

**Negative ion motion in the mixtures of SF<sub>6</sub> with CF<sub>4</sub> and CH<sub>4</sub>-Ar**J. de Urquijo<sup>1,2,\*</sup> and F. B. Yousif<sup>1</sup><sup>1</sup>*Facultad de Ciencias, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, 62210 Cuernavaca, Morelos, Mexico*<sup>2</sup>*Centro de Ciencias Físicas, Universidad Nacional Autónoma de México, Cuernavaca, Morelos P.O. Box 48-3, 62251 Cuernavaca, Morelos, Mexico*

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This paper deals with the measurement of the mobility of negative ions in the mixtures of SF<sub>6</sub> with CF<sub>4</sub> and the CH<sub>4</sub>-Ar (50:50) binary mixture with SF<sub>6</sub> contents up to 50%. The pulsed Townsend technique was used to observe the integrated ionic avalanches over a range of the density-reduced electric field  $E/N$  for which ionization is either negligible or absent, and attachment processes are significant, leading to the formation of mostly SF<sub>6</sub><sup>-</sup>. The  $E/N$  range of measurement was from 1 to 70 Td (1 Td = 10<sup>-17</sup> V cm<sup>2</sup>), over which the measured mobilities were found to be almost constant. The mobility of the negative ions was also measured for trace amounts of SF<sub>6</sub> in CH<sub>4</sub> and Ar and 1% CF<sub>4</sub>, thereby providing a good value of the mobility of SF<sub>6</sub><sup>-</sup> in these pure gases, in order to test the measured mobilities with Blanc's law. We have found good agreement, within quoted experimental uncertainties, between calculated and measured values.

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**I. INTRODUCTION**

Sulfur hexafluoride is a gas of widespread use in the high-voltage and semiconductor plasma processing industries. Its mixtures with other gases have become increasingly important, not only for etching but also for finding SF<sub>6</sub> mixtures with other gases that would retain many of its outstanding thermal and insulating characteristics, while being substantially less harmful to the environment [1]. Mixtures of SF<sub>6</sub> with CH<sub>4</sub>, CF<sub>4</sub>, or Ar are either currently used for practical applications, or have been suggested as potential replacements for using pure SF<sub>6</sub>. The present work is part of a long-term project to investigate the transport properties of SF<sub>6</sub> negative daughter ions in binary and ternary mixtures of this gas with rare hydrocarbon and halocarbon gases. On the other hand, from fundamental point of view, ion mobility measurements provide a means of testing Blanc's law [2,3], which enables the calculation of the mobility of a given species in a gas mixture in terms of the mobility of the same ion in the pure gases constituting the mixture.

Usually, drift tubes with mass spectrometry are used for studying ion transport since these apparatus can provide an almost unambiguous identification of the species under investigation. However, their higher pressure limit of operation is around 10 Torr, since the mass spectrometer(s) must be operated at pressures less than 10<sup>-5</sup> Torr. However, under some special circumstances like the present one, where there is only one negative ion majority species, the identity of which can be established by indirect means, the use of the pulsed Townsend method (PTM), lacking mass spectrometry, can be justified and thereby leads to accurate and reliable results. The use of this method is advantageous with respect to the drift tube-mass spectrometer in its wide range of operating pressures, usually from 0.1 Torr to 1000 Torr, as in the present case. It is well known that SF<sub>6</sub> has a very large electron attachment cross section for slow electrons,

leading to the formation of SF<sub>6</sub><sup>-</sup> with cross sections of 1.5 × 10<sup>-13</sup> cm<sup>2</sup> for 1 meV and 5 × 10<sup>-15</sup> cm<sup>2</sup> for 0.7 eV electrons, in contrast with a fairly constant attachment cross section for SF<sub>5</sub><sup>-</sup> formation of 2 × 10<sup>-16</sup> cm<sup>2</sup> over the same energy range [4,5]. In the present SF<sub>6</sub> mixtures, a negative ion signal can be ascribed to the presence of SF<sub>6</sub><sup>-</sup> as the majority species, since the density-reduced electric field intensity  $E/N$  used here was kept small. Furthermore, ionization processes can be ruled out, since these would have been apparent from the shapes of the ion transient signals as a step [6]. On the other hand, CH<sub>4</sub> and CF<sub>4</sub> are only slightly electronegative in comparison to SF<sub>6</sub> [6–8], forming negative ions by dissociative attachment at energies peaking at several electron volts. Usually, binary mixtures have been used and studied, like the present SF<sub>6</sub>-CF<sub>4</sub> mixture. In this work, we go one step ahead by showing that the negative ion mobility in the SF<sub>6</sub>-CH<sub>4</sub>-Ar ternary mixture can also be successfully predicted by Blanc's law, provided that the mobilities of the same negative ion species in pure gases SF<sub>6</sub>, CH<sub>4</sub>, and Ar are well known. The SF<sub>6</sub> content in the mixture were varied between 3.75 and 60% for SF<sub>6</sub>-CF<sub>4</sub>, and between 0.1 and 50% for SF<sub>6</sub>-CH<sub>4</sub>-Ar, by keeping the CH<sub>4</sub>:Ar ratio fixed at 50:50.

**II. ANALYTICAL BACKGROUND**

The time-resolved pulsed Townsend method relies on the measurement of the total displacement current due to electrons and ions drifting through a parallel-plate capacitor. Figure 1 shows a schematic layout of the experiment. Full accounts of this method can be found elsewhere [6,9,10].

The discharge is initiated by the instantaneous release of photoelectrons from the cathode by the action of Ultraviolet (UV) light. Under the action of the electric field between the electrodes, these photoelectrons will move toward the anode. According to the gas or gas mixture and to the  $E/N$  ranges, on their way to the anode they may ionize and (or) be attached to the gas neutrals. Since the electrons are more mo-

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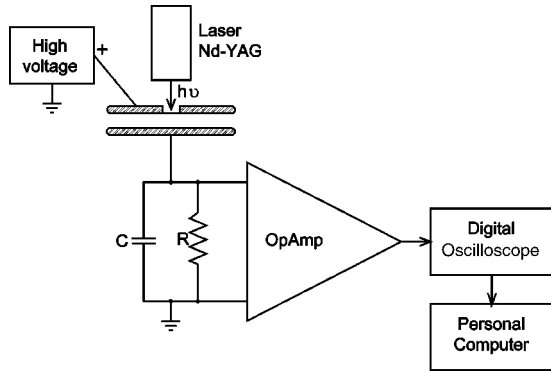


FIG. 1. Schematic diagram of the experiment.

ble (by a factor of 100 or more) than the ions, the latter will remain virtually in their positions of formation during the electron transit. Thus, on a much slower time scale, the ions will move toward their corresponding electrodes. This enables the distinction of two types of current contributions, namely, a fast or electronic component, and a second, slow or ionic component [9,10].

Under the present low  $E/N$  conditions prevailing in this investigation, and because of the relatively high pressures (50–1000 Torr) used, most of the initial photoelectrons become attached to the  $SF_6$  molecules during the first nanoseconds of discharge development. Thus, in the absence of ionization, the negative ion current during the electron transit is [9,10]

$$i_n(t) = \left( \frac{n_0 q_0}{T_n} \right) [1 - \exp(-\eta \nu_e t)], \quad (1)$$

where  $n_0$  is the photoelectron number,  $q_0$  is the ion charge,  $\eta$  is the electron attachment coefficient,  $\nu_e$  is the electron drift velocity, and  $T_n = d/\nu_n$  is the ion transit time, where  $d$  is the gap spacing and  $\nu_n$  is the negative ion drift velocity. Under conditions of strong attachment (low  $E/N$ , high pressure), the negative ion current can reach its maximum value well before the electron transit time  $T_e$ . During the ionic drift regime  $T_e < t < T_n$ , the negative ion current is [9,10]

$$i_n(t) = \left( \frac{n_0 q_0}{T_n} \right) (1 - \exp[-\eta(d - \nu_n t)]). \quad (2)$$

In the present experiment, this displacement current is integrated at the input of a very high impedance amplifier [6,9,11], which relies on the charging of the stray capacitance connected effectively between the input terminals. Moreover, as in the present case, when the gas pressure is high then the  $\eta \nu_e$  product is large, and Eq. (2) approximates very closely to

$$i_n(t) \approx \frac{n_0 q_0}{T_n} \quad (3)$$

for  $T_e < t < T_n$ , which is resemblant of a negative ion lamina formed by a very fast ion conversion process, travels toward the anode without losing its identity, since ion diffusion has been neglected. When the input resistance of the amplifier is

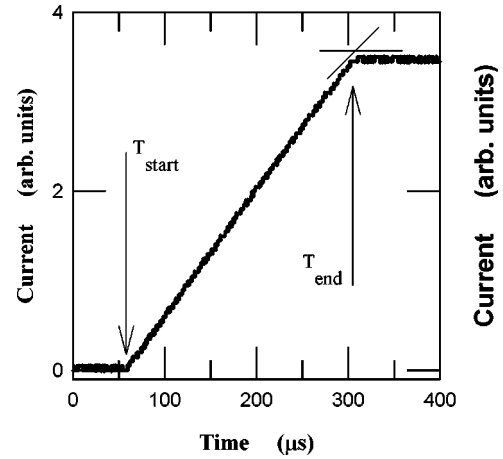


FIG. 2. Sample ionic transient in the  $SF_6-CH_4-Ar$  (20%:40%:40%) mixture,  $E/N = 16$  Td and 505 Torr total pressure.

very large ( $1 \text{ G}\Omega$  in the present case,  $C = 30 \text{ pF}$ ), then the passive resistance-capacitance circuit connected to the amplifier terminals behaves as an integrator. Thus, keeping in mind that  $\eta \nu_e$  product is large, the voltage between the input terminals of the amplifier is, using Eq. (3),

$$V_n(t) = \frac{1}{C} \int_0^t i_n dt \approx \frac{n_0 q_0}{C T_n} t, \quad (4)$$

which is a linear current growth to a maximum of

$$V_n(T_n) = \frac{n_0 q_0}{C}.$$

Figure 2 illustrates the above behavior very clearly for a negative ion transient in the  $SF_6-CH_4-Ar$  mixture. In the same figure, the arrows indicate the start and end of the ion drift regime from which  $T_n = T_{end} - T_{start}$ . The slight rounding edge around the  $T_{start}$  point is due mostly to diffusion. Also note that should there be more than one negative ion species with different mobilities, then the transient would show a break, which is completely absent from this curve thereby supporting the hypothesis that the majority species is  $SF_6^-$ . Finally, the drift velocity is evaluated by

$$V_n = \frac{d}{T_n}, \quad (5)$$

and from it the reduced mobility

$$K_0 = (\nu_d / N_0) / (E/N). \quad (6)$$

### III. EXPERIMENTAL DETAILS

The apparatus has been described for the first time in some detail elsewhere [12]. The vacuum vessel is a stainless-steel, six-way cross sealed with oxygen-free high-conductivity (OFHC) copper gaskets, with an approximate volume of 3 l. The vacuum system consists of 80 l/s turbo-molecular pump backed by a  $1.5 \text{ m}^3 \text{ s}^{-1}$  rotary pump. Nor-

mally, vacuum base pressures of less than  $10^{-6}$  Torr can be readily attained after about 20 min.

The discharge electrodes consist of a stainless steel anode and an aluminum cathode, both of 7 cm in diameter and 1 cm thickness, with rounded edges. The anode holds a central hole of 1 cm in diameter, covered by a flat OFHC copper mesh of 75 lines/mm, to allow the passage of the UV light from the laser, while keeping the electric field homogeneity on its surface. The material (aluminum) of the cathode was chosen because of its larger photoelectron yield in comparison to that of stainless steel. The cathode can be moved from outside via a linear motion feedthrough with 0.0254 mm accuracy. The gap (anode-cathode) distance was kept fixed at 1.360 cm throughout the experiment.

The electric field within the discharge gap was produced by a high stability 0–5 kV regulated power supply, with less than 10 mV residual ripple, and was monitored by a calibrated 10 000:1 voltage divider. The gas pressure was measured by a 0–1000 Torr range absolute pressure gauge (MKS Baratron, 622 C), with 0.02% accuracy.

The initial photoelectrons were generated by a fast flash of UV light from a 300  $\mu$ J nitrogen laser ( $\lambda=337$  nm, 3 ns full width at half maximum duration, and 50 mm<sup>2</sup> cross sectional area). Measurements of the electron component in CH<sub>4</sub>-Ar lead us to estimate that the laser-cathode combination was capable of providing a maximum of  $10^7$  photoelectrons per pulse.

The ionic avalanche was detected by a voltage amplifier of gain 20, 1 G $\Omega$  input resistance, and 15 MHz bandwidth. A stray capacitance  $C=30$  pF was estimated. In view of the relatively slow transit times of the ionic avalanches (50  $\mu$ s–5 ms) the above bandwidth is considered to be adequate. The amplified avalanche pulse was registered by a 60 MHz oscilloscope (Tektronix210), and stored in a personal computer for further analysis. A fast photodiode that detected some stray light from the quartz entrance window provided the synchronized triggering of the oscilloscope.

The gas temperature was read from a digital thermometer with 0.1 C resolution. The measurements were performed at room temperatures over the range 296–303 K. We estimate that the maximum error in the setting of  $E/N$  is less than 0.3%. The gaseous mixtures were prepared inside the discharge vessel by first injecting SF<sub>6</sub> followed by the injection of CF<sub>4</sub> or premade mixture of 50% CH<sub>4</sub> and 50% Ar. The purity of the gases used was 99.8% and 99.3% for SF<sub>6</sub> and CF<sub>4</sub>, and 99.99 for the premade CH<sub>4</sub>-Ar mixture at a ratio of 50:50.

#### IV. RESULTS

For the two mixtures considered in this study, the drift velocity (mobility) of the negative ion species is the average of at least three different measurements at the same  $E/N$  and different gas mixture pressures. Hence, the associated uncertainties correspond to these averages. The overall accuracy in the average values of the drift velocity (mobility) is 2–5%. Some of the SF<sub>6</sub>-CH<sub>4</sub>-Ar mixture mobility data have been reported previously as a conference proceeding [12]. The

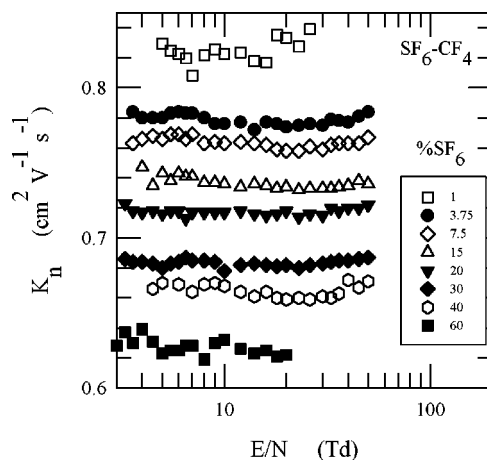


FIG. 3. The reduced mobility of negative ions (assumed SF<sub>6</sub><sup>-</sup>, see text) in the SF<sub>6</sub>-CF<sub>4</sub> mixture.

data reported in this paper, together with those for SF<sub>6</sub>-CF<sub>4</sub> should be considered as final.

#### V. NEGATIVE ION MOBILITY IN SF<sub>6</sub>-CF<sub>4</sub> AND SF<sub>6</sub>-CH<sub>4</sub>-Ar

The reduced mobilities of the SF<sub>6</sub> negative ion species in SF<sub>6</sub>-CF<sub>4</sub> and SF<sub>6</sub>-CH<sub>4</sub>-Ar are displayed in Figs. 3 and 4, respectively, as a function of  $E/N$ . Common to these two plots is the decrease in the value of the reduced mobility with the increase in the SF<sub>6</sub> content in the mixture, which is consistent with the fact that the interaction of the SF<sub>6</sub> daughter negative ion with its parent SF<sub>6</sub> is strongest than within the other gases. Also, one can notice a fairly constant mobility over a rather wide range of  $E/N$ , which is indicative of the regime where the long-range attractive part of the interaction potential is predominant. According to Wannier [13], this regime is characterized by a linear dependence of the drift velocity with  $E/N$  or, equivalently, a constant reduced mobility.

Also in Fig. 4, we have included the mobility curve of

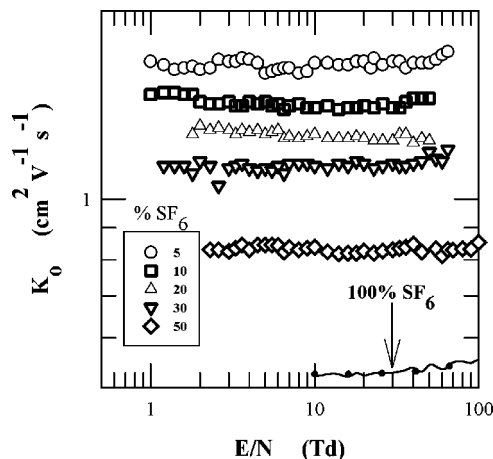


FIG. 4. The reduced mobility of negative ions (assumed SF<sub>6</sub><sup>-</sup>, see text) in the SF<sub>6</sub>-CH<sub>4</sub>-Ar mixture. The broken line corresponds to 100% SF<sub>6</sub> [14].

TABLE I. Values of low-field mobilities for  $SF_6^-$  in Ar,  $CH_4$ ,  $CF_4$  and  $SF_6$  in  $cm^2V^{-1}S^{-1}$ .

$SF_6^-$ in Ar	1.68
$SF_6^-$ in $CH_4$	1.87
$SF_6^-$ in $CF_4$	0.825
$SF_6^-$ in $SF_6$	0.542

$SF_6^-$  in  $SF_6$ , taken from a previous pulsed Townsend measurement [10], which is in excellent agreement with a drift tube-mass spectrometer measurements of  $SF_6^-$  in  $SF_6$  indicated by the arrow at the left-hand side axes [12]. The presence of  $CF_4$ ,  $CH_4$  and Ar in large amounts in the mixture makes them act as efficient electron scatterers, thereby keeping the electron energy distribution centered at low energies, where the electron attachment processes are large, leading to the formation of mostly  $SF_6^-$ . Thus, in the following, we shall assume that the negative ion species under question is  $SF_6^-$ .

## VI. COMPARISON OF MEASURED MOBILITIES WITH THOSE CALCULATED FROM BLANC'S LAW

A second fact that leads us to support our assumption that  $SF_6^-$  is at least the predominant ion in the mixture is the test of the above low-field (up to  $E/N=10$  Td) ion mobilities in the mixture with Blanc's law, from which the negative ion mobility in the  $n$ th gaseous component mixture is [2,3]

$$\frac{1}{K_{mix}} = \sum_{j=1}^n \frac{x_j}{K_{i,j}}, \quad (7)$$

where  $K_{ij}$  is the ionic mobility of species  $i$  ( $SF_6^-$  in the present case) in the pure gas  $j$  and  $x_j$  is the molar fraction of gaseous species  $j$  in the mixture.

In order to evaluate the mobility of the negative ion in these mixtures previous knowledge of the mobility of  $SF_6^-$  in the pure gases  $SF_6$ ,  $CH_4$ ,  $CF_4$ , and Ar is needed. The mobility of  $SF_6^-$  in  $SF_6$  has been widely studied with drift tube-mass spectrometers [12,14,15] with a value of  $0.542 cm^2 V^{-1} s^{-1}$ . However, to the best of our knowledge, no published data exist for the low-field mobility of  $SF_6^-$  in any of the gases listed above. In order to obtain these values, we measured the mobility of negative ions of gas mixtures with small amounts of  $SF_6$  in the other gases. For relatively inexpensive gases like  $CH_4$  and Ar, we used 100 ppm and 50 ppm  $SF_6$ , respectively. For the case of  $CF_4$  we limited our measurements to only 1%  $SF_6$ . However the latter value was found low enough to be used as a limiting value of the mobility of  $SF_6^-$  in  $CF_4$ , as it will be shown below when discussing the low-field mobilities according to Blanc's law. The low-field mobility values are given in Table I. Using these values in Eq. (7), the calculated zero-field reduced mobility of  $SF_6^-$  in the present binary  $SF_6$ - $CF_4$ , and the ternary  $SF_6$ - $CH_4$ -Ar mixture are plotted in Fig. 5 as a function of the  $SF_6$  content. For the  $SF_6$ - $CF_4$  mixture, most of the calculated

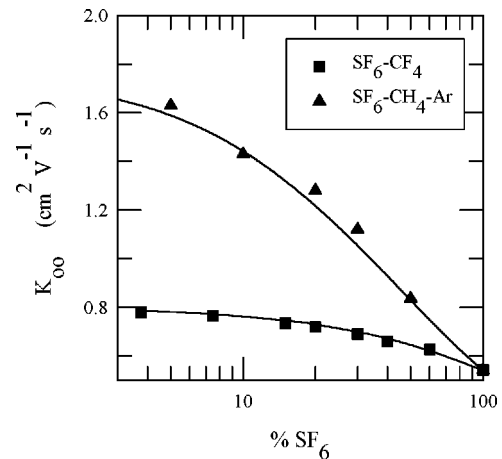


FIG. 5. The measured low-field mobility of  $SF_6^-$  in the  $SF_6$ - $CH_4$ -Ar (closed squares) and the  $SF_6$ - $CF_4$  mixture (closed triangles) and their corresponding calculated curves (solid lines) according to Blanc's law [Eq. (7)], using the low-field mobility data for  $SF_6^-$  in the pure gases (see Table I).

values are higher than those measured, but in all cases these fall within the quoted uncertainties (2–5%).

## VII. CONCLUSIONS

The time-resolved pulsed Townsend method has allowed us to measure the negative ion mobility in the binary  $SF_6$ - $CF_4$  and the ternary mixture  $SF_6$ - $CH_4$ -Ar, over a wide range of  $E/N$  and gas pressure. The shape of the measured transients indicating that there is only one drifting ionic species, together with the low  $E/N$  values used have led us to assume that the majority ion species under question is  $SF_6^-$ . The second abundant ionic species is undoubtedly  $SF_5^-$  but is present in relatively small amounts under the conditions of this experiment, since it is formed with smaller cross sections at higher electron impact energies. Moreover, the good agreement found when testing the low-field mobilities with Blanc's law provide further support to our assumption that the drifting ion is, at least predominantly,  $SF_6^-$ . We have also demonstrated the usefulness of measuring the mobility of the negative ion species at trace concentration, which is almost equivalent to measuring the mobility of the negative ion in a foreign drifting gas. These mobilities have been found essential to test our measurements with Blanc's law. The present data are hoped to be useful both for gaining more insight into the fundamental processes governing ion transport and for the simulation of electrical discharges.

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