by attachment, from Eq. (9) the number of electrons

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[20] It should be noted that since the ions and electrons are separated according to their time of arrival at the control grid the measurements are unaffected by attachment which occurs between the grid and the collector. The only requirement is that the charge not be lost by diffusion, etc., between the grid and the collector.

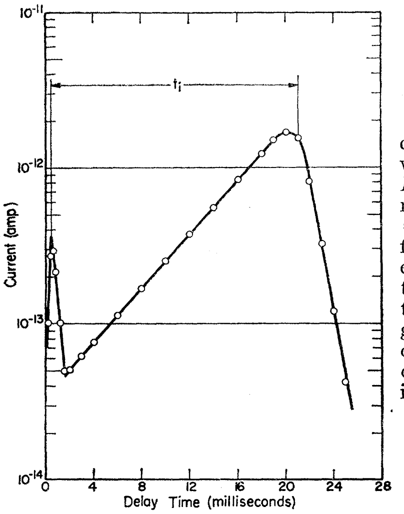

FIG. 3. Observed current waveform with pure O_2 for $E/p=0.25$ volt/cm-mm Hg and $p_{300}=10.5$ mm Hg. The first peak is due to electrons which cross the tube without attaching to the oxygen. The remainder of the waveform is due to the negative ions.

per unit area reaching the control grid is

$$N_e(L)=n_e w_e \delta t=n_e(0) w_e \delta t \exp(-\alpha L) =N_e(0)\exp(-\alpha L), \quad (13)$$

and the number of ions per unit area formed in the drift space and eventually reaching the grid is consequently

$$N_i=N_e(0)-N_e(L)=N_e(0)[1-\exp(-\alpha L)]. \quad (14)$$

Thus, we have

$$\alpha=(1/L)\ln\{[N_i+N_e(L)]/N_e(L)\}. \quad (15)$$

The values of $N_e(L)$ and N_i are determined from the areas under the electron pulse (early spike) and ion current portions of the curve of Fig. 3. In order to use the collector current data it has been implicitly assumed that the control grid has essentially the same transmission factor for electrons and for negative ions. While this method provides a less precise determination of α, several runs at relatively high E/p have been evaluated, and the values obtained by the two methods found to agree within 15%.

Finally, the values of α as a function of applied drift field E and gas pressure p are converted to the desired two-body and three-body coefficients β and K by use of electron drift velocity, w_e, data obtained by other investigators.[21]

IV. EXPERIMENTAL APPARATUS

A. Drift Tube

A schematic diagram of the drift tube and associated circuitry used to determine the attachment coefficients is shown in Fig. 4. It is essentially identical to that designed by Pack and Phelps for electron mobility studies[22] except that one grid is omitted. At the left is a photocathode from which electrons are released in short pulses as a result of incident ultraviolet radiation from a pulsed mercury discharge lamp (Westinghouse type AH4, with the outer glass envelope removed). The uv radiation is admitted to the tube through a fused silica window (85% transmittance at 1850 Å). A series of guard rings is used to maintain a uniform potential gradient between the cathode and the control grid of the tube. Drift distances of 2.54 and 10.16 cm were used in these studies.

The grid consists of a series of fine (0.0025 i.d.) parallel wires, with alternate wires electrically connected.[3] In operation the grid is made nontransmitting by application of equal and opposite bias voltages to the alternate wire sets. The grid is made transmitting during a particular time interval by application of rectangular voltage pulses to the wire sets to reduce the field between the wires to zero and thus allow some of the ions and electrons to pass through the grid. A collector electrode, shielded from stray currents, is connected to a vibrating reed electrometer to measure the ion and electron currents.

By delaying the opening of the grid relative to the photoelectron pulse from the cathode by various time intervals, it is possible to determine the current reaching the grid as a function of time (see Fig. 3). In order to minimize contact potential effects, all electrodes are gold plated. The tube is mounted in a glass envelope with a demountable gold gasketed flange at one end to permit modification of the structure. Electrical leadthroughs are either of glass-metal or ceramic-metal type, and in all cases leakage resistances in excess of $10^{13}\ \Omega$ are obtained.

B. Electronic Circuitry

A simplified block diagram of the electronic circuitry used in these measurements is given in Fig. 4. The apparatus is cycled at repetition rates between 10–200 cps, controlled by the master generator. The light source is turned on and off by means of a pulsed voltage

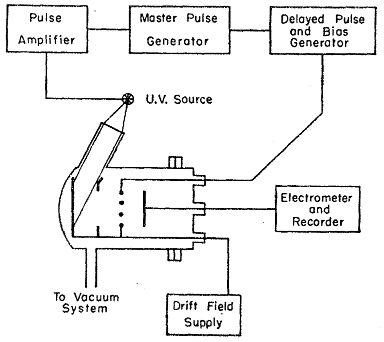

FIG. 4. Schematic diagram of drift tube and associated electronic circuits.

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[21] See Appendix II.

[22] A. V. Phelps, J. L. Pack, and L. S. Frost, Phys. Rev. **117**, 470 (1960) and J. L. Pack and A. V. Phelps, *ibid.* **121**, 798 (1961).

from the modulator and pulse amplifier. A uniform drift field is maintained in the tube by means of dc potentials applied to the photocathode, guard rings, grid, and collector from a variable drift voltage supply. By means of a variable delay generator and balanced pulse generator, voltage pulses are applied to the grid wires at selected times delayed with respect to the uv light pulse. The shapes and times of occurrence of the various voltage pulses are monitored on a synchronized oscilloscope. In all cases the duration of the photoelectron pulse and the open time of the grid are $\leq 5\%$ of the ion transit time. The currents arriving at the collector vary from 10^{-11} to 10^{-15} A.

C. Gas Handling System

The experimental tube is mounted on a glass and metal ultrahigh vacuum system.[23] The entire system is baked at 300°C for approximately 16 h before each series of measurements. Following bakeout, the system pressure is less than $<10^{-8}$ mm Hg and a rate of rise of background pressure of $<10^{-9}$ mm Hg/min is achieved. These values are sufficiently small that no significant impurities are added by the system to the gas sample during the course of the measurements.

The drift tube is separated from the rest of the vacuum system manifold by means of a re-entrant liquid nitrogen trap. No change in results is observed when the trap is not cooled. Measurements at low temperature (77°K) are accomplished by immersing the entire tube, with the exception of the fused silica window, in a liquid nitrogen bath. The gas pressure in the tube, between 0.1 mm Hg and 500 mm Hg, is determined with the aid of a bakeable null reading manometer[24] which isolates the system from the oil and mercury vapors of the measuring manometers. The values of pressure quoted in this paper are normalized to 300°K and should be interpreted as the gas density in units of 3.22×10^{16} molecule/cc. The gases are of reagent grade purity, obtained from the Air Reduction Sales Company.

V. DATA

On the basis of current waveform measurements of the type illustrated in Fig. 3 for a number of pressures of oxygen, the variation of α with the drift field to pressure ratio, E/p, shown in Fig. 5 is found. The ratio α/p is plotted to display two- and three-body pressure dependences in the attachment. Similarly, the quantity E/p, which determines the average energy which the particles attain in the applied field, is used. In the course of the measurements shown in Fig. 5, tests were made to determine whether or not the observed values of α depend on the intensity or wavelength of the uv light used to produce the photoelectrons. The negative results of these tests are consistent with our expectation that insufficient radiant flux is used to cause appreciable excitation of or chemical reactions in the gas under study.

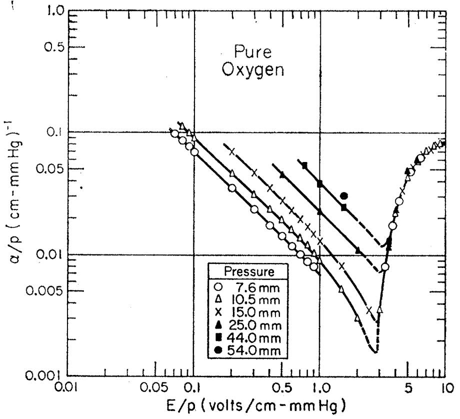

FIG. 5. Measured values of α/p in pure O_2 at 300°K. As discussed in the text the agreement between values of α/p obtained at various pressures for $E/p>3$ V/cm-mm Hg shows that α is directly proportional to p. For lower E/p one finds that α/p^2 is independent of pressure.

It is found that, at low values of E/p (<3), the quantity α/p is proportional to pressure, indicating that a three-body attachment process predominates, while at higher E/p values α/p is independent of pressure (two-body process). The appropriate three- and two-body rate coefficients, K and β [see Eq. (6)], are determined as functions of the average electron energy by conversion of E/p values to average energy using the curves of Appendix II, which represent a composite of previous measurements.

The measurements of Fig. 5 were obtained in pure oxygen; in order to obtain results at smaller drift fields (lower electron energies) one must inhibit diffusion effects in the tube. This has been accomplished by adding helium or nitrogen, both of which have a small effect in stabilizing the three-body attachment reaction, to the oxygen. Under these circumstances, it will be seen from Eqs. (6) and (9) that at low E/p the measured attachment coefficient, α, is given by

$$\alpha=\nu_a/w_e'=(1/w_e')\sum_X K(X)n(X)n(O_2), \quad (16)$$

where w_e' indicates the electron drift velocity in the mixture, and X indicates the various component gases in the mixture. Thus, for oxygen-helium mixtures,

$$\begin{aligned} K'&=\alpha w_e'/n(\mathrm{He})n(O_2)\\ &=K(O_2)[n(O_2)/n(\mathrm{He})]+K(\mathrm{He}). \quad (17)\end{aligned}$$

Measured values of K' for various oxygen-helium mixtures and E/p values are shown in Fig. 6. For these dilute oxygen concentrations, the energy scale and

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[23] D. Alpert, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 12.

[24] D. Alpert, C. G. Matland and A. O. McCoubrey, Rev. Sci. Instr. **22**, 370 (1951).

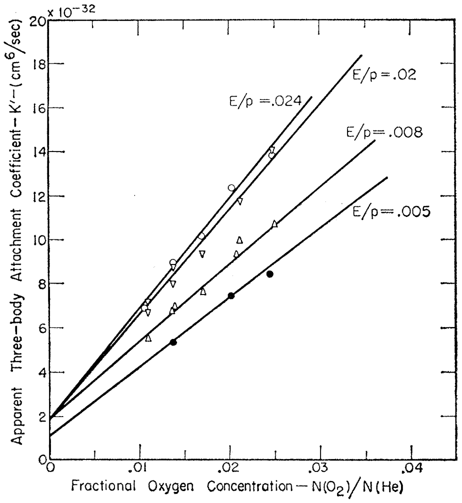

FIG. 6. Apparent three-body attachment coefficient for oxygen-helium mixture vs fractional concentration of oxygen for various values of E/p at 300°K. The slopes of these straight lines give the three-body attachment coefficient for pure oxygen and the intercepts give the three-body coefficient for oxygen-helium collisions. Note that the oxygen concentrations are small enough so that the electron drift velocities and average energies at a given E/p are essentially the same as for pure helium.

electron drift velocities are largely determined by the helium gas (see Appendix II). The slopes of the curves yield values of $K(O_2)$ while the intercepts, $K(\mathrm{He})$, indicate the effectiveness of helium as a third body in stabilizing the attachment.

VI. RESULTS AND DISCUSSION

A. Two-Body Attachment Process

At average electron energies greater than ~1 eV ($E/p>4$) the two-body attachment process predominates (see Fig. 5). A detailed comparison of this portion of the curve, as given in Fig. 7, with the results of the several earlier swarm experiments reveals at best qualitative agreement concerning the magnitude of the attachment coefficient. Since the earlier investigators missed the three-body nature of the attachment process at $E/p<4$, these portions of their curves, which depend on the particular pressure used, should be ignored.

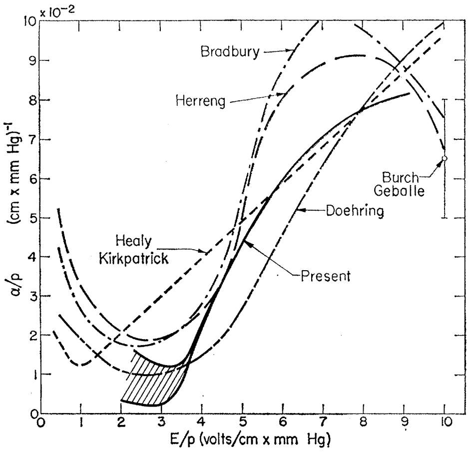

FIG. 7. Comparison of attachment coefficients measured by various experimenters. The shaded region for $E/p<4$ V/cm-mm Hg corresponds to the region of Fig. 5 in which α/p varies with pressure.

The present results are compared with the results of beam experiments in Fig. 8 in a manner similar to that introduced by Craggs, Thorburn, and Tozer.[16] This has been done by converting the values of α/p to the two-body coefficient, β, and comparing the results with values calculated from the beam experiment data[16] of Craggs, Thorburn, and Tozer as corrected by Buchelnikova and by Schulz. Since their data yield the attachment cross section for electrons of narrow spread in kinetic energy, it is necessary to average their data over the electron energy distribution appropriate to our swarm measurements. The exact form of the energy distribution of electrons under the action of a dc electric field in oxygen is not known; we have assumed that it is somewhere between a Maxwellian and a Druyvesteyn energy distribution. The present results are somewhat higher than the average of the beam data over either distribution. Note that these results are plotted as a function of an "average energy" equal to $3D/2\mu$ where D/μ is a measure of the electron energy. D is the electron diffusion coefficient and μ is the electron mobility. Values of D/μ vs E/p are given in Appendix II.

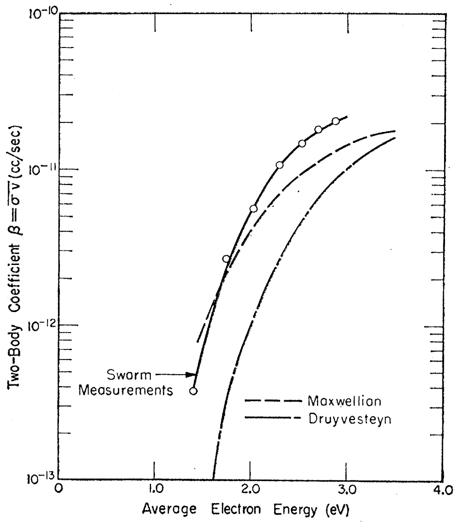

FIG. 8. Comparison of the two-body attachment coefficient for pure O_2 at 300°K obtained from swarm experiments with values calculated from electron beam experiments using Druyvesteyn and Maxwellian electron energy distributions. The "average electron energy" for these purposes is taken as $(3D/2\mu)$, where D is the electron diffusion coefficient and μ is the electron mobility.

The data of Bradbury and of Herreng, Fig. 7, exhibit a maximum in the vicinity of 2.3 eV average energy, in contradiction with the averaged beam results. Thus, it appears that the present results, which are in fair agreement with the swarm experiment data of Healy and Kirkpatrick[2], of Doehring[6] and of Huxley, Crompton, and Bagot,[17] provide a more accurate picture of the two-body attachment process for moderate electron energies.

Since a succession of beam experiments[15–16] have established that this two-body attachment process is the result of dissociative attachment, Eq. (2), the reasonable agreement of the present swarm results with the averaged beam data permits one to dismiss Bradbury's proposed process for the attachment in this energy range. He suggested that the high-energy process ($E/p>3$) was the result of electrons first losing their kinetic energy as a result of inelastic collisions with oxygen molecules and then being captured by the low-energy attachment process. This hypothesis is also ruled out by the present finding that the low-energy process is a *three*-body process, which in Bradbury's picture would imply a similar pressure dependence for the high-energy process.

B. Three-Body Attachment Process

The values of $K(O_2)$ inferred from the E/p measurements in pure oxygen and in oxygen-helium mixtures are shown in Fig. 9 as functions of average electron energy, where the average energy is defined as $3D/2\mu$. At a gas temperature of 300°K the curve exhibits a maximum value of 5×10^{-30} cm^6 sec at ~0.09 eV average electron energy. When these data are extrapolated to thermal energies, i.e., to $\bar{u}_v=3\ kT_{\text{gas}}/2e$, we obtain the thermal attachment coefficients shown in Fig. 10. The thermal value ($\bar{u}_e=0.04$ eV at $T_e=T_{\text{gas}}=300$°K) is 2.8×10^{-30} cm^6/sec. It will be seen that, in pure oxygen, the three-body pressure dependence is followed over the entire measured range, 8 mm–54 mm Hg. Recently, Schulz[25], using a modified electron beam apparatus, has verified the predominance of the three-body attachment process for oxygen pressures from 0.01 mm Hg to 0.1 mm Hg. Also, van Lint, Wikner, and Trueblood[11] have verified the pressure squared dependence for pressures up to 150 mm Hg of oxygen. The data at a gas temperature of 77°K were obtained only by the use of helium-oxygen mixtures and involved substantial errors, as indicated by the vertical lines through some of the solid dots. It appears that the thermal ($\bar{u}_e=0.01$ eV at $T=77$°K) attachment coefficient, $K(O_2)$, is substantially less than 10^{-30} cm^6/sec.

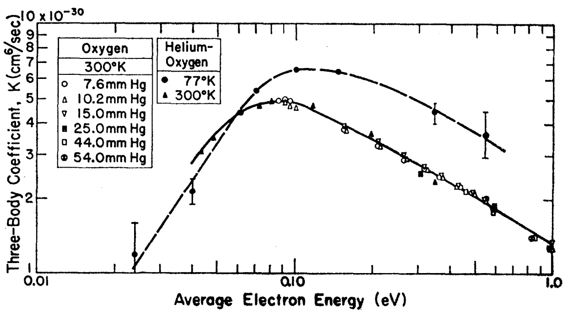

FIG. 9. Three-body attachment coefficient for oxygen vs average electron energy ($3D/2\mu$) for gas temperatures of 77 and 300°K. The open points are computed from the pure O_2 data of Fig. 5 while the solid points were obtained from data such as shown in Fig. 6.

In view of the interest to upper atmospheric physicists of the attachment process in air, studies of the three-body process have also been carried out in oxygen-nitrogen mixtures. The values obtained for $K(O_2)$ are approximately 25% lower than those obtained with pure oxygen and the oxygen-helium mixtures (see Fig. 11). The discrepancy may result from uncertainties in the electron energy distribution function at these values of E/p. The O_2-N_2 data for $K(O_2)$ agree, within the combined experimental errors, with the recent results obtained by Hurst and Bortner[9] from ionization chamber measurements involving similar mixtures.

From the mixture studies, the relative effectiveness of helium, nitrogen, and oxygen as third bodies in stabilizing the attachment of electrons to oxygen molecules [Eq. (5)] has been determined and is indicated in Fig. 12. It will be seen that helium is roughly one hundred times less effective than oxygen at gas temperatures of 300 and 77°K. Nitrogen is intermediate in effectiveness at 300°K. Possible reasons for this behavior will be discussed shortly.

It is clear from the experimental measurements that the end points of the three-body reaction are given by

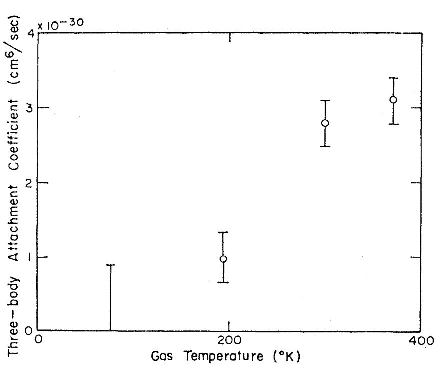

FIG. 10. Three-body attachment coefficients for thermal electrons in oxygen as a function of temperature. The points shown have been obtained by extrapolating curves of the type shown in Fig. 9 to energies of $3kT/2e$ for each temperature. At $T=77$°K only an upper limit is indicated.

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[25] G. J. Schulz, Bull. Am. Phys. Soc. 6, 387 (1961).

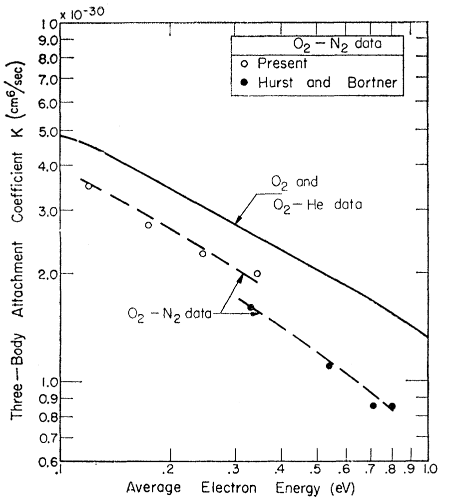

FIG. 11. Three-body attachment coefficient for electrons and oxygen molecules as obtained from pure O_2 and from O_2-He studies (solid line) and from O_2-N_2 studies (dashed lines). The average electron energy used here is equal to $3D/2\,\mu$.

Eq. (5); however, there is more than one process which could conceivably lead to the observed three-body dependence. In the light of present knowledge[19] of the electron affinity of O_2 the Bloch-Bradbury process in pure oxygen would have to involve the sequence;

$$(O_2)_{v=0}+e \rightleftharpoons (O_2^-)_{v=m}, \tag{18a}$$

followed by

$$(O_2^-)_{v=m}+(O_2)_{v=0} \rightleftharpoons (O_2^-)_{v=0}+(O_2)_{v=3}. \tag{18b}$$

Here we have used the published value of the electron affinity,[19] 0.44±0.02 eV, and have assumed the $v=m$ state of the negative ion to occur at an energy of about 0.1 eV above the ground vibration state of the neutral molecule, i.e., near the maximum in the curves of K vs $\bar{u}_e$ in Fig. 10. We also have assumed that the O_2^- is left in its ground vibrational state after the stabilizing collision.[19] The energy to be absorbed by the neutral oxygen is then 0.56 eV, corresponding to excitation to the $v=3$ level. It is also possible to stabilize the negative ion by removal of only enough of its vibration energy to drop it below the ground state of the neutral molecule, with subsequent collisions reducing it to its ground vibration state. It is necessary, however, that this process take place in a time short compared to the measuring time scale in order that a single value of the affinity be obtained.[19] It should be noted that several sharp excited states of the type proposed by Bloch and Bradbury would be required to explain the slow decrease in K with $\bar{u}_e$ shown in Fig. 9 for pure O_2 at $\bar{u}_e>0.1$ eV. Evidence that this is indeed the case has been obtained by Schulz[25] who studied the three-body attachment process with an electron beam with roughly 0.1 eV energy spread. He found indications of structure in the K vs electron energy curve at intervals of ~0.2 eV.

An alternative sequence to the Bloch-Bradbury process involves a three-body, pseudodissociative attachment reaction. In this process an electron passes in the vicinity of two oxygen molecules which are close together (~2Å) at a given instant and could be considered as a temporary O_4 molecule.[26] The system of electron plus two O_2 molecules may be thought of as an unstable state of O_4^-, which begins to dissociate. If the configuration can separate a sufficient distance before the electron moves out of range, the electron will be captured by one of the O_2 molecules, leading to formation of O_2^-. The over-all reaction is, thus,

$$O_2+O_2+e \rightleftharpoons (O_4^-)_{\text{unstable}} \rightleftharpoons O_2^- + O_2 + \text{kinetic energy}. \tag{19}$$

From our experimental measurements it is not possible to determine the relative contributions of reac-

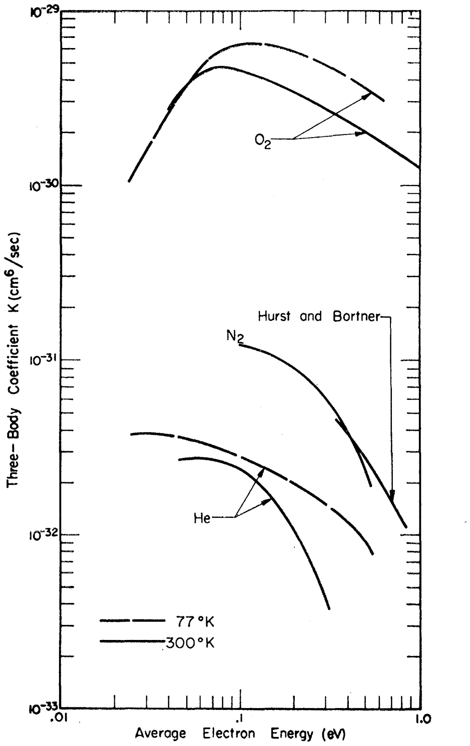

FIG. 12. Comparison of stabilizing effects of O_2, N_2, and He in the three-body attachment to O_2 at 77°K (dashed curves) and 300°K (solid curves).

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[26] Unfortunately, there appear to be wide variations of opinion as to the degree of dissociation of the O_4 molecule. See, for example, Y. K. Syrkin and M. E. Dyatkina, *The Structure of Molecules* (Butterworths Scientific Publications, Ltd., London, 1950), p. 256 and L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), 2nd ed., 273. If the dissociation energy were as large as 0.1 eV, then at a fixed average electron energy, the attachment coefficient due to this process would be expected to be much larger at 77° than at 300°K.

tions (18) and (19) to the observed three-body attachment. However, on the basis of the Bloch-Bradbury process one can make plausibility arguments for the smaller effectiveness of He relative to O_2 and N_2 as a third-body in stabilizing the reaction. Since it is necessary to remove vibration energy to stabilize the negative ion formed in reaction (18a) a molecule such as O_2 or N_2, with its added degrees of freedom, might be expected to be more effective than an atom such as helium which can only carry off the energy as translational motion. There is no particular reason why O_2 should couple to the vibrational modes of O_2^- more effectively than N_2 unless there is an accidental resonance in the vibration spacings of O_2 and O_2^-, leading to a greater efficiency in stabilizing the attachment process. However, it is possible that the potential energy "curves" for O_2^- colliding with O_2 are such that the vibrational de-excitation indicated by Eq. 18b is accomplished by *charge* transfer.[27] Since stable N_2^- is not known, the parallel reaction for nitrogen is not possible. Note that the K values for N_2 and He in Fig. 12 decrease rapidly with increasing electron energy as expected when only a single excited state of the negative ion can be stabilized efficiently.

The present results remove one of the difficulties encountered by Bloch and Bradbury in suggesting their process [Eqs. (3) and (4) or (18a) and (18b)] as an explanation of Bradbury's data. Probably as a result of difficulties in carrying out low E/p measurements, Bradbury mistakenly concluded that, above pressures of ~5 mm Hg, a two-body pressure dependence was obeyed. In the Bloch-Bradbury process this can only occur if the stabilizing reaction [Eqs. (4) or 18(b) going to the right] is fast compared to the autodetachment rate [Eq. (3) or (18a) going to the left]. This required the assumption of a combination of a very long autodetachment lifetime, $\sim 10^{-10}$ sec, and an incredibly large collisional stabilization cross section, $\sim 10^{-12}$ cm^2. The studies by van Lint, Wikner, and Trueblood of the three-body pressure dependence show no evidence of saturation[11] up to pressures of about 150 mm Hg. This observation and the assumption that *all* of the attachment occurs via the modified Bloch-Bradbury process lead to limits[28] on the autodetachment time of from 10^{-13} sec to 3×10^{-10} sec and a stabilization cross section of 10^{-14} cm^2.

C. Collisional Detachment

The inverse of the three-body attachment process, reaction (5) going to the left, is the collisional detachment of electrons from O_2^-. An experiment was carried out in which the control grid of the drift tube was operated as an electron filter.[3] This device permits the electrons to be collected by the filter, yet transmits the massive negative ions. In this way it is possible to separate the current reaching the collector into a negative ion and an electron component. A search was made for a detached electron current in pure oxygen at gas temperatures of 300 and 370°K. No electrons other than those in the original photoelectric pulse were detected. In view of the detection sensitivity of the apparatus an upper limit for the detachment coefficient, β_d, defined by the relation:

$$\left.\frac{dn_e}{dt}\right|_d = \beta_d n_- n(O_2), \tag{20}$$

was set at $\beta_d < 10^{-16}$ cc/sec at 300°K. Using the thermal attachment coefficient at 300°K and detailed balancing[19,29] one calculates that the O_2^- formed in these experiments exhibits an affinity in excess of 0.35 eV. The recent extension of these studies by Phelps and Pack[19] to higher gas temperatures leads to a value of the affinity of 0.44 ± 0.02 eV for the O_2^- state formed in these experiments.

D. Comparison with Microwave Afterglow Studies

The present experiment was undertaken in part to investigate the apparent discrepancy between the Bradbury[1] results, which extended down to average electron energies of ~0.2 eV, and the thermal energy ($T_e=300$°K) attachment coefficients deduced from microwave afterglow studies.[5,12,13] The several microwave studies, which involved observation of the decay of electron density during the afterglow following a microwave discharge in oxygen, each indicated a *two*-body pressure dependence at pressures of the order of 10 mm Hg, with an attachment cross section of $\sim 10^{-22}$ cm^2. Thus, at 10 mm Hg, the microwave studies indicated an electron decay frequency of $\sim 3\times10^2$ sec^{-1}, while the three-body attachment process should lead to a rate of decay of $\sim 3\times10^5$ sec^{-1}.

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[27] D. R. Bates and H. S. W. Massey, Phil. Trans. Roy. Soc. (London) **A239**, 269 (1943).

[28] In these considerations one assumes that the cross section for the initial formation step, Eq. (18a) going to the right, cannot exceed an average value of 10^{-15} cm^2 or else the temporary negative-ion formation would lead to electron scattering in this energy range in excess of that observed in electron collision frequency measurements by van Lint *et al.* (see reference 9). If, in addition, one assumes the excited O_2^- density to electron density ratio in Eq. (18a) to be given by thermal equilibrium considerations, with an excitation energy of 0.1 eV, then the cross section for reaction (18b) required to give the measured K is approximately 10^{-14} cm^2. Combining this result with the limiting initial formation cross section yields a lower limit to the autodetachment time of about 10^{-13} sec. Combining the stabilization cross section with the lower limit for the saturation pressure yields an upper limit of the autodetachment time of about 3×10^{-10} sec. D. C. Conway, Bull. Am. Phys. Soc. 7, 131 (1961), proposes that both the Bloch-Bradbury and the pseudodissociative processes are important, so that our stabilization cross section is too large and the upper limit to the autodetachment time is too small. He finds an autodetachment time of 10^{-9} sec from an analysis of O_2-CO_2 and $O_2-C_2H_4$ data. Unfortunately, the data do not cover a sufficiently large range to make his analysis unique.

[29] R. E. Meyerott, R. K. M. Landschoff, and J. Magee, Lockheed Aircraft Corporation Report LMSD-48361, (unpublished).

Nicholls and Hopwood[30] suggested that the low rate of electron loss in microwave afterglows resulted from a near equilibrium between attachment of electrons to oxygen molecules and detachment of electrons as a result of collisions between the negative ions and vibrationally excited molecules left over from the discharge. It can be shown that, if the attachment and detachment times are short compared to the measuring time scale, the final decay rate of the electron density will be determined by the decay rate of the vibrationally excited molecules.

Unfortunately, this attractive hypothesis for removing the apparent discrepancy between the microwave and the drift tube attachment determinations is difficult to reduce to a quantitative argument. If the detachment results from vibrationally excited molecules, they must be at least in the $v=3$ state [see Eq. (18) and the associated discussion]. Such excited molecules will be de-excited by vibration transfer collisions or by collisions in which the vibration excitation is converted into translational energy between the colliding particles, e.g.,

$$(O_2)_{v=3}+(O_2)_{v=0}\rightleftharpoons(O_2)_{v=2}+(O_2)_{v=1}, \qquad (21)$$

and

$$(O_2)_{v=3}+(O_2)_{v=0}\rightleftharpoons(O_2)_{v=2}+(O_2)_{v=0}+\text{kinetic energy}. \qquad (22)$$

In the case of near energy resonance, vibration transfer, Eq. (21), should occur much too rapidly[31] to fit the observed electron decays. On the other hand, the rate of vibration-translation conversion, Eq. (22), can be deduced from sound dispersion measurements[32] and is much too slow to explain the observed electron decays. This problem has been independently examined by Chantry, Wharmby, and Hasted,[33] who arrive at similar conclusions but suggest that, as a result of convergence of the vibration levels, the energy discrepancy of Eq. (21) may be sufficient to slow the process to the decay times observed in microwave afterglows.

An alternative possibility is that the detachment results from collisions of the negative ions with O_2 molecules in low-lying, long-lived electronic excited states (for example, the $a^1\Delta_g$ state). Here again, no rates of collisional de-excitation of this state are available; consequently, one cannot make quantitative comparisons with the microwave decays. Another possible detachment process is associative detachment,[34] which requires the presence of oxygen atoms, i.e., $O_2^-+O\rightarrow O_3+e$. Thus far, we do not see how this process can give the two-body pressure dependence of the attachment coefficient observed in the microwave studies.

Additional evidence that an explanation of the general attachment-detachment type is probably correct is found in microwave studies of electron decay following formation of a low-density plasma by irradiation of a gas with high-energy (MeV) electrons.[11,35] These studies, in which, as a result of the mode of excitation and ionization, the concentration of low-lying excited states relative to that of electrons produced by ionization is expected to be much smaller than in a conventional microwave discharge, yield three-body attachment coefficients within about 20% of the values shown in Fig. 10 for temperatures between 195° and 370°K.

E. Implications for Ionospheric Studies

The principal implication of the present work for ionospheric studies is that the electron attachment frequencies in the lower ionosphere due to molecular oxygen are considerably lower than the previously accepted values.[27,34,36] Typical lifetimes of electrons against three-body attachment as calculated from our data are 10^{-4}, 0.5, and 5×10^3 sec at 30, 60, and 90 km, respectively. The lifetime of O_2^- against photodetachment during daylight has been calculated by Branscomb[14] to be 2.3 sec. The work of Burch, Smith, and Branscomb,[14] together with our results indicates that radiative attachment to O_2 can be neglected compared to three-body attachment to all altitudes of interest. However, at altitudes above 90 km the atomic oxygen concentrations are large enough[37] so that the electron loss via negative-ion formation is by radiative attachment to atomic oxygen.[14,38] We have not considered here the possibility of attachment to minority species such as NO_2.[11]

ACKNOWLEDGMENTS

The authors wish to express their appreciation for valuable discussions of this work with members of the Atomic Physics group, especially T. Holstein and G. J. Schulz. They are particularly indebted to J. L. Pack for much valuable assistance in the design of the electronic apparatus.

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[30] J. D. Craggs, *Proceedings of the Third International Conference on Ionization Phenomena in Gases, Venice, Italy, June, 1957* [The Italian Physical Society, 1958] (unpublished), p. 207.

[31] C. Zener (private communication) has modified the conclusions reached previously [Phys. Rev. **37**, 556 (1931)] and agrees that the transfer of vibrational excitation should occur with a reasonably large probability.

[32] J. G. Parker, J. Chem. Phys. **34**, 1763 (1961).

[33] P. J. Chantry, J. S. Wharmby, and J. B. Hasted, *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1962), p. 630.

[34] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A187**, 261 (1946).

[35] C. M. Crain, J. Appl. Phys. **29**, 1605 (1958) and C. M. Crain, J. Geophys. Research **66**, 1117 (1961).

[36] D. R. Bates and H. S. W. Massey, J. Atmospheric and Terrest. Phys. **2**, 1 (1952).

[37] M. Nicolet, in *Physics of the Upper Atmosphere,* edited by J. A. Ratcliffe (Academic Press Inc., New York, 1960), Chap. 2.

[38] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

APPENDIX I

Ion Mobilities

Figure 13 shows the negative-ion mobilities determined from waveforms such as that of Fig. 3. These data show that at 300°K in the E/p range from 0.15 to 1.5 V/cm-mm Hg the mobility of the negative ion in pure O_2 is 2.7 cm²/Vsec at a density of 2.69×10^{19} molecules/cc, in excellent agreement with Doehring.[6] The rather rapid variation of the ion mobility in O_2 and in He with temperature in this E/p range is shown in Table I. As discussed in the text, we believe that the stable ion formed by the low energy attachment process is O_2^-. However, the theoretical value of the mobility of O_2^- in the low temperature or polarization limit[39] is 2.8 cm²/Vsec. One possible explanation for a lower mobility at low temperatures is the formation of complex ions. Thus far, the only evidence for more than one ion species in our experiments is a distortion of the ion waveform observed in O_2 at 77°K and E/p less than about 0.2 V/cm-mm Hg. Considerations of the energy required[40] allow us to rule out conversion to O_3^- (but not O_4^- formation) in a three-body collision. The recent prediction by Arthurs and Dalgarno[41] of a rapidly varying ion mobility in H_2 at low temperatures appears unlikely to be applicable in a gas as heavy as O_2, where many rotational states are thermally excited at the temperatures of our experiments. Obviously, further work on this subject is desirable.

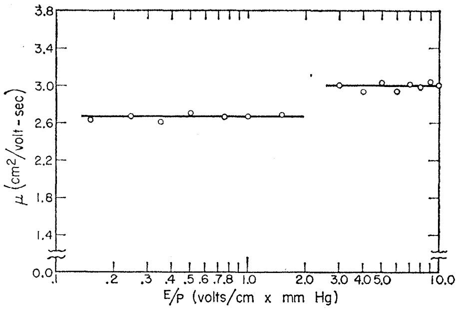

FIG. 13. Negative ion mobilities in oxygen at 300°K normalized to a gas density of 2.69×10^{19} cc^{-1}. Note that the range of E/p for which the lower mobility ion is observed is the same as that over which the three-body attachment process dominates. Similarly, the high-mobility ion corresponds to the two-body attachment process. In either case, the E/p values are sufficiently small so that the ions are essentially in thermal equilibrium with the gas.

In the high E/p range the discussion in Sec. VI A presents evidence that the negative ion formed initially is O^-. This ion would have a mobility in the low energy or polarization limit of 3.3 cm²/Vsec compared to the value of 3.0 cm²/Vsec from Fig. 13. In this case Burch and Geballe[42] have suggested that the O^- ion may be converted into either an O_3^- ion in a three-body collision with two O_2 molecules or into O_2^- in an energetic collision with O_2. The latter process can only occur before the O^- loses its kinetic energy of dissociation, and our waveforms show no evidence of distortion due to ion conversion in the E/p range from 3 to 10 V/cm-mm Hg. We have not investigated this problem as a function of temperature.

TABLE I. Normalized ion mobilities[a] in O_2 and He at low E/p. (Mobilities in cm²/V sec at 2.69×10^{19} molecules/cc.)

Temperature	O_2^- in O_2	O_2^- ions in He
77°K	1.8[b]	0.75
195°K	2.2[c]	1.5
300°K	2.7	
375°K	2.8	1.3

[a] The mobilities were computed using the peak of the ion waveforms such as shown in Fig. 3 as the ion transit time.

[b] At the very lowest E/p at 77°K there is evidence for the formation of an ion with a mobility of about 1.1 cm²/Vsec.

[c] Data obtained by J. L. Pack (private communication).

Although the above discussion indicates considerable uncertainty regarding the possibility that the initial ions are converted into more complex forms, the absence of distortion of the waveforms in the range of the data indicates that possible errors introduced in the attachment coefficient measurements from this source are small.

APPENDIX II

Electron Drift Velocities and Average Energies

The calculation of electron attachment frequencies, ν_a, from the values of α using Eq. (9) and of the attachment coefficients, K and β, requires a knowledge of the electron drift velocity under the conditions of the measurement. Figure 14 shows the available experimental

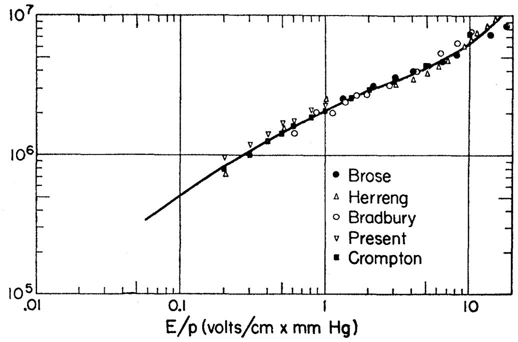

FIG. 14. Electron drift velocity in oxygen as a function of E/p. The solid curve gives the drift velocities used in our calculations.

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[39] P. Langevin, Ann. Chem. Phys. **5**, 245 (1905).

[40] H. O. Prichard, Chem. Rev. **52**, 529 (1953).

[41] A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) **A256**, 540 and 552 (1960).

[42] D. S. Burch and R. Geballe, Phys. Rev. **106**, 188 (1957).

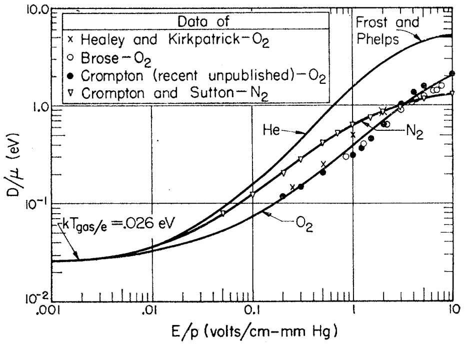

FIG. 15. Characteristic energy, D/μ for electrons in O_2, He, and N_2 as a function of E/p. The smooth curves give the values used in our calculations.

measurements[1,7,43,44] of the electron drift velocity in oxygen. The solid curve shows the variation of drift velocity with E/p which we used in our analysis. The drift velocity data used for the analysis of the measurements in oxygen-helium and oxygen-nitrogen mixtures are those given by Pack and Phelps[22] for pure helium and pure nitrogen, respectively. In using these data we have neglected the small change in electron drift velocity resulting from the fact that the elastic and inelastic cross sections for oxygen are different than those for the main gas, i.e., helium or nitrogen. The resultant error is considerably less than the fractional concentration of O_2, i.e., less than 5%.

The attachment coefficients obtained at various values of E/p are plotted in Figs. 8, 9, 11, and 12 as a function of an average electron energy $\bar{u}_e = 3D/2\mu$, using the smooth curves of Fig. 15. In the case of O_2 and N_2 these curves are averages of the available measurements of D/μ by Healy and Kirkpatrick,[2] Brose,[43] Crompton and Sutton,[45] and Crompton.[44] At low E/p the curves are extrapolated to the thermal value of D/μ, i.e., kT/e. In the case of helium the smooth curve is theoretically calculated by Frost and Phelps.[46]

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[43] H. L. Brose, Phil. Mag. **50**, 536 (1925).

[44] R. W. Crompton (private communication).

[45] R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) **A215**, 467 (1952).

[46] L. S. Frost and A. V. Phelps (unpublished).