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Measurement of negative ion mobilities in oxygen at high pressures with a pulsed Townsend technique

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Abstract. Using a pulsed Townsend technique, the mobility of a single, negative ion species in oxygen has been measured over the reduced field strength range $12 \times 10^{-17} \leq E/N \leq 59 \times 10^{-17}$ V cm^2 at high gas pressures of 20.7 and 68.9 kPa (155 and 510 Torr); E is the electric field intensity and N is the gas number density. Over this range, a mobility value of 2.16 ± 0.08 cm^{2}V^{-1}s^{-1} was determined, which compares well with those obtained by Snuggs and by McKnight, who could state the ion identity at pressures substantially lower than those of the present research. This agreement suggests that the ion species of concern is O_4^-, being formed by a three body collision process from the parent ion O_2^-. Further support to our hypothesis is provided by a simple analysis applied to the ion transients.

Resumen. Utilizando la técnica pulsada de Townsend, se ha medido la movilidad de un ion negativo en oxígeno, dentro del intervalo de intensidad de campo eléctrico reducido $12 \times 10^{-17} \leq E/N \leq 59 \times 10^{-17}$ Vcm^2, a altas presiones gaseosas de 20.7 y 68.9 kPa (155 y 510 Torr); E es la intensidad de campo eléctrico y N es la densidad del gas. Dentro de este intervalo, se determinó una movilidad de 2.16 ± 0.08cm^{2}V^{-1}s^{-1}, que está en buen acuerdo con las debidas a Snuggs y a McKnight, quienes pudieron establecer la identidad del ion a presiones sustancialmente menores que las usadas en la investigación presente. Este acuerdo sugiere que la especie iónica en cuestión es O_4^-, formado a partir de un proceso de tres cuerpos, del ion paterno O_2^-. Para dar mayor apoyo a esta hipótesis, se presenta un análisis simple, aplicable a los pulsos iónicos.

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1. Introduction

Because of the important role of oxygen in many gas discharge processes, it has been a gas of widespread research, for instance, on the complex ion chemistry of the atmosphere [1], in the chemical ionization in flames [2], in ozone production [3], and in the dielectric characteristics of air [4].

Although there exists a fair degree of qualitative agreement in what refers to the many ion-molecule reactions taking place in oxygen, there is still a need of more measurements on the various swarm parameters and reaction rate coefficients, and of increasing the ranges of measurement, both in reduced field strength, E/N, and in gas pressure (E is electric field intensity and N is gas number density). The ionic mobility, an important swarm parameter, provides a means of determining the effective temperature of the ionic species in the swarm; hence, the importance of determining it both theoretically and experimentally.

When a weak uniform electric field, $\mathbf{E}$, is applied throughout a gas, the ions will undergo a steady motion along the field lines with an average, drift velocity, $\mathbf{v}_d$, superimposed on the much faster random motion. In particular, $\mathbf{v}_d$ and $\mathbf{E}$ are related by the (scalar) mobility K as

$$\mathbf{v}_d = K\mathbf{E}.$$

This paper deals with the application of the Pulsed Townsend Method (PTM) to the measurement of the mobility of a single negative ion species in oxygen at the high gas pressures of 20.7 and 68.9 kPa (155, 510 Torr), and reduced field strengths, E/N, in the range 12–59 Td (1 Townsend, $Td = 10^{-17}$ Vcm^2). A comparison of the present mobility values with those of other authors taken at pressures substantially lower than those of this research (up to 0.8 kPa), strongly suggests that the ion of concern is O_4^-.

2. Experimental apparatus and measurement technique

The Pulsed Townsend Method is based on the observation of the total displacement current due to the individual charge carriers drifting across a parallel-plate discharge gap, to which an external, homogeneous electric field is applied. Well accounted reviews on this method can be found elsewhere [11–13]. The apparatus used in this research has been described in detail previously [14]. A schematic diagram of the setup is shown in Fig. 1. Briefly, the discharge gap consisted of two 13.4 cm nickel-plated electrodes with a 90° Rogowski profile. Initial electrons were generated by a very short flash of UV light (17 ns FWHM) from a ruby laser with frequency doubling ($\lambda = 347$ nm). The central portion of the cathode (1.5 cm radius) was covered with a thin layer of CuI to improve the photoelectron yield to about 3×10^8 electrons per pulse. The anode had a plane mesh covering a central hole of 2.6 cm in diameter to allow the light beam to reach the cathode.

Vacuum base pressures of less than 4×10^{-6} kPa were normally obtained. Gas pressures were measured from a KDG pressure transducer (0.2% full scale accuracy). The research gas had a quoted purity of 99.7% (BOC Ltd.). Prior to injection into the discharge vessel, the gas was passed through a liquid nitrogen trap to remove condensible impurities. Accuracies in the setting of gas density and of E/N were estimated to be about 2%.

The total current was measured by a resistor, R, inserted in series with the cathode and earth terminals, to which a stray capacitance, C, of about 40 pF was effectively connected. The voltage signal was further amplified by a video amplifier and recorded from a Tektronix 556 oscilloscope (time base accuracy 3%).

3. Analysis

Briefly, the most relevant processes taking place in oxygen, in the discharge gap over the pressure and E/N ranges referred to above, are as follows. At $E/N < 40$ Td, the three-body reaction

$$e + 2\mathrm{O}_2 \xrightarrow{k_a} \mathrm{O}_2^- + \mathrm{O}_2 \qquad (1)$$

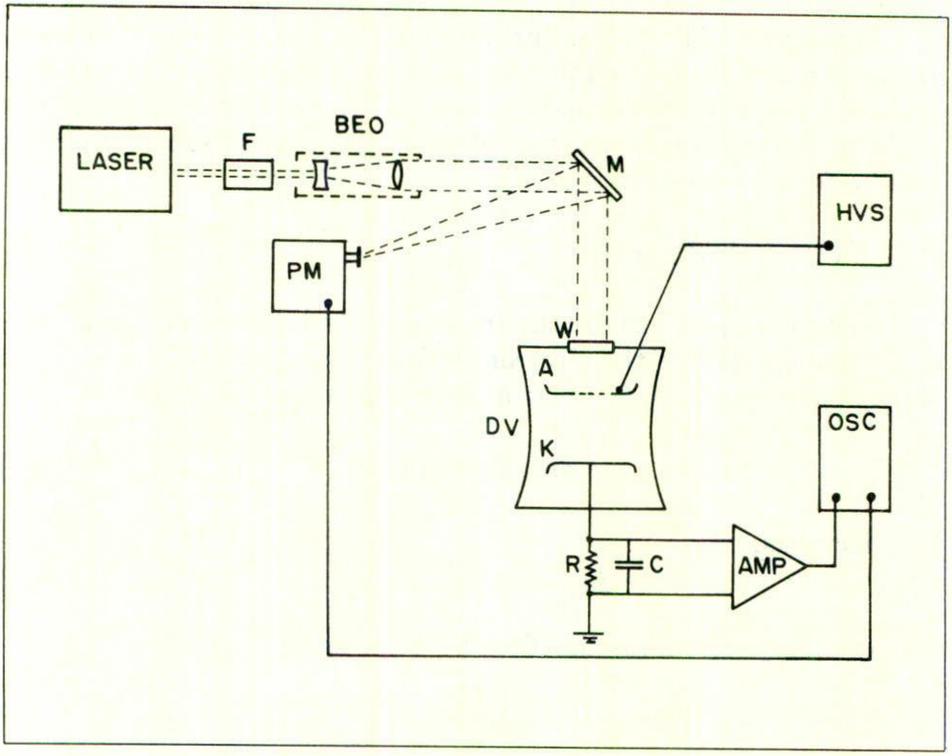

FIGURE 1. Schematic diagram of the apparatus. F-liquid filter to remove unconverted red light; BEO-beam expanding optics; M-mirror; PM-photomultiplier used for triggering the oscilloscope, OSC; DV-discharge vessel; W-quartz window; HVS-high-voltage stabilized power supply; A-anode; K-cathode; AMP-video amplifier.

predominates [5–7]. For gas pressures of above a few Torr, evidence of formation of the cluster ion O_4^- from O_2^- occurs via the three-body process [6, 8–10]

$$O_2^- + 2O_2 \xrightarrow{k_c} O_4^- + O_2. \tag{2}$$

Here, k_a and k_c are the attachment and clustering rate coefficients for reactions (1) and (2), respectively.

In the aim of providing further support to our measurements in terms of reactions (1) and (2), we shall present here a simple analysis based on the particular conditions of the experiment. Details on the steps to follow in the derivation of the current in the external circuit can be found elsewhere [14, 15].

3.1. Electron drift regime

The rate equations for the temporal development of charge carrier numbers during the electron drift regime, $0 \leq t \leq T_e = d/v_e$ (d is gap spacing and v_e is electron drift velocity), are

$$dn_e/dt = -\nu_a n_e \tag{3}$$

for electrons,

$$dn_1/dt = \nu_a n_e - \nu_c n_1 \tag{4}$$

for ions of species 1 (assumed to be O_2^-), and

$$dn_2/dt = \nu_c n_1 \tag{5}$$

for ions of species 2 (assumed to be O_4^-). Here, $\nu_a = k_a N^2$ and $\nu_c = k_c N^2$ are the respective attachment and clustering frequencies.

On the assumption that the initial photoelectrons are released at $t = 0$ as a delta pulse, then $n_e(0) = n_0$, and with $n_1(0) = n_2(0) = 0$, the solution of the above set of Eqs. (3–5) for the electron drift regime is

$$n_e(t) = n_0 e^{-\nu_a t}, \tag{6}$$

$$n_1(t) = n_0 C_1 \left[e^{-\nu_a t} - e^{-\nu_c t}\right], \tag{7}$$

$$n_2(t) = n_0 \left[1 + C_1 e^{-\nu_c t} - C_2 e^{-\nu_a t}\right], \tag{8}$$

where $C_1 = \nu_a/(\nu_c - \nu_a)$ and $C_2 = \nu_c/(\nu_c - \nu_a)$.

3.2. Ion drift regime

After the electron transit has elapsed, all electrons have been absorbed at the anode, leaving behind a cloud of much slower negative ions that remain virtually in their positions of formation, since $v_e \gg v_1, v_2$, the latter two being the drift velocities of ions of species 1 and 2, respectively. It is interesting to notice at this stage that at the high pressures used in this experiment, an evaluation of Eqs. (7) and (8) at $t = T_e$, results in $n_1 \ll n_2 \simeq n_0$, thus indicating that a saturated reaction, leading to the formation of mostly ions of species 2 has been accomplished. In doing this, we have taken values for the electron attachment coefficient, $\eta = \nu_a/v_e$, from Grünberg [7], and v_e and k_c data as compiled by Dutton [16], and Parkes [6], respectively. From k_c, $\nu_c = k_c N^2$ is obtained. Then, we are led for the analysis of the ion drift regime with only ions of species 2, the linear distribution of which, $N_2(x,t)$, obeys the continuity equation

$$\partial N_2(x,t)/\partial t + v_2 \partial N_2(x,t)/\partial x = 0, \tag{9}$$

which is solved according to the boundary conditions

$$N_2(x,0) = n_0 \eta C_2 \Big[e^{-\eta x} - e^{-\mu_c x} \Big] \tag{10}$$

and $N_2(0,t) = 0$, since there are no ions at the cathode, and with $\mu_c = \nu_c/v_e$. In deriving Eq. (10) from Eq. (8), we followed the arguments given in Refs. 14 and 15. Solution of Eq. (9) results in

$$N_2(x,t) = n_0 \eta C_2 \Big[e^{-\eta(x - v_2 t)} - e^{-\mu_c(x - v_2 t)} \Big] u(x - v_2 t), \tag{11}$$

where u is the unit step function. Finally, the measurable current in the external circuit is obtained by integrating Eq. (11) between the limits $v_2 t$ and d [15],

$$I_2(t) = (n_0 q_0 / T_2) \Big[1 + C_1 e^{-\mu_c(d - v_2 t)} - C_2 e^{-\eta(d - v_2 t)} \Big], \tag{12}$$

which is valid for $T_e \leq t \leq T_2$; q_0 is elementary charge and $T_2 = d/v_2$ is the ion transit time.

Since the time constant, RC, of the measuring circuit was kept small (≈ 40 ns, see section 2), then we could make use of the so called "differentiated pulse condition" [11]. Hence the measured voltage developed across resistor R is simply

$$V = RI_2(t). \tag{13}$$

An example of a measured transient in oxygen, and its fitting curve, calculated from Eq. (12) for three different values of k_c is shown in Fig. 2. Here, the transient shape gives a clear indication of the ion transit, *i.e.*, the time at which the current reaches zero value at $t = T_2$, from which v_2 is determined. The small spike at $t = 0$ is due to the influence of the RC time constant on the much faster electron component, but this is of no importance in the present case [14]. To fit the transients, values of v_e and η were taken from the references already cited. Then, we were led with only two free parameters to vary. Thus we found that the fitting process was very sensitive to variations in v_2 ($\sim 3\%$), which could be easily determined by the method outlined above; however, variations in k_c gave much lower sensitivity, between 50 and 100%. This is discussed below.

4. Results

It is customary to report reduced mobilities, K_0, instead of drift velocities; K_0 is calculated from v_2 as [17, 18]

$$K_0 = (v_2/N_0)(N/E), \tag{14}$$

where $N_0 = 2.69 \times 10^{19}$ cm^3 is gas number density at STP.

Present K_0 values are shown plotted in Fig. 3 as a function of E/N. No particular pressure dependence was observed at the two pressures used in this experiment. In fact, the K_0 data show a slight scatter of 0.08 around a mean value of 2.16 cm^{2}V^{-1}s^{-1}. This is in very good agreement with the zero-field mobilities for the O_4^-

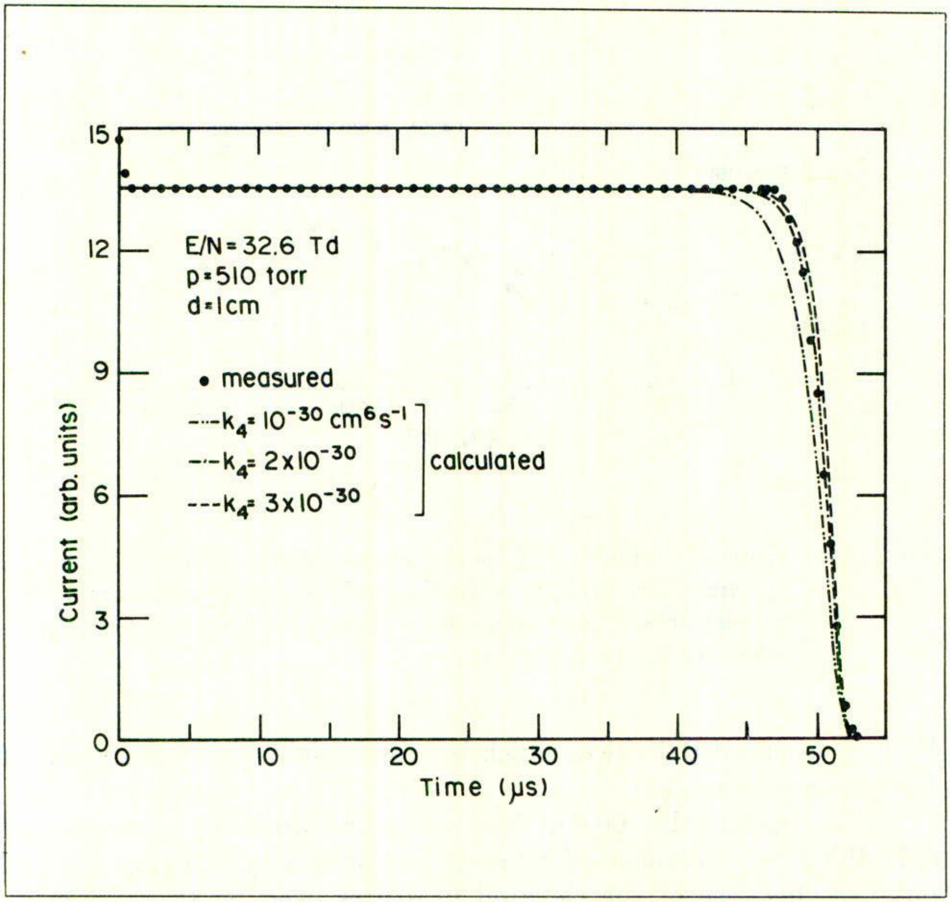

FIGURE 2. Sample measurement of an ion transient in oxygen (dots) and three calculated curves (Eq. 12) for different values of k_c. Other parameters used in the calculation were $\eta = 37$ cm^{-1}, $v_e = 6.6 \times 10^6$ cm s^{-1}, $v_2 = 1.33 \times 10^4$ cm s^{-1}.

species as reported by Snuggs *et al.* [10] (2.14 ± 0.08 cm^{2}V^{-1}s^{-1}) and by McKnight [9] (2.2 ± 0.1 cm^{2}V^{-1}s^{-1}), who performed their measurements in drift tubes with a mass spectrometer attached to the exit end, so that a clear identification of the drifting species could be assessed. However, their highest working pressure limit had to be

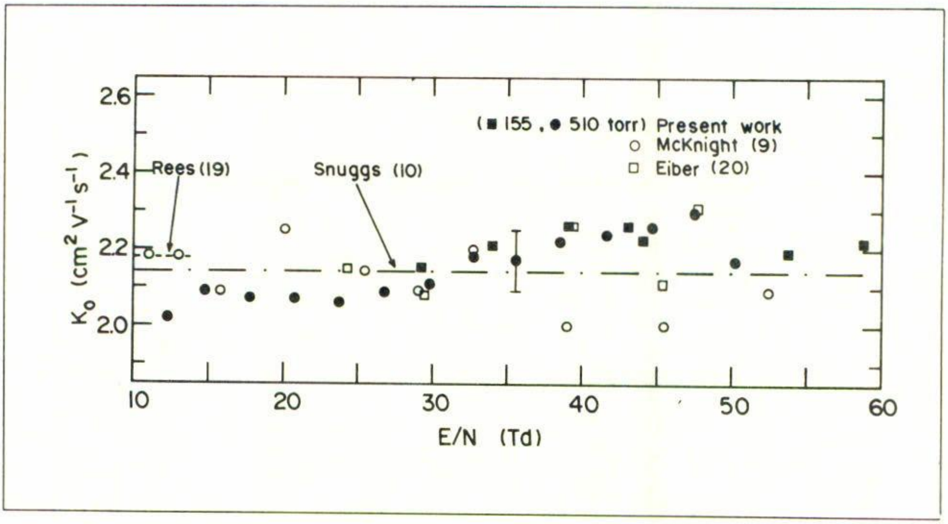

FIGURE 3. Reduced mobilities, K_0, in oxygen, as a function of E/N from this research. The error bar is indicative of the typical uncertainty of the present data. Values from other workers are also shown for comparison with the present data.

limited to about 0.08 kPa, which is substantially lower than that of the present research.

In discussing the data of Rees [19], who worked at pressures of 0.33–9.5 kPa, and those of Eiber [20] (1.3–49 kPa), Snuggs pointed out that because of the elevated pressures used by these workers, their detected ions, labeled by them as O_2^-, must have been spending most of their drift time as O_4^-, in clear reference to reaction (2). Indeed, this statement gives further support to our assumption of the ion under question as being O_4^-, on which we attempted to give some more insight into the interpretation of the ion transients.

As regards the clustering coefficients, k_c, we found that the "best" fits to the ion transients over the whole E/N range covered here, were achieved for mean values around 2×10^{-30} cm^{6}s^{-1}, with overall uncertainties between 50–100%. This apparent reaction coefficient turns out to be six times higher than that reported by

McKnight [9]. However, this author has pointed out that his values for $E/N > 20$ Td showed an apparent decrease which might not be real; moreover, the scatter around his mean k_c values ranged from 50–90%, and his data were obtained for pressures < 0.8 kPa. Consequently, it seems to us that a direct comparison cannot be made here. On the other hand, we are of the opinion that should less uncertain values of this coefficient be reported, the present technique deserves further improvements. Indeed, as can be seen from Fig. 2, the influence of k_c is only appreciable on the falling portion of the transient and, at the time scale we used in the measurement this represents only a small share of the whole transient shape. In view of this, no values of this coefficient can be reported at this time with a fair degree of confidence.

5. Conclusions

In the present paper, we have reported the reduced mobility of a single negative ion species in oxygen by using the Pulsed Townsed Method, over the E/N range 12–59 Td, and at elevated gas pressures of 20.7 and 68.1 kPa. Thus we have found that the mobilities of this ion are in very good agreement with those of other workers who could mass-analyze the ion, it being O_4^-. To our knowledge, no previous work in oxygen has been carried out with this method over the present E/N range at the high pressures used here. In view of the enormous difficulties of using mass spectrometers in drift tubes at pressures higher than about 1.3 kPa, we see here that the PTM can be applied successfully to the measurement of ion mobilities at pressures of up to several atmospheres provided that only one stable ion species becomes predominant at the early stages of discharge development, and that it remains stable during its drift through the gap. The simple analysis presented in this paper indicates that this is the case. As far as the determination of the clustering coefficients, further improvements to the measurement technique are underway.

Acknowledgements

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