Effect of small admixtures of N₂, H₂ or O₂ on the electron drift velocity in argon: experimental measurements and calculations

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Abstract. The electron drift velocity in argon with admixtures of up to 2% of nitrogen, hydrogen or oxygen is measured in a pulsed Townsend system for reduced electric fields ranging from 0.1 Td to 2.5 Td. The results are compared with those obtained by Monte Carlo simulations and from the solution of the electron Boltzmann equation using two different solution techniques: a multiterm method based on Legendre polynomial expansion of the angular dependence of the velocity distribution function and the Sₑ method applied to a density gradient expansion representation of the distribution function. An almost perfect agreement between the results of the three numerical methods and, in general, very good agreement between the experimental and the calculated results is obtained. Measurements in Ar-O₂ mixtures were limited by electron attachment to oxygen molecules, which contributes to the measured drift velocity. As a result of this attachment contribution, the bulk drift velocity becomes larger than the flux drift velocity if attachment is more probable for electrons with energy below the mean value and smaller in the opposite case. Attachment also contributes to the negative differential conductivity observed in Ar-O₂ mixtures.

1 Introduction

Trace amounts of molecular gases in an atomic gas background have a large impact on the values of the electron transport properties and rate coefficients. Although this effect is known and has been studied for some time, numerous industrial and research applications [1] of discharges in argon with molecular admixtures sustain a continued interest in this problem.

The presence of small amounts of molecular admixtures in argon plasmas modifies the emission characteristics in glow discharge optical emission spectrometry [2,3], radio-frequency glow discharges [4,5] and glow discharge mass spectrometry [6]. A controlled addition of either hydrogen [7], nitrogen [8] or oxygen [9] is used to enhance the emission yields of certain spectral lines and thus to improve the detection limits. In addition, molecular admixtures influence the electrical characteristics and sputtering rate when used in these analytical techniques [10]. Mixtures of argon with CO₂, O₂ or H₂ are also used as a shielding gas for arc welding of metals and alloys [11,12].

In addition, applications of discharges in argon-molecular gas mixtures include surface treatment [13] and sterilization of heat sensitive materials [14].

Admixtures of molecular gases are also known to improve stability of discharges in argon. It was found in [15,16] that steady-state partially constricted glow discharges, i.e. glow discharges where the diffuse and constricted form of the positive column exists simultaneously, can easily be realized and reproduced when adding small amounts of N₂ to argon, while the formation of such discharges is rather accidental than regular in pure argon. Correct assessment of the impact of impurities on discharges in rare gases is therefore necessary in order to obtain meaningful quantitative results or to improve agreement with simulation results [17,18].

The measurement of transport properties in mixtures of atomic and molecular gases is also useful for testing and adjusting electron-collision cross section sets. Collisions leading to vibrational excitation increase the energy losses thereby reducing the average electron energy. For the same values of reduced electric field E/n, the transport properties for different concentrations are sensitive to different energy ranges of the cross sections [19].

In the present work we measure the electron drift velocity in argon with small admixtures of nitrogen, oxygen and hydrogen, respectively, at low reduced electric field values. We compare the results with those obtained numerically using updated cross sections and discuss how the changes in the electron energy distribution function

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with the admixture concentration explain the results obtained.

2 Experimental setup

The results are obtained at ambient pressure of 100 kPa using a single shutter drift tube shown schematically in Figure 1. Electrons are generated by a corona discharge in a point-to-plane geometry. The point electrode is a 100 µm diameter tungsten wire tip, which acts as a cathode. The plane electrode is made of nickel plated brass, with a central aperture of 5 mm through which electrons are transmitted. The distance between the electrodes is 10 mm and the voltage applied to them is in the range from 2 to 2.5 kV. The discharge is fed by an Ar-N₂ mixture with a mixing ratio of 25:1 and total flow of 26 ml/min. The admixture of N₂ is necessary to keep a stable discharge current as discharges in pure Ar have a tendency to spark. The discharge current is also stabilized using a 6 MΩ resistor.

The electron drift velocity \( W \) is determined from the flight time of electrons through a drift tube with a fixed length of 111 mm. Electrons are periodically released into the drift tube in 1 µs or 2 µs pulses controlled by a shutter grid formed by coplanar parallel wires according to the Bradbury-Nielsen design [20]. The electron current is measured at the collector at the end of the drift tube. The collector is shielded by a fine Ni mesh placed 1 mm in front of it to prevent charge induction by the approaching electrons. The electron current is amplified by a variable gain current/voltage amplifier (model DHPA-100, FEMTO GmbH). The amplified signal is averaged and recorded with a digital oscilloscope.

The drift tube is composed of brass rings separated by PTFE rings. The metal rings are attached to a resistor chain in order to form a homogeneous electric field inside the drift tube. The pressure inside the drift tube is measured using a capacitive gauge, while the temperature of the gas exiting the instrument is measured by a K-type thermocouple. The voltage on the drift tube is set to the desired value of \( E/n \) with the help of a HV probe. The accuracy of the \( E/n \) values is estimated to be within ±2%. The maximum value of \( E/n \) that can be applied to the drift tube is 2.5 Td (1 Td = \( 10^{-17} \) V cm²) and is limited by electric breakdown.

The drift tube is fed by a gas mixture prepared using MKSTM mass flow controllers. The total flow rate is 1000 ml/min for all the mixtures used. The drift tube is separated from the rest of the instrument by an aperture of 6 mm to prevent the diffusion of the discharge gas into the drift tube. The indicated purity of the gases used is 99.9996% for argon and 99.999% for H₂, N₂ and O₂. The gas inlet system is made of high purity materials, PTFE and stainless steel. Prior to each measurement, the instrument is baked out and pumped down by a dry membrane pump to a pressure of 4.5 mbar and subsequently flushed with argon for about one hour.

The electron drift time is determined from the time difference between the opening pulse of the shutter grid and the position of the maximum of the electron current peak recorded by the oscilloscope. In order to minimize errors, transition effects in the shutter and in the collector are taken into account by subtracting half of the shutter opening interval and the delay of the shutter response (0.1 µs) from the measured drift time. The delay of the amplifier response is also subtracted from this time interval. In order to determine the delay of the amplifier response, the electron current waveform is recorded with different amplifications (see Fig. 2). A 10⁶ amplification is used to study the Ar-N₂ and Ar-H₂ mixtures while amplification factors of 10⁷ and 10⁸ are used for the Ar-O₂ mixtures. Comparing the waveforms in Figure 2, the delay of the electron peak due to the amplifier response is determined to be 0.1 µs, 0.5 µs and 1.5 µs for amplification factors of 10⁶, 10⁷ and 10⁸, respectively. We estimate the accuracy of drift time measurements to be within ±250 ns for amplifications of 10⁶ and 10⁷ and within ±500 ns for an amplification of 10⁸, resulting in an uncertainty of drift velocity values between 2.5% and 6.5% and increasing with \( W \).
3 Simulation of the electron swarm

The experimental results are compared with computed drift velocity values using three different approaches: a Monte Carlo simulation [21,22] and two different approaches for the solution of the Boltzmann equation for the electron swarm. The two approaches differ in their initial physical assumptions and in the numerical algorithms used.

3.1 Multiterm method

The first solution technique (referred to as I) considers that the electrons move in a steady-state plasma where the microscopic and related macroscopic properties are determined by the time- and space-independent Boltzmann equation for the velocity distribution function \( f(v) \). For constant electric field the distribution function acquires a reduced dependence on the magnitude \( v \) of the velocity \( v \) and the direction cosine \( \cos \theta \), where \( \theta \) is the angle between the velocity and the field direction. It can be expanded with respect to \( \cos \theta \) into Legendre polynomials \( P_k(\cos \theta) \) according to

\[
f(v, \cos \theta) = n_e \frac{1}{2\pi} \left( \frac{m_e}{2} \right)^{3/2} \sum_{k=0}^{l-1} f_k(U) P_k(\cos \theta),
\]

where the velocity magnitude was replaced by the kinetic energy \( U = m_e v^2 / 2 \) on the right-hand side. Here, \( n_e \) and \( m_e \) are the density and mass of the electrons. Employing expansion (1) up to an arbitrary number \( l \) of expansion coefficients a set of partial differential equations for the expansion coefficients \( f_k(U) \) results. The equation system with typically eight expansion coefficients is solved by means of a generalized version of the multiterm solution technique [23] adapted to account for non-conservative electron collision processes. In particular, the electron attachment to O\(_3\) is treated as an electron loss process when using the present method and the other two approaches. Assuming positive electric field strength, the magnitude of the flux drift velocity \( v_d \) [24] is obtained from the first contribution \( f_1 \) to the distribution anisotropy according to

\[
v_d = -\frac{1}{3} \left( \frac{2}{m_e} \right)^{1/2} \int_{0}^{\infty} U f_1(U) dU. \tag{2}
\]

3.2 Density gradient expansion

The second approach (referred to as II) takes into account space gradients in the electron density, considering that after a certain time and far from boundaries, the electrons move in a hydrodynamic regime where the swarm electron velocity distribution can be expanded in terms of powers of the density gradients according to

\[
F(r, v, t) = \sum_{i=0}^{\infty} f_i^{[0]}(v) \otimes (\nabla)^i n_e(r, t),
\]

where the functions \( f_i^{[0]}(v) \) are tensors of rank \( i \) and \( \otimes \) indicates an \( i \)-fold scalar product [25]. The numerical method used is based on the discrete ordinates \( S_\alpha \) [26]. The use of (3) in the electron Boltzmann equation results in a set of equations for the cartesian components of each function \( f_i^{[0]}(v) \), all with the same structure. These are solved on a \( (v, \theta) \) grid.

In order to compare the results obtained by both approaches for the solution of the Boltzmann equation and to help in the interpretation of the results, it is necessary to discuss the meaning of the first two of these functions. \( f_i^{[0]}(v) \) is the space averaged velocity distribution function of the swarm and is proportional to the distribution function (1). The expansion of \( f_i^{[0]}(v) \) in Legendre polynomials with respect to \( \cos \theta \) results in expansion coefficients \( f_i^{[0]} \) identical to those in (1). Accordingly, from now on we will drop the superscript \( [0] \) of these expansion coefficients. The function \( F_i^{[1]}(v) \) is proportional to \( f_i^{[0]}(v) \) and to the difference between the average position of electrons with velocity \( v \) and the average position of the swarm.

In this approach the drift velocity measured in time-of-flight experiments includes an explicit contribution from reactions occurring in the gas. White et al. [24] use the term bulk drift velocity to designate this value and flux drift velocity for the conventional definition. The relationship is

\[
W = v_d + S^{[1]} \tag{4}
\]

where \( W \) and \( v_d \) represent bulk and flux drift velocities, respectively, and \( S^{[1]} \) is the contribution from non-conservative processes. The flux drift velocity here is the same as in (2) and \( S^{[1]} \) is

\[
S^{[1]} = \int \nu_{eff} f_i^{[1]}(v) dv \tag{5}
\]
where $f^{[1]}(v)$ is the component of $f^{[1]}(v)$ along the field direction and $\nu_{eff}$ the effective ionization frequency (i.e. the difference between the ionization and attachment frequencies). Expanding this component with respect to $\cos \theta$ into Legendre polynomials, only the isotropic term, $f^{[1]}_{2n}$, contributes to $S^{[1]}$.

### 3.3 Monte Carlo simulation

The Monte Carlo code (MC, referred to as III) simulates the transport of electrons in a homogeneous external electric field. The task to be solved in this approach is twofold: one has to (i) follow the trajectories of the particles between collisions and (ii) handle the collisions of the particles with the background gas. (Here we consider only collisions of the traced particles with the atoms/molecules of the background gas, and neglect e.g. electron-electron collisions). The present code uses the null-collision technique, which makes it possible to assign random durations of free flights to electrons between their collisions with the background gas [27]. The positions of the collisions are obtained from the equation of motion. Whenever a collision occurs, the type of the collision is assigned in a random manner, taking into account the ratios of cross sections of all possible processes (weighted by the densities of the gases in the mixture). All collision processes are assumed to result in isotropic scattering; the scattering and azimuth angles in the collision events are assigned using random numbers. The simulations are set to run “long enough” to ensure that the swarm reaches hydrodynamic conditions, where transport coefficients do not change in time. The method of data collection and the calculation of the transport coefficients is based on [28]. In order to achieve sufficient accuracy a high number of electrons is traced, the results presented in this paper have been obtained from simulation runs handling $\sim 10^{11}$ collisions for each set of conditions.

These three approaches and solution techniques have previously been compared with other techniques and have found to be highly accurate [29]. Using the values obtained by approach I for the flux drift velocity and mean energy as reference, we computed the relative differences to these values using the two other approaches. Table 1 summarizes the average and standard deviation of the differences obtained for the range of electric field and concentration values studied. The results obtained by these three approaches show an almost perfect agreement.

### 3.4 Cross sections

All three solution techniques shared the same cross sections. We used the recommended data on electron collision cross sections from [30–35]. In addition, we used the more recent elastic momentum transfer cross sections for collisions of electrons with $N_2$, $H_2$ and $O_2$ from [36].

Collisions of second kind with vibrational levels were not included as vibrationally excited levels have negligible population. Assuming e.g. that the vibrational temperature is the same as the gas temperature, the ratio between the first two vibrational levels of the ground electronic state is of the order of $10^{-4}$ for $O_2$ and even lower for $N_2$ and $H_2$.

The $O_2$ cross section set includes a three body attachment cross section in pure oxygen. As discussed in [37], however, the efficiency as third body, $\varepsilon$, for $O_2$ is expected to be higher than for other gases. We have found only one measurement [38] of the relative efficiency of argon but the authors report large errors for measurements with rare gases. Because of the uncertainty of this value we have considered two cases: (a) $\varepsilon_{Ar} = \varepsilon_{O_2}$ and (b) $\varepsilon_{Ar} = 0.025\varepsilon_{O_2}$, the value indicated in [38]. In case (b) the cross section or the $O_2$ concentration are too small for this process to have any influence on the results.

Figure 3 shows the weighted sum of cross sections per type of process in pure argon and argon with 1% of each admixture.

### 4 Results and discussion

We have measured the electron drift velocity for $Ar$ with admixtures of $N_2$ or $H_2$ for values of admixture concentration between 0% and 2% and at reduced electric field strength, $E/n$, between 0.5 Td and 2.5 Td. Measurements in $Ar-O_2$ mixtures were limited by electron attachment and covered the range between 0.1 Td and 1.5 Td. At higher values of $E/n$ the electron current was below the sensitivity of the collector, indicating a strong electron attachment to $O_2$. In these ranges of reduced electric field the ionization frequencies are negligible and the bulk and flux drift velocities in $N_2$ and $H_2$ are equal. However in $O_2$ the bulk and flux drift velocities are expected to be different because of the contribution of electron attachment to $S^{[1]}$.

The results for the drift velocity are represented in Figures 4–6 as a function of the calculated mean energy as this allows a better comparison between the three mixtures and a better understanding of the results. The error bars on the experimental values correspond to an uncertainty of 1σ. The lines connect the numerical values at constant concentration and constant reduced field. When the differences between the results of the three approaches are too small to be clearly identified in the figures, only one set of numerical results is represented (usually from I) and

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar-H_2$</td>
<td>(0.05 ± 0.12)%</td>
<td>(0.62 ± 0.12)%</td>
<td>(0.62 ± 0.12)%</td>
</tr>
<tr>
<td>$Ar-N_2$</td>
<td>(−0.03 ± 0.05)%</td>
<td>(−0.44 ± 0.11)%</td>
<td>(−0.44 ± 0.11)%</td>
</tr>
<tr>
<td>$Ar-O_2$</td>
<td>(0.01 ± 0.08)%</td>
<td>(1.56 ± 1.18)%</td>
<td>(−0.44 ± 0.61)%</td>
</tr>
</tbody>
</table>

Table 1. Average value and standard deviation for the relative difference between the results on $v_d$ (first line) and mean energy (second line) obtained by approach II or III and approach I.
Fig. 3. (Color online) Weighted sum of cross section per type of process in pure argon and argon with 1% of N$_2$, H$_2$ or O$_2$. [m]: momentum transfer; [r]: rotational excitation; [v]: vibrational excitation; [x]: excitation of electronic levels; [i]: ionization; [3ba]: three body attachment at 1 atm and 300 K for $\varepsilon_{Ar} = \varepsilon_{O2}$. If $\varepsilon_{Ar}$ is reduced by 0.025, the combined cross section is too small to be visible in the figure; [2ba]: two body attachment.

Table 1 should be kept in mind as reference to the other results.

The experimental values in Ar-N$_2$ (Fig. 4) and Ar-H$_2$ (Fig. 5) mixtures are in very good agreement with the numerical results. In Ar-H$_2$ mixtures, however, experimental data at $E/n \geq 1.5$ Td and [H$_2$] $\geq$ 1% are below the calculated results but the differences are not statistically significant. On the other hand, most of the experimental data in Ar-O$_2$ mixtures (Fig. 6) are above the calculated results of W using $\varepsilon_{Ar} = \varepsilon_{O2}$ with most prominent differences at low $E/n$ and high O$_2$ admixture.

The present results are also compared with other experimental results. Figure 4 includes results for pure Ar [39–41] and for mixtures with 0.1% and 1% of N$_2$ [42]. Very good agreement is obtained for the 1% [N$_2$] mixture, while for 0.1% [N$_2$] few points are below the present data.

For the Ar-H$_2$ mixtures (Fig. 5) we compare the present results with the result of Haddad and Crompton [43] at 0.5 Td for 0.5% [H$_2$], and with the data shown in the work of Engelhardt and Phelps [44]. The original sources of these values for 1% and 1.5% [H$_2$] were not published. The data for the 1% [H$_2$] mixture significantly exceed both our experimental and calculated results. Considering the good agreement with the values from other authors as well as the data for 1.5% [H$_2$], we conclude that the data for 1% [H$_2$] reported in [44] are less accurate.

Figure 6 includes results from Jeon and Nakamura [45] in an Ar-O$_2$ mixture with 1.01% [O$_2$] and covering the
present range of $E/n$. Most of the data slightly exceed the calculated values for $W$. They are, however, in a very good agreement with the present experimental results. At 0.1 and 0.15 Td for 1% [O$_2$], however, both the present experimental values and those from [45] are well above the numerical results. The differences could not be attributed to impurities (see next section) or other experimental errors. A possible explanation relies on incorrect values for the cross sections for $U < 0.6$ eV, in particular of the cross section for three body attachment in O$_2$, or the vibrational excitation of O$_2$.

Notice that the contribution of $S^{[1]}$ in (4) decreases and $v_d$ increases and approaches the values $W$ shown in Figure 6 when assuming $\varepsilon_{Ar} = 0.025\varepsilon_{O_2}$ for the three body attachment cross section.

### 4.1 Effect of impurities on the results

The present experimental results show small deviations from the experimental data for pure argon reported in [39,40] (cf. Fig. 4). The most probable explanation for this disagreement is the presence of impurities in the argon filling gas and/or in the experimental system due to wall degassing or small leaks. To estimate the level of impurities that may be present, we calculated the electron drift velocity in Ar with traces of N$_2$, up to 20 ppm using method I (Fig. 7). At an admixture of 5 to 8 ppm of N$_2$ the experimental values were reproduced for all studied values of $E/n$. We therefore assume that the presence of trace amounts of air around 7 ppm explains the observed experimental values of $W$ for pure Ar. The effect of these trace amounts, however, should become negligible once a much higher concentration (up to 2%) of a molecular gas is added to Ar. Therefore, we conclude that impurities do not affect to a considerable extent the measured values of $W$ for the gas mixtures studied.

### 4.2 Electron velocity distribution function

In order to understand the observed behaviour of the drift velocity, it is important to look at the effect of the admixtures on the two first expansion coefficients of the electron velocity distribution function (evdf), $f_0$, $f_1$ and on $f_{\infty}^{[1]}$, with expressions (1)–(5) in mind.

#### 4.2.1 Isotropic component $f_0$

Figure 8 shows the isotropic component $f_0(U)$ of the evdf in pure argon and in argon with 1% of each of the admixtures for $E/n = 2.5$ Td calculated using either of the Boltzmann methods. The admixture of molecular gases causes a depletion of the high energy tail of $f_0$ and an increase of the number of low energy electrons. Among the three gases, N$_2$ has the strongest and O$_2$ the weakest impact.

In mixtures with N$_2$ we observe a strong increase in the number of electrons with energies below 2 eV followed by a steep drop of two orders of magnitude resulting from the very intensive impact of the electron collision processes mainly leading to vibrational excitation of N$_2$.

The position of the drop corresponds to the energy of the maximum of the vibrational and rotational cross sections (see Fig. 3). This is followed by a less abrupt decline at around 7 eV corresponding to the threshold of electronic excitation processes.

The results are in accordance with experimental detections of the isotropic distribution in glow discharges in Ar-N$_2$ mixtures [46] and in Ne-N$_2$ mixtures [47,48] showing that $f_0$ depends sensitively on the amount of N$_2$. 

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**Fig. 6.** (Color online) Computed bulk and flux drift velocities in Ar-O$_2$ mixtures as a function of the mean energy for several admixture concentrations assuming that both gases have the same efficiency as third body in three body collisions. Symbols: experimental values from this work and [45]; lines: numerical results from approach II: continuous lines: bulk drift velocity, $W$; dotted lines: flux drift velocity, $v_d$.

**Fig. 7.** (Color online) Drift velocity in Ar with N$_2$ admixtures on the ppm level calculated using approach I (lines). The symbols indicate the drift velocity measured in argon without admixtures.
Comparing with the previous case, the drop in $f_0$ in mixtures with H$_2$ is more monotonous but with a shorter tail, which is explained by a lower maximum amplitude of the vibrational and rotational cross sections compensated by a larger energy spread of these cross sections.

Mixtures with O$_2$ show the smallest increase on the number of low energy electrons but with a steep drop of the tail in the range between 6 and 9 eV.

Comparing with Figure 3 we observe that the sharp peaks of the O$_2$ vibrational cross section between 0.3 and 1.5 eV have a minor influence and the electronic excitations with thresholds starting above 0.98 eV are responsible for the drop of $f_0$.

4.2.2 First anisotropy component $f_1$

The changes in the first contribution $f_1(U)$ to the anisotropy of the evdf with the admixture concentration are shown in Figure 9 for $E/n = 2.5$ Td and mixtures of Ar plus N$_2$, H$_2$ and O$_2$, respectively. Because $f_1$ is negative, its magnitude is shown here. In pure Ar $|f_1|$ shows a minimum at 0.23 eV, which is the result of the Ramsauer minimum of the momentum transfer cross section.

Elastic collisions are efficient in randomizing the direction of the electrons and the maximum of $|f_1|$ has a relatively low value with the main contribution to $v_d$ coming from electrons with energies between 4 eV and 8 eV.

As soon as we admix any of the molecular gases, the number of electrons losing energy in inelastic processes increases. These electrons are subsequently accelerated in the field direction and the maximum of $|f_1|$ starts to increase forming a peak in the region of the vibrational and rotational cross sections. This explains the increase of $v_d$ most of which comes from electrons with progressively lower energies. However, the three gases show very different behaviour:

(a) The admixture of 0.1% of N$_2$ has already a large impact on $|f_1|$ with the formation of a maximum one order of magnitude larger than in pure Ar for electrons with energies between 1 eV and 3 eV. The maximum increases with the N$_2$ concentration but at a progressively slower pace and, above a concentration of 1% it starts to saturate. This corresponds to the observed behaviour of $W$ in Figure 4, showing a strong increase at low N$_2$ concentration and becoming almost constant above a given value.

(b) H$_2$ has a similar effect but the formation of the maximum occurs only for higher values of H$_2$ concentration, has a smaller value and is broader. However, contrary
to the case for N₂, it continues to increase with H₂ concentration. The behaviour of W in Figure 5 is consistent with these observations.

(c) O₂ has also the weakest impact on f₁. The resonances on the vibrational excitation cross sections of O₂ are responsible for the formation of an oscillatory structure at energies below 1 eV that, when the O₂ concentration increases, becomes the most intense. Above this region and roughly between 1 eV and 5 eV, the shape of f₁ changes with concentration, but the values are within the same order of magnitude. The changes in f₁ become less pronounced when the concentration increases. The peak in the drift velocity with concentration occurs around (0.3–0.5) eV and is contributed by two factors: (a) the resonances of the vibrational cross section and, (b) the three body collision attachment as the curves for the flux drift velocity v_d and bulk drift velocity, W, in Figure 6 show. This is discussed in the following section.

4.2.3 Isotopic component f₁[0] in Ar-O₂ mixtures

The electron attachment to O₂ contributes to the drift velocity measured in the present experiment. A comparison between the bulk and flux drift velocities computed by approach II considering that both gases have the same efficiency as third body in three body collisions, shows two different regions (Fig. 6): (a) for low mean energy values, W is higher than v_d; (b) above a certain value, depending on the O₂ concentration, the two curves cross and v_d becomes slightly higher than W. If we consider the efficiency as third body of argon at a fraction of the efficiency for O₂, the two curves become indistinguishable in region (a) but region (b) is unchanged. This is an indication that region (a) is determined by three body attachment, while region (b) by two body attachment. This is confirmed in Figure 10 showing the isotopic component f₁[0] in mixtures with 0.8% of O₂ for two values of E/n, (0.15 Td and 2.5 Td), respectively, together with the product of the effective ionization frequency with v² for the two values of three body efficiency of Ar discussed in Section 3.4. As explained in Section 3.2, the negative or positive values of f₁[0] correspond to electrons with average position respectively behind or in front the average position of the swarm. For E/n = 2.5 Td (blue line) the main contribution to the integral in equation (5) comes from the range (5–8) eV where f₁[0] is positive (corresponding to electrons with energy above the mean energy) and the negative peak in v_d v² (from two body attachment) dominates. In this region S₁ is negative and W < v_d. However, for E/n = 0.15 Td (red line), the negative region of f₁[0] gives the main contribution to the integral in (5), and we need to consider the two cases for three body attachment: (a) when the Ar efficiency as third body is the same as O₂ (green line), S₁ is positive and W > v_d; (b) when the Ar efficiency is a small fraction of the efficiency of O₂, three body attachment has a negligible contribution and W ≈ v_d.

![Fig. 10. (Color online) Isotopic component of f₁[0] in mixtures of Ar with 0.8% of O₂ for E/n = 2.5 Td (blue line) and 0.15 Td (red line). The product of the effective ionization frequency with v² is also shown for two values for the efficiency of argon as third body in three body attachment: (a) ε_Ar = ε_O₂ (green line) and, (b) ε_Ar = 0.025 ε_O₂ (yellow line).](image)

4.3 Negative differential conductivity

We observe a local maximum of the drift velocity with the reduced field in several mixtures. This effect is known as “negative differential conductivity” (NDC) and has been previously reported in mixtures of an atomic and a molecular gas, also in some pure gases [49], and in RF fields [50]. To explain the processes behind the NDC, substantial work has been conducted. It has been recognized that conditions for the NDC to occur are given by relative changes of the momentum transfer cross section and the cross section for inelastic processes at low electron energy [51,52]. In particular, an increasing momentum transfer cross section as well as a decreasing inelastic collision cross section favour NDC, while superelastic collision processes tend to reduce NDC. Occurrence of the NDC is limited to the range of E/n where inelastic collisions significantly contribute to the average loss of electron energy per collision. It can be shown that a decrease of the electron energy and of the collision frequency for momentum transfer at given E/n results in an increase on drift velocity. This increase within a finite range of E/n may result in the formation of a local maximum followed by a decrease in W when E/n increases. Conditions for the presence of NDC are very favourable in argon with a small admixture of a molecular gas [53]. The Ramsauer-Townsend minimum in the momentum transfer cross section of argon is followed by a rapid increase in the cross sections for inelastic collisions with the molecular gas. The details in each mixture, however, are significantly different.

4.3.1 Ar-N₂ mixtures

For constant field W increases significantly for very small amounts of N₂ and stabilizes afterwards (cf. Fig. 4). This
increase is accompanied by a reduction of the mean energy to a value close to 1 eV.

At very low mean energy, few of the swarm electrons have an energy above the threshold for inelastic processes and \( W \) approaches asymptotically its value in pure Ar. This approach at low mean energy and the decrease of the mean energy with increasing \( N_2 \) concentration results in a saturation of \( W \) with increasing \( N_2 \) concentration. It also explains that at low \( E/n \) the saturation is reached at lower admixture concentration than at high \( E/n \).

### 4.3.2 Ar-H\(_2\) mixtures

\( NDC \) is also observed in Ar-H\(_2\) mixtures for some values of \( H_2 \) concentration although in a much less visible way (cf. Fig. 5). The maximum of \( W \) is not so pronounced as in the case of \( N_2 \). We do not observe a saturation of \( W \) with increasing \( H_2 \) concentration and, in general, a higher amount of \( H_2 \) is necessary to produce a comparable effect. This can be attributed to lower cross sections for inelastic processes than in the case of \( N_2 \) and to a much larger spread of the cross sections without sharp slopes. Both a fast increase or decrease of the inelastic cross sections are important for the occurrence of \( NDC \) [51].

### 4.3.3 Ar-O\(_2\) mixtures

The local maximum of \( W \) in Ar-O\(_2\) mixtures takes place at a much lower mean energy ((0.3–0.5) eV) just above the Ramsauer minimum, where the momentum transfer cross section increases rapidly and the vibrational and rotational cross sections show a series of sharp peaks. Both conditions favour the occurrence of \( NDC \) [51,52]. However in this case three body attachment can also contribute to the increase of the local maximum, depending on the value of \( \varepsilon_{Ar} \). In any case the contribution of attachment to the \( NDC \) is expected to increase with \( O_2 \) concentration. Because attachment reduces the number of electrons significantly, it becomes increasingly difficult to determine the drift velocity then [54].

The relatively large effect of attachment on inducing the \( NDC \) has already been noticed and discussed for model cross sections in [55]. Furthermore, Goyette et al. [56] supposed that the \( NDC \) found in their electron drift studies of Ar-C\(_4\)F\(_6\) mixtures could partially be induced by the electron attachment properties of C\(_4\)F\(_6\). To our best knowledge the contribution of attachment to \( O_2 \) to the \( NDC \) has not yet been reported.

### 5 Conclusions

Measurements of the drift velocity of electrons in argon-molecular gas mixtures have been carried out using a drift tube. The experimental results were obtained with an uncertainty below 4% for most of the conditions. The admixture concentration was varied between 0.1% and 2%, and the reduced electric field ranged between 0.1Td and 2.5Td.

The measurements were accompanied by numerical computations using three different methods. Good agreement between the experimental and the calculated results was obtained, with most of the calculated results lying within the uncertainty band of the experimental results. The three numerical methods used show almost identical results.

Gas impurities were estimated to be lower than 8 ppm and only influence the results for the lowest values of admixture concentration.

\( NDC \) can be observed in mixtures of Ar with any of the molecular gases studied, depending on the admixture concentration.

The analysis of the first anisotropic component \( f_1 \) of the evfd aided the understanding of the variation of \( W \) with the admixtures concentration and shows that the main contribution for \( W \) comes from electrons with energy between 1 eV and 3 eV for \( N_2 \) and \( H_2 \).

The contribution of attachment to \( O_2 \) on \( W \) has to be considered under the present experimental conditions and can either increase or decrease \( W \) in comparison with \( v_g \). It was shown that, in this case, attachment also contributes to the \( NDC \).

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