

Electron avalanches in oxygen: Detachment from the diatomic ion $O_2^{-\dagger}$

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The current transients of prebreakdown electron avalanches in uniform electric fields in oxygen are studied with a bakable drift tube and a time resolution of about 1% of the ion transit time involved. At this low time resolution, electronic-current components are discovered which are attributed to detachment from the diatomic ion O_2^- . Detachment rates of O_2^- in O_2 are measured over a range of pressures from 1 to 32 Torr, and over a range of field strength to pressure ratios from 35 to 130 V/cm Torr, corresponding to mean ion swarm energies for O_2^- between about 0.2 and 1.5 eV. The detachment rates observed depend linearly on pressure, indicating a two-body detachment reaction, and are consistent with a detachment cross section near threshold (0.44 eV) of approximately 0.7×10^{-16} cm². Also obtained are effective electron attachment rates for O_2^- and O_3^- in oxygen, which show a characteristic pressure dependence consistent with attributing the observed detachment to diatomic O_2^- . These rates reflect the formation of the diatomic ion O_2^- by charge transfer from the primary atomic ion O^- . The pressure dependence observed, however, is inconsistent with the trial assumptions that either the atomic ion O^- , or the triatomic ion O_3^- , detach their electrons at the rates reported here. The mass-spectrometric study undertaken supports these conclusions.

I. INTRODUCTION

If a uniform electric field is set up between two plane parallel electrodes in an atmosphere of oxygen, electron avalanches can be initiated by a short-duration uv light flash onto the cathode. The current transients of avalanches are observed on an oscilloscope. Such transients are the superimposed current contributions of the drifting and reacting electrons and of the various positive- and negative-ion species (O^+ , O_2^+ , O_3^+ , O_4^+). A detailed study of the shapes of these transients can then be used to obtain information as to what particular reactions occur. Certain reaction rates, such as the frequencies of ionization, electron attachment, electron detachment, charge transfer of ions, and ion conversion can be measured if a trial model of the reactions thought to be occurring in the gas is adopted and if the superposition of the individual currents calculated from the model is compared to the experimentally determined total current.

Previous experiments indicate that oxygen is a gas in which several electronic and ionic reactions occur over a broad range of pressures and mean energies of electrons and ions. As a consequence, several negative and positive ion species of differing mobilities exist. Harrison and Geballe¹ showed that electron attachment was important under conditions where electrons are energetic enough to ionize O_2 . The primary negative ion in oxygen for the pressures and electric field strength to pressure ratios (E/p), of the present experiment, is atomic O^- , which is formed via dissociative attachment²⁻⁶



Burch and Geballe⁷ in a study of the "ion component" of avalanches have shown the primary negative ion undergoes charge transfer to O_2^- ,



and at high enough pressures three-body ion conversion to O_3^-



thus giving rise to two "secondary ions" O_2^- and O_3^- . The identification of these secondary ions was later confirmed by Moruzzi and Phelps.⁸

Using fast time resolution for the investigation of the "electron component" of avalanches one of the present authors showed the presence of an electron detachment process,⁹ according to the reaction



The presence of detachment processes in avalanches in inhomogeneous fields was invoked previously by Loeb¹⁰ many years ago in an attempt to explain certain features of an experiment by Cravath.¹¹ Thermal electron detachment from the diatomic ion O_2^- is also known to exist from the study of Pack and Phelps,¹² which seems to suggest the significance of that reaction in avalanches at the higher E/p under conditions of prevailing O_2^- abundances



In this paper it is shown that avalanches in oxygen, in addition to the "fast" detachment reactions

of the primary atomic ion⁹ [Eq. (4)] exhibit a *slow* detachment process. The detachment rates are measured and shown to be consistent with the assumption of O_2^- detachment¹³ [Eq. (5)]. A mass-spectrometric investigation shows that at low pressures ($p \lesssim 8$ Torr), O_2^- is the prevailing ion under the conditions of this study. Apparent attachment rates that describe the formation of O_2^- are also obtained and indicate that O_2^- is formed from the primary, atomic ion O^- via reaction (2).

It is found that the apparatus and principles of the measurement as discussed in Secs. II and III, respectively, are sensitive to the reaction rates of the various charge carriers, but especially so to reactions leading to free electrons (i.e., ionization and electron detachment), since the mobility and hence the current signal of free electrons is 100 times that of ions. Also, by the design of the apparatus, electrons could not escape detection by radial diffusion to the walls. As a result of the analysis of the transients, electronic currents are found to persist (Sec. IV) for times much longer than the transit time of the primary electron swarm. These electronic currents are attributed to electron detachment from a negative ion (O_2^-) and the measured detachment rates are reported in Sec. V. The method used to measure this slow detachment process in the presence of the fast one is observation on a time scale adequate to just resolve the effects of the slow reaction. In this way the atomic ion O^- may be considered a virtual intermediary state, that is, merely an unresolved step in the formation of the diatomic ion O_2^- . [The reactions (2) and (3) compete with the detachment reaction (4) and further shorten the lifetime of the atomic ion.]

After analyzing pulse shapes taken at both fast and slow time resolution, it became apparent that two different sets of detachment rates resulted and therefore, that two different ions must be detaching according to the time resolution being used. Under the conditions of this experiment the fast process lasts for only (1–10%) of the time of the slow process and is significant only in the early formative phase of an avalanche. We conclude that substantial concentrations of the primary ion O^- exist only initially, and for a very short time interval. After the bulk of the O^- is lost, essentially only the molecular negative ions (and also the positive ions) remain in the gap. Their reactions can then be studied with little interference from the fast reactions of the atomic ion. This study of the many reactions known to occur in oxygen led to the development of a theory of avalanche growth in which all reactions of known importance were included.¹⁴

In Sec. VI auxiliary data describing the effective

formation rates of the ion undergoing electron detachment (O_2^-) and of a stable negative ion (O_3^-) are reported and briefly discussed. Finally, Sec. VII contains some comments concerning previous studies of O_2^- detachment and the differing values of the electron affinity of O_2^- which have resulted.

II. APPARATUS

A block diagram of the bakable (400 °C) stainless-steel drift tube used for this work is shown in Fig. 1. The total diameter of the solid copper cathode is 10 cm. A "Rogowsky profile"¹⁵ was joined smoothly to the 2.54-cm-diam flat central region. The anode diameter is 15 cm and the gap width was fixed for most of the work to be $d = 2.54$ cm. In this way the maximum electric field distortions of the 2-cm² central area is less than 2%, and the "mean distortion" along any line of force of this central area is well below 1%. Hence, no guard rings are necessary for further improving the field uniformity. The drift-tube walls are cylindrical and of 19-cm i.d. Thus none of the reactive species (electrons or ions) are lost to the side walls and radial diffusion is insignificant due to the absence of an azimuthal boundary.

Since it is known that the work function of most surfaces, when exposed to an electronegative gas like oxygen, increases to about 5–7 eV,^{16–18} it is necessary to increase the photoelectric yield of the cathode by creating a sensitization layer which is both bakable and minimally affected by oxygen in order to improve the signal-to-noise ratio. It was found that depositing copper iodide¹⁹ on the central 2-cm diameter of the cathode increased the photoelectric yield by one to two orders of magnitude. In this way essentially all the avalanches

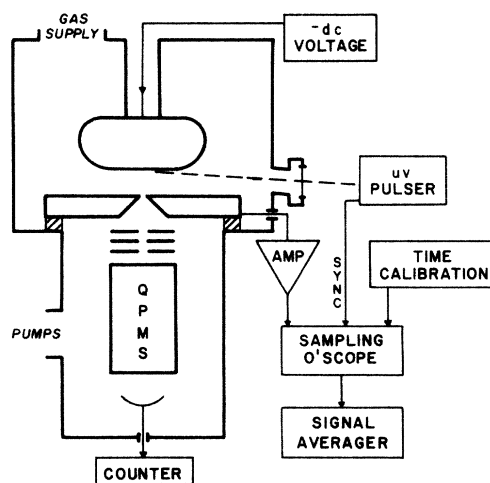


FIG. 1. Block diagram of the apparatus.

are initiated in this central region, in spite of lens aberrations of the high-aperture light collimating system and some unavoidable stray light.

The light source consists of a 1-cm spark gap in a deuterium atmosphere (~ 10 Torr) to which a rectangular pulse of about 8 kV is applied from a 50- Ω source for 5 nsec. The photoelectrons produced at the cathode may be observed by using the drift tube as a vacuum photodiode. Approximately 10^5 photoelectrons are produced in vacuum in each 5-nsec pulse. Integration of the photoelectron pulses shows no detectable electron signal produced after the first 5 nsec.

The bandwidth of the preamplifiers is either from dc to 150 MHz (for fast reactions) or from dc to 2 MHz (for slow reactions). The output of the preamplifiers is connected to a sampling oscilloscope and a 500 channel signal averaging computer. The pulse repetition rate is approximately 250/sec, and the lowest signals are recovered after about 1 h of averaging.

A frequency tuned quadrupole mass spectrometer is used by replacing the anode with one in which an effusion hole (0.01-in. diameter by 0.01 in. depth) is placed in the center. The exit side of the effusion hole is flaired to a 120° cone.

A diaphragm-type bakable pressure-gauge head (MKS Baratron type 90H-30) is employed. Pressure readings are reduced to a temperature of 20°C . Measurements were taken at temperatures between 24 and 28°C .

The input impedance of the preamplifier is $R = 1$ M Ω for the fast-time-resolution and $R = 10$ M Ω for the slow-time-resolution unit. The stray capacitance of the drift tube anode to ground is approximately $C = 80$ pF. As a consequence, the avalanche transients, which typically last for less than 50 μsec , are integrated by the resulting large time constant²⁰ ($RC = 0.8$ msec for the slow-time resolution preamplifier):

$$u(t) \approx \frac{1}{C} \int_0^t i(t') dt'. \quad (6)$$

These "voltage pulses" or "integrated current pulses" $u(t)$ have a more favorable signal-to-noise ratio than a direct recording of $i(t)$ and therefore are preferred. From these recordings the total current pulse can be obtained by graphical differentiation.

Certain features of an avalanche signal can be studied better in the "differentiated" form $i(t)$, while others can be observed better in the "integrated" form $u(t)$. Both forms were used in analyzing the pulses. For example, rapidly varying current components, such as those of detached electrons, are better studied as currents. Small, but persistent current contributions such as those

due to stable negative ions, can quantitatively better be investigated from voltage pulses.

III. METHOD OF PULSE-SHAPE ANALYSIS

In a previous paper, the equations describing the avalanche growth in oxygen have been presented.¹⁴ These equations are time-dependent continuity equations with gain and loss terms. Solutions are given for the cases of fast and slow time resolution, the latter of which will be used for this work. For easy reference we repeat here the equations necessary for the present work [Eqs. (36)–(40) of Ref. 14]:

$$\text{Electrons: } \frac{\partial n_0}{\partial t} + v_0 \frac{\partial n_0}{\partial x} = b_{00} n_0 + b_{02} n_2, \quad (7)$$

$$\text{O}_2^-: \quad \frac{\partial n_2}{\partial t} + v_2 \frac{\partial n_2}{\partial x} = b_{20} n_0 + b_{22} n_2, \quad (8)$$

$$\text{O}_3^-: \quad \frac{\partial n_3}{\partial t} + v_3 \frac{\partial n_3}{\partial x} = b_{30} n_0, \quad (9)$$

$$\text{O}_4^-: \quad \frac{\partial n_4}{\partial t} + v_4 \frac{\partial n_4}{\partial x} = b_{42} n_2, \quad (10)$$

$$\text{Pos. ions: } \frac{\partial n_5}{\partial t} - v_5 \frac{\partial n_5}{\partial x} = b_{50} n_0. \quad (11)$$

Here, $n_0 = n_0(x, t)$ is a function of space x and time t , designating electron number densities. $n_2 = n_2(x, t)$ is the number density of the ion undergoing detachment (it will be identified with the diatomic ion O_2^- below). n_3 and n_4 are densities of stable negative ions (O_3^- and O_4^- , respectively)²¹ and n_5 designates the densities of positive ions. Equations (7) and (8) form a set of coupled equations which can be solved with appropriate boundary conditions given. Equations (9)–(11) then require simple integrations over these known solutions for n_0 and n_2 . The atomic negative ion O^- is assumed to be a "virtual" intermediary state for this slow-time-resolution study as explained elsewhere.¹⁴ The v_i are drift velocities of the i th ionic species. The b_{ik} are "effective reaction rates" and are defined as (i) $b_{50} = \alpha v_0$ is the electron impact-ionization frequency (α is often called Townsend's first ionization coefficient); (ii) b_{20} is the effective electron-attachment frequency for the formation of the ion undergoing attachment (O_2^-); (iii) b_{30} is the effective electron-attachment frequency for the formation of the stable negative ion (O_3^-); (iv) $b_{00} = b_{50} - b_{20} - b_{30}$; (v) b_{02} is the electron-detachment frequency of the "unstable" ion (O_2^-); (vi) b_{42} is the ion-conversion frequency of the "unstable" ion (O_2^- to form O_4^-); and (vii) $-b_{22} = b_{02} + b_{42}$ is the total loss frequency of the "unstable" ion (O_2^-).

Using trial values for these b_{ik} , the densities $n_i(x, t)$ can be obtained by integration of Eqs. (7)–(11) and the various current components computed according to

$$i_i(t) = \frac{ev_i}{d} \int_0^d n_i(x, t) dx. \quad (12)$$

The total current is the sum over all of these currents ($i=0, \dots, 4$) and the voltage pulse $u(t)$ is obtained by integration of the total current. At this time scale, the voltage pulse $u(t)$ is not continuous at $t=0$ due to the primary electron swarm arriving at the anode. This δ -function-like behavior of the avalanche current at $t=0$ is a consequence of the initial avalanche conditions. It is suppressed in the current pulse shapes obtained by graphical differentiation, but it is visible in the integrated curves as a voltage jump at zero time. An example of such pulse shapes is given in Fig. 2.

The computed pulse shapes are compared to the experimental ones and by reiterated adjustments of the trial values for b_{ik} , a good match is obtained for every one of the experimental pulse shapes of this work. That set of b_{ik} which is consistent with the pulse shapes is called the measurement of the respective reaction frequencies.

IV. EXPERIMENTAL PULSE SHAPES

The most prominent feature of the avalanche pulse shape in oxygen is the initial exponential-like drop in the total current pulse (Fig. 2). Such a rapidly decreasing current component of this amplitude is surprising at that time scale, because the current contributions of the drifting oxygen ions should vary much more gradually over the whole duration of the event. Also due to the smallness of the attachment coefficients, under most of our conditions they should be of a smaller amplitude. Even if ion conversion is considered, such quasiexponentials, with an average duration of only (10–20)% of an ion transit time, cannot be understood because the drift velocities of the product ions (O_2^- , O_3^- , O_4^-) are too small. Furthermore, if one increases the mean energies (or E/p) slightly, under otherwise unchanging conditions, the mean duration of this quasiexponential is seen to decrease, and its amplitude to increase much more rapidly than one could explain on the basis of increasing drift velocities of any oxygen ion. It thus appears impossible to understand this initial exponential decay on the basis of ion drift or ion conversion alone.

We have found that a consistent alternative is the assumption that electrons produce this feature. The drift velocity of electrons is very much larger than that of ions. Thus, very small concentrations of electrons produce currents which, although

being of short duration, can be quite comparable to, or even larger than the sum of all ionic currents. If electrons are observed during the initial 10 or 20% of the pulse duration, there must be a source for these electrons, namely, detachment from a negative ion. (We remind the reader that the electrons of the ordinary ionization avalanche process remain in the gap for an electron transit time only, $\sim 10^{-7}$ sec for an electrode separation of 1 in. Electrons that are found in the gap microseconds after the initiating light flash are detached electrons, or are produced in ionization processes of detached electrons.)

This interpretation of the rapidly decreasing currents leads to the following hypothesis: In avalanches in oxygen there is an electron detachment

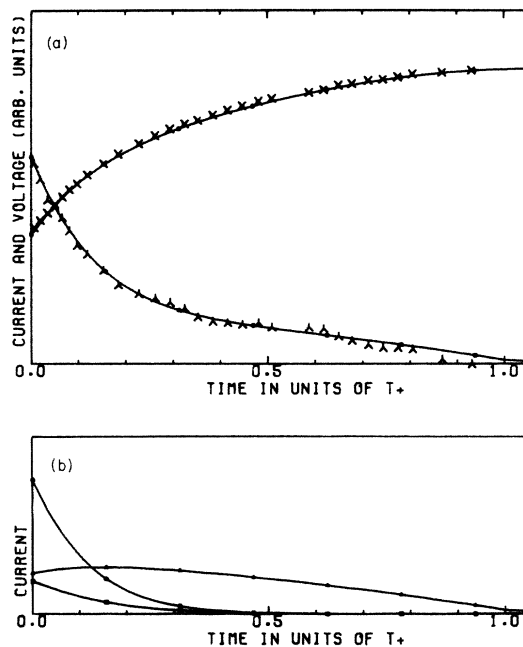


FIG. 2. (a) Electron avalanche in oxygen; comparison of experiment and theory. Experimental data: $E/p_{20} = 44.8$ V/cm Torr; $p_{20} = 7.9$ Torr; gap width $d = 2.54_0$ cm. The upper curve represents the integrated avalanche current (or total charge) vs time. The lower curve is current vs time obtained by graphical differentiation of the upper curve. The jump to a large value of the total charge curve at $T=0$ is due to the integrated primary electron component which occurs in the first 10^{-7} sec; this initial current has been suppressed on the lower curve. The solid line represents the best computer fit to the data: $\alpha d = 1.0$; $\eta d = 0.9$; $\eta_0 d = 0$; $\nu T_+ = 8$; where the ion transit time $T_+ = 36.3 \times 10^{-6}$ sec. (b) The components of computed current shown above. In order of magnitude at $T=0$: detached electron current (from O_2^-); positive ion current; current of unstable negative ions (O_2^-). (Very little O_3^- and O_4^- were discovered by mass spectrometer at this pressure.) (Experimental points are indicated by \times and \wedge .)

process occurring on a microsecond time scale. This is a relatively slow detachment process clearly discernible from a fast detachment process, which has been described earlier⁹ and which typically persists for small fractions of a microsecond under these conditions. The fast process was shown to be due to the atomic ion O^- , a conclusion which is fully supported by a recent extension of the earlier work.²² Hence, the slow detachment reaction must arise from one of the molecular ions O_2^- , O_3^- , O_4^- . Evidence for identifying the detaching ions as O_2^- is given in Sec. V.

The set of continuity equations (7)–(11) contains two parameters which describe the rapidly decreasing detached electron currents; b_{20} is the effective electron attachment rate for O_2^- and $-b_{22}$ is the total loss rate of O_2^- . The amplitude of this exponential is controlled in the main by the product of b_{20} and $-b_{22}$. The mean duration of it is controlled mainly by the loss frequency $-b_{22}$. Thus, by matching amplitude and duration of this exponential component, the two parameters b_{20} and $-b_{22}$ can be evaluated individually as an approximation.

The resultant b_{20} and $-b_{22}$ do depend to some extent on the choice of b_{50} (electron impact-ionization frequency) and, to a lesser degree, on b_{30} (attachment frequency leading to formation of stable negative ions). With decreasing pressure (approximately below 8 Torr), b_{30} becomes so small that stable negative-ion contributions have no noticeable effect on the observed pulse shape or on b_{20} and $-b_{22}$.

The influence of the ionization frequency b_{50} was such that larger apparent b_{20} and $-b_{22}$'s resulted from an increase of the trial value b_{50} . b_{50} is determined approximately by fitting the details of the positive-ion component near $t = \text{transit time}$ of the positive ions, as previously described.⁹ The precision of this approach, however, was not high and a range of consistent b_{50} values could vary between 20 and 50%. This uncertainty in b_{50} produced an approximately equal relative range of consistent b_{20} values but did not affect the loss rate $-b_{22}$ nearly as much. (This error was in addition to the uncertainties of b_{20} and $-b_{22}$ stemming from fitting the pulse shapes.) A different approach that could be utilized for measurement of b_{50} , however, was capable of yielding b_{50} values with a much higher accuracy,²³ particularly at the lower pressures of the experiment. With this improved b_{50} measurement the precision of the attachment and loss frequencies b_{20} , and $-b_{22}$ is also improved. If all assumptions concerning the reactions occurring in the oxygen avalanche are correct, then the remaining uncertainty in $-b_{22}$ does not exceed 20%. This uncertainty is due to the curve-fitting procedure and the dependence on auxiliary reaction rates which

are not known with higher accuracy. In no case is there an ambiguity in these data apparent which would lead us to doubt the uniqueness of the $-b_{22}$ and b_{20} measurement for any given recording.

Where stable negative ions had some influence on the observed pulse shape, the computed curves would not fit the experimental curves if $b_{30} = b_{40} = 0$ was assumed. Either $b_{30} \neq 0$ or $b_{40} \neq 0$ had to be assumed for a close fit, and under conditions of just discernible stable ion contributions there was an ambiguity as to which of the two, b_{30} or b_{40} , was the nonvanishing one. In such cases we chose $b_{40} = 0$ because, as pointed out elsewhere,¹⁴ $b_{40} \neq 0$ meant a pressure-square dependency of the loss frequency $-b_{22}$, which was not observed at low pressures. Also, the results of the mass-spectrometric investigation in this work indicated O_4^- concentrations to be smaller than those of O_3^- .

For this paper, accurate values of the electron drift velocity v_0 were not required because on a microsecond time scale the actual speed of the electrons does not influence the observed pulse shapes. Furthermore, all b_{ik} can be expressed in a dimensionless form which does not contain v_0 at all. (See the caption of Fig. 2 for an example.) The drift velocities of negative and positive oxygen ions in oxygen were taken from Refs. 24–27. Drift velocities of positive ions could be obtained directly in the present measurement, with lesser accuracy than in Refs. 24–27. In every case, our v_5 values were consistent with these values²⁷ to within a few percent.

V. MEASURED DETACHMENT RATES

The results of the measurements of the loss frequency over pressure ($-b_{22}/p$) are given in Fig. 3. At many E/p values, this frequency was measured at two or three pressures differing by a factor of 2 or 4, respectively. $-b_{22}/p$ is seen to be nearly independent of pressure. Thus we conclude that the loss is largely by a simple two-body process. We therefore have a three-body conversion frequency b_{42} , which is much smaller than the loss frequency $-b_{22} = b_{02} + b_{42}$, i.e.,

$$-b_{22} \approx b_{02}, \quad (13)$$

essentially everywhere for our condition of not too high pressures ($p \leq 32$ Torr). Hence, the loss of the unstable ion is predominantly by detachment, and Fig. 3 thus reports the detachment rate to pressure ratio of an ion species to be identified as O_2^- . Data are plotted as a function of E/p , which is a monotonic increasing function of the mean energy of the ion swarm. b_{02}/p increases rapidly with increasing mean ion energy suggesting an endothermic detachment reaction with a threshold

larger than the available mean ion energy. (Only the high-energy tail of the ionic distribution function is capable of undergoing detachment in a collision with a neutral gas molecule.)

The fact that the experimental data $-b_{22}/p$ form a smooth curve if plotted as function of E/p is considered a first confirmation for the correctness of the detachment hypothesis formulated in Sec. IV.

The question now arises as to why, of the four ions (O^- , O_2^- , O_3^- , O_4^-), the observed detachment reaction is attributed to O_2^- . We raise two arguments, one theoretical and one experimental, to show that this detachment arises from the diatomic ion O_2^- . (The discussion in Sec. VI concerning the formation of the ion undergoing detachment will further support this conclusion.)

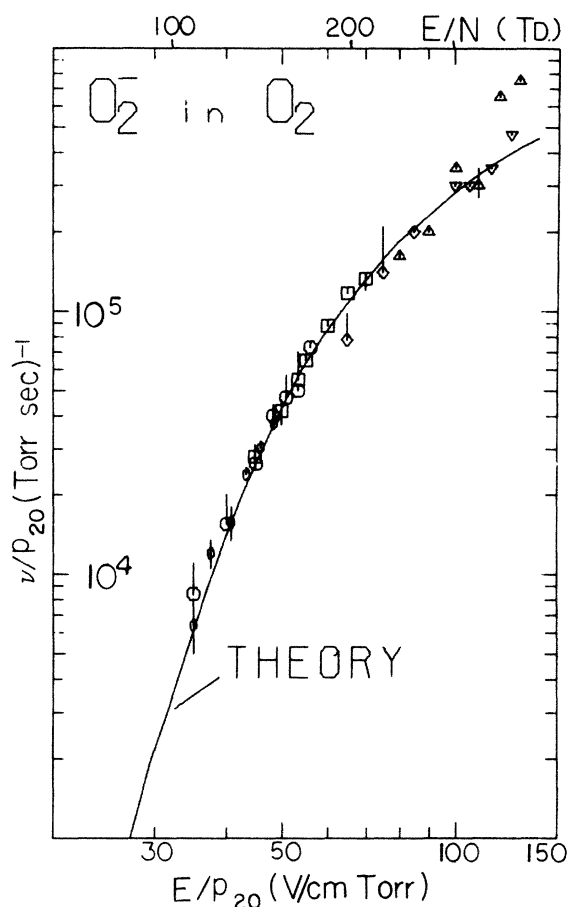


FIG. 3. Detachment frequencies, normalized to p_{20} , determined in this experiment. The solid line represents a calculation using the theory of Kagan and Perel (Ref. 31) described in the text. No pressure dependence is discernible for the ν/p_{20} values; identical values were obtained for as many as three different pressures differing by factors of 2 and 4, respectively. (\circ , 32 Torr; \square , 16 Torr; \diamond , 8 Torr; \diamond , 4 Torr; \triangle , 2 Torr; ∇ , 1 Torr.)

A. Theoretical argument

With a few simple assumptions, detachment frequencies for the various negative ions can be estimated according to

$$\frac{b_{0i}}{p} = N_1 \int \sigma_d(v) v F(v, \bar{e}) f(v_g, kT) d^6V, \quad (14)$$

where $i = 1, 2, 3, 4$ refers to one of the four negative ions O^- , O_2^- , O_3^- , or O_4^- . Here N_1 is the neutral density at a pressure of 1 Torr and σ_d is the cross section for detachment as function of the relative velocity v of the collision partners. $F(v, \bar{e})$ and $f(v_g, kT)$ are the distribution functions of ions and neutrals, with the mean energies \bar{e} and $\frac{3}{2}kT$ for ions and neutrals, respectively.

First we use Eq. (14) to estimate detachment frequencies for the various ions. The detachment cross section σ_d will be assumed to be zero below threshold and for easy comparison, constant (1 \AA^2) above threshold. The threshold energy is determined by the electron affinity A and relative speed v according to

$$\frac{1}{2} \mu v^2 \geq A, \quad (15)$$

where μ is the reduced mass of the collision partners. Furthermore, for this simple estimate here, the gas may be assumed at rest

$$f(v_g, kT) \equiv \delta(v_{gx}) \delta(v_{gy}) \delta(v_{gz}). \quad (16)$$

The mean energy of the ions is obtained from their drift velocities by means of an approximate formula of Wannier²⁸

$$\bar{e} = \frac{1}{2} (m + M) v_i^2 + \frac{3}{2} kT, \quad (17)$$

with m and M being the mass of the ion and neutral, respectively. With these simplifying assumptions and the electron affinities: $A(O^-) = 1.45 \text{ eV}$,²⁹ $A(O_2^-) = 0.44 \text{ eV}$,¹² $A(O_3^-) = 1.9 \text{ eV}$,³⁰ $A(O_4^-) = 1 \text{ eV}$.¹⁴ Estimates of the detachment frequencies of the four oxygen ions are given in Fig. 4 together with our experimental data. The estimates for O_3^- and O_4^- at the lower E/p are many orders of magnitude too small and certainly do not explain the experimental data. Even when the cross sections $\sigma_d(v)$ are somewhat adjusted, their slopes are generally too steep. (In a semilogarithmic plot such as Fig. 4, an adjustment of the cross section corresponds to a simple vertical shift of a computed curve as a whole, without changing the slopes of the curve.) These ions (O_3^- and O_4^-) can safely be eliminated from further discussion and will be considered to be stable (for $E/p \lesssim 100 \text{ V/cm Torr}$). The atomic ion O^- can also be eliminated as a generally poor fit of the data. Furthermore, in previous as well as in current work,^{9, 22} detachment rates of the atomic ion were measured and found to be larger

than the rates in Fig. 3 over most of the range of E/p in agreement with the theoretical estimates. The remaining ion is thus the diatomic ion O_2^- , for which we obtain agreement at least for the higher energies or E/p values.

At the lower E/p one expects the measured detachment rates to be larger than the simple estimate above, since the thermal energy of the neutrals, which was neglected [Eq. (16)], actually tends to increase the reaction rates. By proper accounting for the thermal energies, the overall fit is significantly improved. The reason is that the mean energies of O_2^- in O_2 are 0.125, 0.24, and 0.60 eV at $E/p = 30, 50,$ and 100 V/cm Torr, respectively, and thus are all relatively small compared to the critical energy X of the Boltzmann factor $e^{-X/\bar{\epsilon}}$. The value of X for O_2^- in O_2 is given by $X = 3mA/2\mu = 3A = 1.32$ eV. [This Boltzmann factor results from the use of a Maxwellian distribution function for the ions, $F \approx \exp(-3mv^2/4\bar{\epsilon})$.] As a consequence, the resulting reaction rates $b_{O_2^-}/p$ have a very strong energy dependence and even a small addition to the available energy by the thermal motion of the gas (0.04 eV) raises $b_{O_2^-}/p$ significantly. Therefore, for this case of the diatomic ion O_2^- , a more accurate evaluation of Eq. (14) is included.

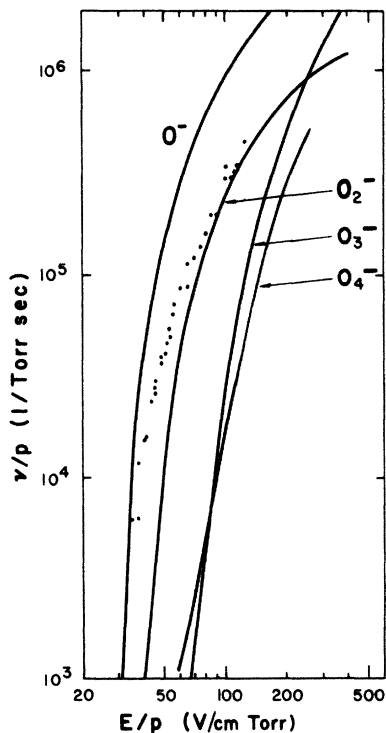


FIG. 4. Comparison of the crude estimates of the detachment rates for the four ions O^- , O_2^- , O_3^- , and O_4^- in oxygen. The dots represent the experimental points of Fig. 3.

The main interaction of O_2^- with O_2 is charge transfer, as is evidenced by the small mobility of O_2^- in O_2 in comparison with the other ions. Hence, the ion distribution function and mean ion energies can be obtained from the theory of Kagan and Perel,³¹ who consider charge transfer as the prevailing interaction in their theory of mobility

$$F(v, \bar{\epsilon}) = \left(\frac{3m}{\bar{\epsilon}}\right)^{1/2} \exp\left(-\frac{0.75mv^2}{\bar{\epsilon}}\right), \quad (18)$$

$$\bar{\epsilon} = \frac{1}{2} \pi m v_2^2. \quad (19)$$

A Maxwellian distribution function for the neutrals is assumed. With these expressions and recent measurements of O_2^- drift velocities²⁷ we obtain a mean energy of the O_2^- ion swarm of 0.16 eV at $E/p = 30$ V/cm Torr, and of 1.6 eV at $E/p = 150$ V/cm Torr, at the lower and upper end of our measurement, respectively. The theoretical curve $b_{O_2^-}/p$ vs E/p thus obtained is plotted in Fig. 3. It does reproduce the shape of the experimental curve very well. By adjusting the magnitude of the cross section

$$\sigma_d(v) = \begin{cases} 0 & \text{for } \frac{1}{2} \mu v^2 \leq A(O_2^-), \\ 0.65 \text{ \AA}^2 & \text{for } \frac{1}{2} \mu v^2 \geq A(O_2^-), \end{cases} \quad (20)$$

the experimental values of the detachment frequencies were matched (see the curve marked "theory" in Fig. 3). These results strongly favor the conclusion that in this work detachment from the diatomic ion O_2^- is being studied.

B. Experimental argument

In order to obtain more experimental evidence for such a conclusion, a mass-spectrometric study of the abundances of the various oxygen ions was conducted. At drift-tube pressures between 2 and 8 Torr, at E/p above 30 V/cm Torr, the prevailing negative ion was found to be diatomic O_2^- . The atomic ion O^- was also present at five to ten times smaller concentration. The ions O_3^- and O_4^- were found in still smaller concentrations at only the highest pressures. These findings are qualitatively consistent with the high E/p data of a similar mass spectrometric study by Moruzzi and Phelps.⁸ The conclusion is that for $E/p > 30$ not too high pressures ($p \leq 8$ Torr) only the atomic and diatomic ions are available for reactions.

The atomic ion O^- is lost very rapidly by electron detachment^{9,22} and charge transfer⁸ and is thus present in only small concentrations. Assuming on a trial basis that really the atomic ion O^- undergoes the observed detachment, then one must expect sizable current components due to the stable diatomic ion. At low pressures, however, there is no noticeable signal of a stable ion (see

Fig. 2, for example) in contradiction to the trial assumption above. The conclusion, therefore, is unavoidable that the most abundant ion (O_2^-) undergoes the detachment observed here.

Furthermore, for comparison with Eq. (20), the detachment cross section of O_2^- in O_2 can be estimated from Pack and Phelps's data of thermal detachment. Assuming now a Maxwellian distribution for both the ions and neutrals and using the detachment frequencies of Ref. 12, another estimate for the detachment cross section can be obtained (assuming again a constant σ_d above threshold). From Pack and Phelps's data¹² we obtain a detachment cross section of $0.62 \pm 0.07 \text{ \AA}^2$ over a temperature range from 375 to 450 °K,³² and slightly higher values at the higher temperatures (1.2 \AA^2 at 573 °K). This is consistent with our value [Eq. (20)], which we believe to be accurate to about 20%. (The apparent increase of the cross section with temperature may have to do with the changing rotational populations.)

Summarizing, it can be said that theoretical and experimental evidence indicates that the electron-detachment rates presented in Fig. 3 are those of the diatomic ion O_2^- . Another piece of supporting evidence for this conclusion will be given in Sec. VI.

VI. AUXILIARY DATA

As described in Sec. IV, a measurement of the detachment rate b_{02} will usually also produce rates b_{20} of formation for the ion undergoing collisional detachment, and under suitable conditions a rate b_{30} of formation of a (relatively) stable negative ion. These rates b_{20} , b_{30} are not necessarily attachment frequencies in the rigorous sense of the word and do not necessarily describe direct electron attachment processes. As it is outlined elsewhere,¹⁴ they rather represent "apparent" or "effective" attachment rates and depend critically on the time resolution of the experiment. For the present work the time resolution was chosen such that the lifetime of the primary, atomic ion O^- is too short to be resolved. As a consequence, "direct" electron attachment to form O_2^- and O_3^- is seemingly possible via charge transfer and ion conversion from the virtual state O^- , which was eliminated from the analysis. The meaning of the effective attachment rates become [see Eqs. (47) and (45) of Ref. 14]

$$\frac{b_{20}}{N} = \frac{\eta_2 v_0}{N} = KN + (\sigma_d v)_{av} ({}^{ct}p_0 + {}^{nr}p_0 {}^{ct}p_1), \quad (21)$$

$$\frac{b_{30}}{N} = \frac{\eta_3 v_0}{N} = (\sigma_d v)_{av} ({}^{ic}p_0 + {}^{nr}p_0 {}^{ic}p_1), \quad (22)$$

if one accepts the trial assumptions of O_2^- being the unstable and O_3^- the stable ion. In these expressions, K is the three-body attachment coefficient, which at the large E/p and the low pressures of our experiment may be expected to be negligible. $(\sigma_d v)_{av}$ is the cross section for dissociative attachment [Eq. (1)] by electron collision times the speed of the electrons, averaged over the electron distribution function. ${}^{ct}p_0$ is the probability that an atomic ion O^- undergoes charge transfer [Eq. (2)] in its first collision upon being formed, and ${}^{ct}p_1$ is the same probability of undergoing charge transfer in a collision, but after O^- has had at least one nonreactive collision with O_2 . The remaining ${}^{nr}p_0$ is the probability that the first collision of a newly formed O^- is a nonreactive one:

$${}^{ct}p_0 = [\sigma_{ct} v] / \{[(\sigma_d + \sigma_{ct} + \sigma_{nr}) v] + C_A N\}, \quad (23)$$

$${}^{ct}p_1 = \langle \sigma_{ct} v \rangle / \{ \langle (\sigma_d + \sigma_{ct}) v \rangle + C_B N \}, \quad (24)$$

$${}^{nr}p_0 = [\sigma_{nr} v] / \{[(\sigma_d + \sigma_{ct} + \sigma_{nr}) v] + C_A N\}, \quad (25)$$

$${}^{ic}p_0 = C_A N / \{[(\sigma_d + \sigma_{ct} + \sigma_{nr}) v] + C_A N\}, \quad (26)$$

$${}^{ic}p_1 = C_B N / \{ \langle (\sigma_d + \sigma_{ct}) v \rangle + C_B N \}. \quad (27)$$

Similarly, ${}^{ic}p_0$ and ${}^{ic}p_1$ are the probabilities that an O^- undergoes ion conversion in its very first collision with an O_2 , or after it has had at least one nonreactive collision, respectively.

Square brackets $[\dots]$ indicate averaging over the distribution function of such "new" O^- that have not had a collision since their formation. Angular brackets $\langle \dots \rangle$ indicate averaging over the distribution function of "old" O^- after many collisions, when an equilibrium with the field is established. The cross sections σ_d , σ_{ct} , σ_{nr} of electron detachment, charge-transfer, and nonreactive collisions are multiplied by the relative speed v of the collision partners (O^- and O_2). C_A and C_B are three-body rate constants for ion conversion of new and old O^- , respectively. The denominators reflect the selection of the competing reactions channels accounted for. It is worthwhile to note that the first three of these probabilities show a dependence on the gas density N according to $1/(\alpha + \beta N)$. Hence, the product ${}^{nr}p_0 {}^{ct}p_1$ of Eq. (21) exhibits a strong inverse pressure dependence, particularly at large pressures. Also note that the pressure dependence of the latter two probabilities is different from that of the preceding three, namely, ${}^{ic}p \sim N/(\alpha + \beta N)$. Here, a strong pressure dependence of Eq. (22) can be expected at small densities N , due to the numerator of Eqs. (26) and (27).

The quantities $b_{20}/N = \eta_2 v_0/N$ and $b_{30}/N = \eta_3 v_0/N$ become equal to the normalized apparent detachment coefficient η_2/p and η_3/p of Figs. 5 and 6, respectively, by multiplication with the gas density

$N_1 = 3.3 \times 10^{16} \text{ cm}^{-3}$ at 20 °C, and division by the electron drift velocities v_0 taken from Ref. 9.

Most striking in Fig. 5 is the strong pressure dependence of the effective attachment coefficient for the formation of the ion undergoing collisional detachment (O_2^-). At a constant mean energy, $E/p = 45 \text{ V/cm Torr}$ for example, the measured attachment coefficient to pressure ratios relate approximately as 1:3:6 for pressures of 32, 16, and 8 Torr, respectively. At the highest pressures, this indicates nearly an inverse pressure-squared dependence. Although the error bars of these data are at present still of considerable magnitude (particularly for the smallest η_2/p), the data clearly indicate that the reciprocal pressure dependence is stronger than linear at the highest pressures and at any E/p of our measurement. As outlined above, such a pressure dependence is to be expected for the diatomic ion O_2^- and stems mainly from the product $^m p_0^{ct} p_1$ in Eq. (21); the dependence on pressure of the remaining term $^{ct} p_0$ is probably not sufficient to account for the data. In any case, the peculiar pressure dependence of the data (Fig. 5) is quite consistent with our assumption of the diatomic ion O_2^- being responsible for the collisional detachment reaction observed here.

On the other hand, the data obtained for the stable ion increase (at constant E/p) with increasing pressure (Fig. 6). This increase is consistent with our identification of this ion (O_3^-) as outlined above and reflects the three-body nature of the ion conversion reaction, via the numerator in Eqs. (26)

and (27).

The rapid decrease of the apparent attachment coefficients η_2/p and η_3/p (Figs. 5 and 6), with energy (E/p) can be explained by the increasing loss of the intermediate atomic ion O^- by charge transfer and electron detachment, via the denominators in Eqs. (23)–(27).

Note that the data of Fig. 5 support further our identification of O_2^- undergoing the observed electron detachment. The trial assumption of the atomic ion O^- (rather than O_2^-) undergoing the observed detachment does not allow one to explain the strong pressure dependence observed. Furthermore, the pressure dependence in Fig. 6 reflects the three-body process according to Eq. (26) and hence supports our identification of O_3^- being the stable ion. It also shows that the observed detachment is not related to the triatomic ion O_3^- , because the pressure dependence of the effective attachment rates for the electron detaching ion would then have to be consistent with Eq. (26), which is certainly not the case as the data in Fig. 5 show.

Summarizing, it can be said that the “effective” rates of formation of O_2^- and O_3^- (Figs. 5 and 6) are consistent with our identification of the ions and lend further support to it. The ion undergoing collisional detachment can be the diatomic O_2^- , but not the atomic or triatomic ion, for which cases a very different pressure dependence of the data (Fig. 5) would be required. The relatively stable ion can only be the triatomic, and certainly not the diatomic ion, as the pressure dependence of the

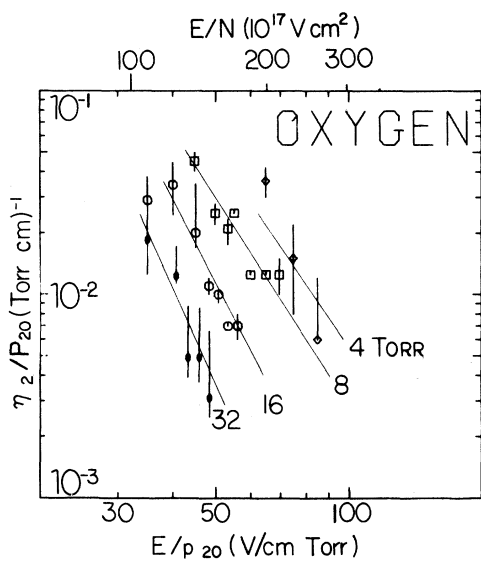


FIG. 5. Apparent attachment rates of the ion undergoing the observed detachment (O_2^-). (Lines drawn are for orientation only.)

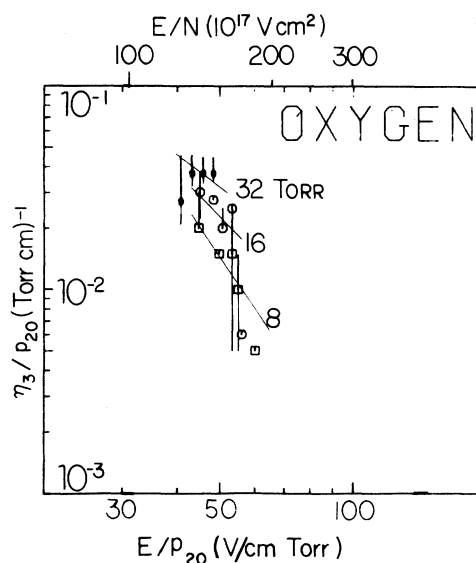


FIG. 6. Apparent attachment rates of the comparatively stable ion (O_3^-). (Lines drawn are for orientation only.)

data in Fig. 6 suggest. At present we are attempting to improve the accuracy of the attachment data η_2 and η_3 and a more detailed description of such data will be available in the near future.

VII. COMPARISON WITH OTHER WORK

Recently, from beam experiments it was concluded that the electron affinity of the diatomic ion O_2^- is 1.12 eV or larger,³³ and that the electron-detachment cross section of O_2^- in collisions with O_2 is very small, if not zero, for energies near the threshold and up to about 4 eV in the center-of-mass frame.³³⁻³⁵ Both statements appear to be inconsistent with our results above. Clearly, if an affinity $A(O_2)$ of 1.12 eV or more is assumed in our theory of detachment frequencies (Figs. 3 and 4), the resulting detachment frequencies would be orders of magnitude smaller and inconsistent with the experimental data. If the threshold for detachment was near 4 eV as suggested in those papers, the disagreement between theory and experiment (Fig. 3) would be disastrous.

The large value of the affinity of O_2 proposed by Bailey *et al.* is clearly inconsistent with the earlier measurement of Pack and Phelps,¹² as well as with a number of more recent determinations,³⁶⁻⁴⁰ in particular with the high-precision measurement of Celotta *et al.*⁴¹ All of these investigations are direct measurements of the affinity and agree on a value of about 0.433 eV. Bailey *et al.* derive their lower bound $A(O_2) \geq 1.12$ eV from a weakly developed extremum in the charge-transfer cross section of O^- in O_2 near 90 eV, using a rather sketchy theory of charge-transfer reactions. It is felt that the affinity of a molecular negative ion should not be inferred from such high-energy reactive scattering data, particularly not in the absence of charge-transfer cross-section measurements at still higher energies near 160-kV center-of-mass energy, where according to theory the maximum should appear if the well supported value of $A(O_2) = 0.43$ eV is used. A measurement of the electron affinity, or of the detachment energy, should be attempted near threshold and in a straightforward manner.

With regard to the electron detachment cross section near threshold, we remind the reader that the present measurement at mean ion energies between approximately 0.2 and 1 eV is consistent with the assumption of a constant cross section ($\sim 0.7 \times 10^{-16}$ cm²) near threshold. In support of this situation is our evaluation of the detachment cross sections from the work of Pack and Phelps,¹² with mean ion energies near 0.05 eV. If one assumes also a nearly constant cross section, Pack and Phelps' work requires that it be of about the same

magnitude. These two observations lend strong support to the assumption of a nearly constant cross section $\sigma_d \approx 0.7 \times 10^{-16}$ cm² near a threshold of 0.43 eV, and in Fig. 7 we have plotted this result together with the beam measurements³³⁻³⁵ at the higher energies. One observes that near threshold the detachment cross section is small, about only $\frac{1}{10}$ of its maximum value. This low-energy nonvanishing detachment cross section does not contradict the beam data, due to the absence of such data at these energies. Bailey *et al.* state that the beam experiment loses precision where the detachment cross sections are small.³³ Furthermore, the difficulties of beam experiments below beam energies of 1 eV are generally known. Summarizing, it can be said that the present results appear to be consistent with the beam experiments and supplement them for the low energies.

Recently, in oxygen at high pressures (~ 100 Torr), another electron detachment process was reported,⁴² which is thought to be due to the triatomic ion O_3^- . The results of that and the present work appear to be consistent; at these high pressures the lifetimes of both O^- and O_2^- are very short such that in a current-versus-distance experiment no curvature due to these ions is expected. On the other hand, at these pressures much O_3^- is formed and the lifetime of O_3^- is possibly sufficiently shortened to account for the apparent differences between Moruzzi's and the present experiment.

In a paper by Wagner,⁴³ detachment coefficients in oxygen are obtained, which are consistent with our earlier detachment frequencies of O^- in O_2 .⁹ However, on the basis of the present work (and of

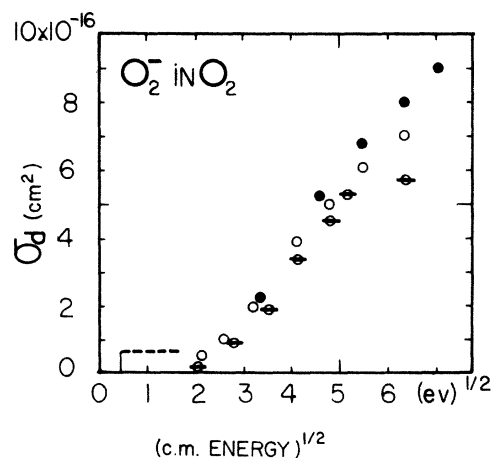


FIG. 7. Electron detachment cross section of O_2^- in O_2 . Dashed line: present results; \oplus , from Ref. 33; \circ , from Ref. 34; \bullet , from Ref. 35. Energies are in the center-of-mass frame.

Moruzzi's results⁴²) one would assume that a more complex reaction scheme than Wagner has proposed is necessary to account for detachment of several negative ions (O^- , O_2^- , O_3^-). Since Wagner uses only one continuity equation, for one negative ion undergoing detachment, his results must be considered an illdefined average over several detachment rates of the various negative ions present and cannot be used to support the present results for O_2^- . In any case, the detachment coefficients he obtained are of comparable magnitude as the ones reported here and generally support the conclusion of the significance of electron detachment reactions in current growth experiments in oxygen.

In a paper by Kinsman and Rees,⁴⁴ it is suggest-

ed that the reverse of the ion conversion reaction [Eq. (3)] is important under avalanche conditions. However, in our work at the highest pressures (32 Torr) we find avalanche pulse shapes which require the assumption of a nonreactive O_3^- . If significant amounts of O^- was produced from O_3^- , we should expect to see electron detachment from O^- as well as ionization processes due to these detached electrons, which would affect the observed pulse shapes noticeably. Instead, we observe transit times of the stable ions (O_3^-) which are only about 14% shorter than those of the positive ions, and no such ionization processes. We conclude that essentially all O_3^- is lost upon impact on the anode, but not by reaction in the gas.

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