Electron swarm parameter measurements of perfluorobut-2-ene (2-C_4F_8)

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In this contribution, the electron swarm parameters of perfluorobut-2-ene (2-C_4F_8) mixtures with the buffer gases N_2, CO_2 and Argon are experimentally investigated. The effective ionization rate constant and electron drift velocity are measured in the entire *E/N* range up to the critical density-reduced electric field.

1. Introduction

Sulphur hexafluoride (SF_6) is widely used nowadays in high voltage gaseous insulation. It has many advantages such as high electric strength, low boiling point and chemical stability. However, due to the high global warming potential (GWP) of SF_6, considerable efforts are made to find alternative gases.

An approach was used for screening a large number of gases [1] for their predicted GWP, electric strength and boiling point. 2-C_4F_8 came out as a very promising candidate, its predicted electric strength is 1.6 ± 0.35 times that of SF_6.

The electron swarm parameters of 2-C_4F_8 are investigated using a pulsed Townsend experiment. The effective ionization rate and electron drift velocity are measured in diluted mixtures of 2-C_4F_8 with respectively N_2, CO_2 and Ar. The present results are compared to calculations using the attachment cross sections of 2-C_4F_8 obtained by earlier investigators [2, 3].

2. Structure of 2-C_4F_8

The molecular structure of 2-C_4F_8 is given in figure 1.

Figure 1: Molecular structure of 2-C_4F_8.

The second and third carbon atoms are linked by a double bond. The crossed double bond stands for both cis/trans isomeric configurations. The investigated gas is a mixture of the cis- and trans- configurations of 2-C_4F_8 in unknown proportions. The sample has a quoted purity of 97 %.

3. Experimental setup

3.1. Principle

The Pulsed Townsend experiment was described in detail in [4]. Approximately 2×10^7 electrons are released in the gas vessel from a 12 nm thick palladium photocathode, which is back illuminated by a 266 nm laser. The laser pulses have a duration of 1.5 ns and a 20 Hz repetition rate. The released electrons drift in the homogeneous electric field between two Rogowski profile electrodes. Upon collision with sample gas molecules, ionization and attachment events lead to a growth or decrease of the electron swarm. The displacement current is measured and analysed to extract the electron swarm parameters. An example current waveform is shown in figure 2. The drift time is taken as $T_e - T_0$ to calculate the electron drift velocity. The exponential growth or decrease between T_1 and T_2 gives the effective ionization rate ν_{eff}.

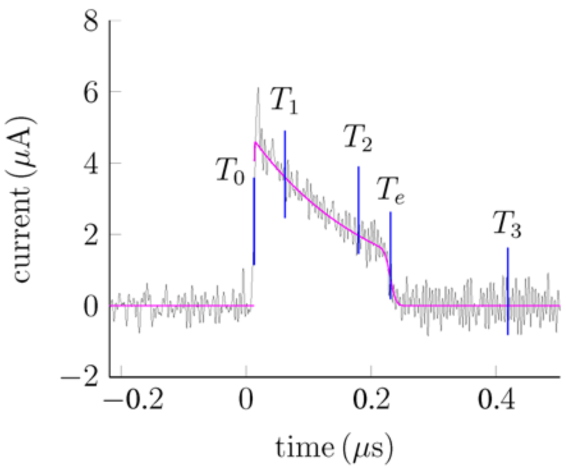

Figure 2: Current waveform in 0.0286 % of 2-C_4F_8 in N_2 at a pressure 100 mbar, *E/N* of 60 Td and for an electrode gap distance of 15 mm.

3.2 Experimental range

Mixtures of 2-C_4F_8 with the buffer gases N_2, CO_2 and Argon are investigated. It was only possible to investigate very diluted mixtures (< 0.04 %), the limiting factor for measurements with higher 2-C_4F_8 concentrations was the photocathode efficiency.

The measurements are performed at gas pressures ranging from 30 to 100 mbar, electrode gap distances ranging from 12 to 19 mm, density-reduced electric fields *E/N* ranging from 2 to 130 Td (1 Td = 10^{-21} V.m^2), and at room temperature about 298 K.

4. Results

4.1. Measurements in mixtures of 2-C_4F_8 with N_2

The measured effective ionization rate constant ν_{eff}/N and electron drift velocity w are shown as functions of E/N in figure 3 (a) and (b) for pure N_2 and for different concentrations of 2-C_4F_8 in N_2.

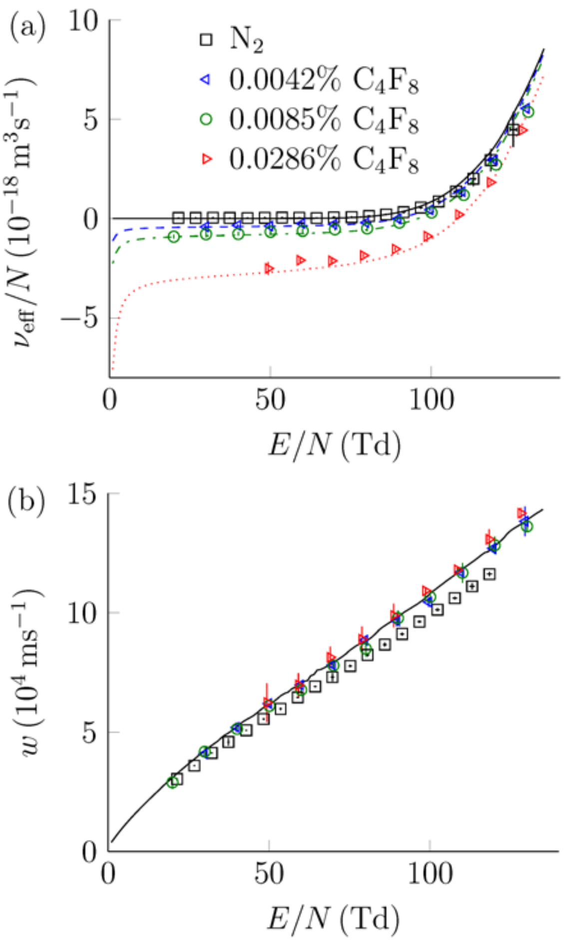

Figure 3: Swarm parameters in N_2 and 2-C_4F_8/N_2 mixtures at a pressure of 100 mbar and concentrations of 2-C_4F_8 ranging from 0.004 to 0.0286 %. (a) Effective ionization rate constant. (b) Electron drift velocity.

The measurement points are marked with symbols. The full lines are calculations for pure N_2 using the Boltzman solver Bolsig+ [5] with the cross section set of Biagi [6]. The broken lines are calculations of ν_{eff}/N in the 2-C_4F_8/N_2 mixtures according to (1):

$$\frac{\nu_{\text{eff}}}{N} \approx (1-k)\,\frac{\nu_{\text{eff}}^{\text{B}}}{N} + k\sqrt{\frac{2}{m_e}}\int_0^{\infty}(\sigma_i-\sigma_a)\epsilon f\,d\epsilon, \quad (1)$$

where $\nu_{\text{eff}}^{\text{B}}/N$ is the effective ionization rate constant in the buffer gas, presently N_2. k is the ratio of 2-C_4F_8 in the gas mixture. σ_i and σ_a are the ionization and attachment cross sections of 2-C_4F_8. f is the electron energy distribution function (EEDF) in the buffer gas. (1) is based on the approximation that f is not disturbed by the addition of small amounts of 2-C_4F_8. $\nu_{\text{eff}}^{\text{B}}/N$ and f are calculated using the solver Bolsig+ as previously mentioned. The attachment cross section σ_a of 2-C_4F_8 is taken from [2], completed with that from [3] for energies $\varepsilon < 0.04$ eV. The ionization cross section σ_i of 2-C_4F_8 is taken from [7].

The addition of very small amounts of 2-C_4F_8 in N_2 significantly decreases ν_{eff}/N. The critical reduced electric field strength $(E/N)_{crit}$ of 2-C_4F_8/N_2 mixtures, for which $\nu_{eff}/N = 0$, increases steadily with increasing percentage of 2-C_4F_8.

4.2. Measurements in mixtures of 2-C_4F_8 with CO_2

The measured effective ionization rate constant ν_{eff}/N and electron drift velocity w in CO_2 and in different 2-C_4F_8/CO_2 mixtures are shown in figure 4 (a) and (b).

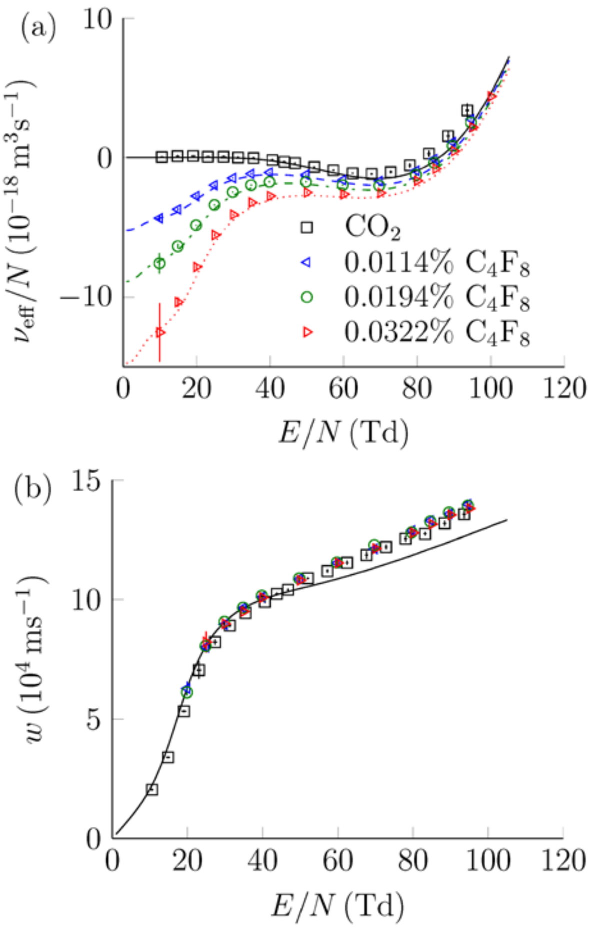

Figure 4: Swarm parameters in CO_2 and 2-C_4F_8/CO_2 mixtures at a pressure of 100 mbar and concentrations of 2-C_4F_8 ranging from 0.011 to 0.032 %. (a) Effective ionization rate constant. (b) Electron drift velocity.

The full lines are Bolsig+ calculations in CO_2 using the cross section set of Phelps [8]. The broken lines are calculations of ν_{eff}/N in the 2-C_4F_8/CO_2 mixtures using (1). The addition of 2-C_4F_8 in CO_2 considerably enhances electron attachment at $E/N < 50$ Td. The critical density reduced electric field $(E/N)_{crit}$ also increases steadily, although not as dramatically.

4.3. Measurements in 2-C_4F_8/Ar mixtures

Some of the current waveforms in 2-C_4F_8/Ar mixtures display unusual features. The waveforms shown in figure 5 are slightly U-shaped, which corresponds to an initial decrease followed by an increase of the current. Additionally, a substantial after-current is observed, which is not present in pure Ar, nor in 2-C_4F_8/N_2 and 2-C_4F_8/CO_2 mixtures.

Obtaining ν_{eff}/N and w is in this case not possible within our model [4]. Therefore, w is derived only for the most diluted mixture where the waveforms are not visibly disturbed. ν_{eff}/N is derived nonetheless for all mixtures, although this is questionable, especially in the range 20-22 Td

The measured effective ionization rate constant ν_{eff}/N and electron drift velocity w in Ar and in different 2-C_4F_8/Ar mixtures are shown in figure 6 (a) and (b). The full lines are Bolsig+ calculations in Ar using the cross section set Siglo [9]. The broken lines are calculations of ν_{eff}/N in the 2-C_4F_8/Ar mixtures using (1). In contrast to 2-C_4F_8/N_2 and 2-C_4F_8/CO_2 mixtures, the calculated ν_{eff}/N in 2-C_4F_8/Ar mixtures differ from the measurements. In particular the measured $(E/N)_{crit}$ is lower. The measured w in the mixture 0.0015% 2-C_4F_8 in Ar is similar to that in pure Ar for $E/N \leq 20$ Td but is slightly lower at higher E/N.

5. Discussion

5.1 Comparison with previous investigations

The swarm measurements in 2-C_4F_8 mixtures with N_2 and CO_2 are compared to previous investigations [2,3,7]. The attachment cross section of 2-C_4F_8 from [2] was unfolded using measurements at very low E/N (< 5 Td) in N_2 and Ar. It was used to calculate ν_{eff}/N at higher E/N and in another background gas CO_2, and good agreement was found with present measurements.

Only the calculations in 2-C_4F_8/Ar mixtures differ from the measurements. A direct comparison is not possible with the swarm measurements from [2], which were performed in different conditions (1000 times more diluted mixtures, lower E/N).

It could be that in the present measurements the EEDF of Ar is disturbed by the addition of 2-C_4F_8. Thus, the calculation of ν_{eff}/N would be inexact. But the observed difference could have another cause. The current waveforms measured in 2-C_4F_8/Ar mixtures display an unusual U-shape and a substantial after-current while this was not reported in [2]. These features could be due to detachment of electrons from negative ions $C_4F_8^-$, as attachment to 2-C_4F_8 was reported to be dominantly non-dissociative [10].

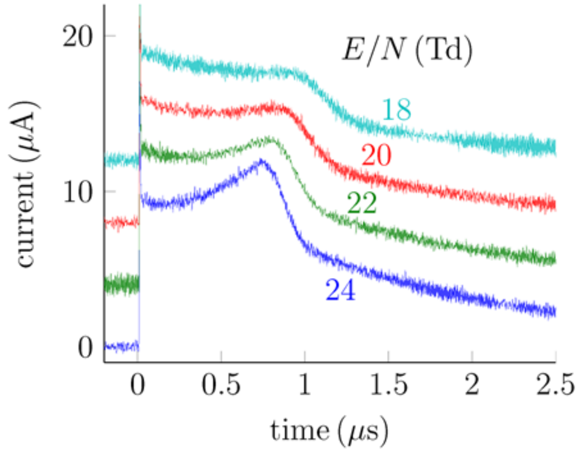

Figure 5: Measured current for 0.0305 % 2-C_4F_8 in Ar, at the pressure of 100 mbar, electrode distance of 19 mm, and E/N between 18 and 24 Td. Offsets of +4 μA have been added between measurements for better visibility.

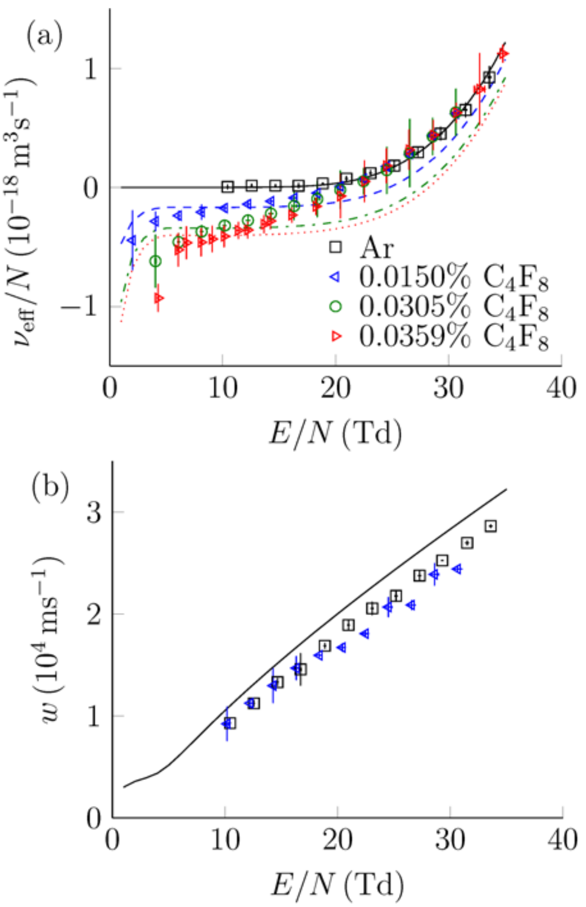

Figure 6: Swarm parameters in Ar and 2-C_4F_8/Ar mixtures at a pressure of 100 mbar and concentrations of 2-C_4F_8 ranging from 0.015 to 0.036 %. (a) Effective ionization rate constant. (b) Electron drift velocity.

However, it is unclear why this would not happen as well in the previous measurements and in other buffer gases.

Another possible cause for this difference between measurements and calculations could be the Penning ionization of 2-C_4F_8, which has an ionization threshold of 12 eV [7], by excited Argon Ar^*. Highly excited states of Ar (> 12 eV) are already populated at $E/N \geq 10$ Td, as verified with Bolsig+ simulations. Excited Ar^* can be still present for some microseconds after the arrival time of the electron swarm. As they ionize 2-C_4F_8 this can result in an after-current. In addition, this coincides with the fact that Penning ionization of 2-C_4F_8 would be negligible at E/N < 2 Td, such as in [2].

5.1 Relevance for high voltage insulation

At -20°C the vapour pressure of 2-C_4F_8 is about 0.4 bar. Thus, a gas mixture with a total pressure of 5 bar could contain up to 8 % of 2-C_4F_8. Since a direct measurement was not possible, we calculate ν_{eff}/N using (1), assuming that the EEDF of the mixture is the same as that of the buffer gas. The attachment cross section of 2-C_4F_8 is similar to that of SF_6. We verified for SF_6 that this assumption on the EEDF is reasonable for concentrations up to 8 % in N_2 or CO_2, compared to the full calculation using the solver Bolsig+.

The critical reduced electric field $(E/N)_{crit}$ of SF_6 mixtures and 2-C_4F_8 mixtures is shown in figure 7, as a function of their percentage in N_2 or CO_2. For SF_6, $(E/N)_{crit}$ was calculated with the two above mentioned methods.

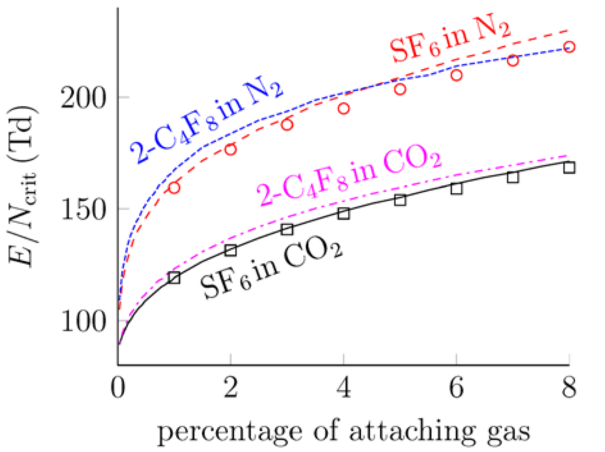

Figure 7: $(E/N)_{crit}$ of SF_6 mixtures and 2-C_4F_8 mixtures as a function of their percentage in the buffer gases N_2 or CO_2. The lines are calculations using (1). The markers are simulations of SF_6 mixtures with N_2 or CO_2, using the solver Bolsig+ with the complete cross section sets [6] for N_2, [8] for CO_2 and [9] for SF_6.

The addition of up to 8 % 2-C_4F_8 in N_2 or CO_2 leads to a similar increase of $(E/N)_{crit}$ as the addition of the same quantity of SF_6.

6. Conclusion

The effective ionization rate constant and electron drift velocity were measured for diluted mixtures of 2-C_4F_8 in the buffer gases N_2, CO_2 and Ar. The measurements are available on the ETHZ database of the LXcat project (www.lxcat.net).

A good agreement was found between measurements in 2-C_4F_8/CO_2 and 2-C_4F_8/N_2 mixtures and calculations using attachment cross sections from literature. The 2-C_4F_8/Ar measurements revealed an unusual time dependence of the swarm displacement current.

For high voltage insulation purposes, the addition of 2-C_4F_8 in N_2 or CO_2 has a comparable impact on $(E/N)_{crit}$ as the addition of SF_6. It could therefore be used as an additive. However due to the relatively high boiling point of 2-C_4F_8 (1.2°C), the percentage of 2-C_4F_8 that can be achieved is limited compared to that of SF_6.

7. Acknowledgements

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8. References

[1] M. Rabie, C.M. Franck, *IEEE Transactions on Dielectrics and Electrical Insulation* **22** (2015)

[2] A.A. Christodoulides, L.G. Chrisophorou, R.Y. Pai, and C.M. Tung, *J. Chem. Phys* **70** 1156 (1979)

[3] A. Chutjian and S.H. Alajajian, *J. Phys B: At. Mol. Phys.* **18** 4159 (1985)

[4] D.A. Dahl, T.A. Teich, C.M. Franck, *J. Phys. D: Appl. Phys.* **45** 485201 (2012)

[5] G.J.M. Hagelaar and L.C. Pitchford, *Plasma Sources Sci. Technol.* **14** 722 (2005)

[6] Biagi-v8.9 database, extracted from Magboltz v8.9, www.lxcat.net, retrieved on March 18, 2014.

[7] C.Q. Jiao, C.A. DeJoseph Jr., R. Leeb, A. Garscadden, *International Journal of Mass Spectrometry* **274** 14 (2008)

[8] Phelps database, www.lxcat.net, retrieved on July 5, 2014.

[9] SIGLO database, www.lxcat.net, retrieved on June 30, 2014.

[10] S. Feil, T.D. Märk, A. Mauracher, P. Schreier, C.A. Mayhew, *International Journal of Mass Spectrometry* **277** 41 (2008)