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Measurement of the electron attachment properties of SF_5CF_3 and comparison to SF_6

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Abstract.

The electron attachment properties of SF_5CF_3 are experimentally investigated using a pulsed Townsend setup. Different $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures, with SF_5CF_3 mole fractions ranging from 2×10^{-4} to 1, are characterized. The effective ionization rate coefficient, electron drift velocity and reduced longitudinal electron diffusion coefficient in these mixture are obtained. For low mole fractions of SF_5CF_3 , the effective ionization rate coefficient is compared to calculations from available electron scattering cross sections, and is also used for estimating the electron attachment cross section of SF_5CF_3 . For pure SF_5CF_3 , the present data is compared to early data from a steady-state Townsend experiment. The presentation of the measurement results is followed by a discussion on the properties of SF_5CF_3 and SF_6 and their significance for gaseous electrical insulation.

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Introduction

When trifluoromethylsulphur pentafluoride ($\text{SF}_5\text{-CF}_3$) was synthesized for the first time in 1949 [1], it immediately attracted interest as a potentially good electrical insulator due to its high number of fluorine atoms, its low boiling point (-20°C [2]) and its similarity to SF_6 . Sulphur hexafluoride (SF_6) is indeed widely used in its gaseous form as an electrical insulator for high voltage equipment, such as gas insulated lines, gas insulated substations and switchgear. The electric strength of SF_5CF_3 was found to be superior to that of SF_6 [3], SF_5CF_3 is therefore an excellent insulating gas. However, in the same work SF_5CF_3 was found to dissociate rapidly and completely into SF_4 and CF_4 during electrical breakdown, and the produced SF_4 and CF_4 did not subsequently recombine into SF_5CF_3 . Therefore, SF_5CF_3 is hardly recommended for use in switching applications, where arcing is frequent. Further applications were envisioned for SF_5CF_3 , such as refrigerant gas [2] and hydrologic tracer [4]. However, the environmental impact of SF_5CF_3 regarding global warming has been lately intensely discussed [5, 6, 7, 8], as it was found that SF_5CF_3 is a potent greenhouse gas with a 100-year integrated global warming potential (GWP) of 17 400 [9] relative to CO_2 . This compromises the use of SF_5CF_3 in the aforementioned applications. The GWP of SF_6 is even higher, namely 23 500 [9], and atmospheric measurements show an accumulation of atmospheric SF_6 and a global emission increase [10, 11]. Therefore, environment-friendly gases to substitute SF_6 in electrical insulation applications are actively sought.

The performance of a gas as an electrical insulator can be assessed by experimental methods, such as swarm experiments, electron beam experiments and breakdown experiments. Swarm experiments such as pulsed or steady-state Townsend setups can be used to measure electron swarm parameters, i.e. rate and transport coefficients, which serve as input for fluid models to simulate electrical discharges. Electron beam experiments serve to measure electron scattering cross sections, which can be used in turn to calculate rate and transport coefficients. These methods are technically challenging and time consuming. Considering the large number of gases that could be investigated, it would be desirable to gain a better understanding of the link between molecular structure and electron attachment properties in order to select good electrical insulators prior to performing experiments. Recently several attempts have been made to correlate the electric strength and boiling point of gases with numerically calculated predictor variables and some useful correlations were identified [12, 13, 14, 15]. However, these methods are

hindered by the relatively small size of the training data set, that is, the small number of gases for which the electric strength is known.

While SF_5CF_3 can hardly be considered as a low-GWP alternative to SF_6 in electrical insulation, the comparative study of SF_5CF_3 and SF_6 could give an insight into the effect of replacing a single F atom from the SF_6 molecule by a CF_3 group [15, 16]. For this purpose, the electron attachment properties of SF_5CF_3 are experimentally characterized in this work. The electron swarm parameters in pure SF_5CF_3 and in $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures are measured in a pulsed Townsend setup, and the data is made available online [17]. The results are compared to previous investigations of SF_5CF_3 and SF_6 , such as measurements of the electron attachment and ionization cross sections of SF_5CF_3 [18, 19] and SF_6 [20, 21] in electron beam experiments and measurements of the attachment and ionization rate coefficients of SF_5CF_3 in a steady-state Townsend setup [22].

This work starts with the description of the experimental setup, the experimental conditions and the analytic tools used for the measurement analysis and for the comparison of data from different sources. In the second part of this work, measurement results for diluted mixtures of SF_5CF_3 in N_2 and CO_2 are presented. These results are compared to calculations based on SF_5CF_3 cross sections from other works. An estimation of the attachment cross section of SF_5CF_3 calculated from the present data is also presented. In the third part of this work, measurement results for mixtures with higher SF_5CF_3 content in N_2 and CO_2 are presented, including measurements in pure SF_5CF_3 , and the latter are compared to early measurements in pure SF_5CF_3 from a steady-state Townsend setup. In the last part of this work, the properties of SF_5CF_3 and SF_6 are discussed.

1. Methods

1.1. Swarm experiment

The measurements are performed in a pulsed Townsend setup that was described in a previous work [23]. The gases used in this work have the following purity: the SF_5CF_3 has a purity of 99%, the N_2 has a purity of 6.0 and the CO_2 a purity of 5.0. The gases are filled into a stainless steel vessel previously evacuated to a pressure of ~ 0.5 Pa. The vessel contains two electrodes separated by a distance d . A negative high voltage U is applied to the cathode, whereas the anode is grounded. The electrodes are shaped with a Rogowski profile in order to create a homogeneous electric field E . The center of the cathode consists in a 12-nanometer-thick palladium film coated on a quartz

window. A short laser pulse (1.5 ns FWHM) directed at the back of the palladium film, releases 10^6 to 10^7 electrons, which initiate an electron avalanche. The electron swarm drifts in the uniform electric field towards the anode. Upon collision, an electron may ionize a gas molecule, forming a cation and an additional free electron. An electron may also attach to a gas molecule and form an anion. The ions formed by ionization and attachment events drift in the electric field, but are slower than electrons by 2-3 orders of magnitude. The current I_{exp} resulting of the displacement of all charged particles drifting through the gap is measured at the anode. The measurements are performed at room temperature, for several gas pressures from 2 to 10 kPa, and several gap distances between the electrodes from 11 to 17 mm. The applied voltage is varied from 50 V to 9.5 kV. Sample measurements of current transients are shown in figures 2 and 6. The electron and ion components of the current are separated using an iterative procedure [24], and the electron component I_e is then analyzed.

1.2. Electron current analysis

Assuming that the one-dimensional electron density along the propagation axis is Gaussian, the electron current I_e can be expressed analytically for $t \geq 0$ as [23, 24]

$$I_e(t) = \frac{I_0}{2} \exp(k_{\text{eff}} N t) \left(1 - \text{erf} \left(\frac{t - T_e}{\sqrt{2\tau_D t}} \right) \right), \quad (1)$$

$$I_0 = q_0 N_e(0)/T_e, \quad (2)$$

where I_0 is the electron current at time $t = 0$, k_{eff} is the effective ionization rate coefficient, N is the number density of the gas, T_e is the electron drift time, which relates to the electron drift velocity w_e via $T_e = d/w_e$, τ_D is the characteristic time for longitudinal electron diffusion, which relates to the longitudinal diffusion coefficient D_L via $2D_L = w_e^2 \tau_D$, $N_e(0)$ is the initial number of electrons and q_0 is the elementary charge. The determination of the effective ionization rate coefficient k_{eff} , the electron drift velocity w_e and the longitudinal electron diffusion coefficient ND_L using this model was described in detail previously [24].

The quantities k_{eff} , w_e and ND_L depend on the density-reduced electric field E/N , given in Townsend ($1 \text{ Td} = 10^{-21} \text{ V m}^2$). The final values of k_{eff} , w_e and ND_L are given with error bars corresponding to the spread of the values obtained in measurements with different electrode gap distances, and the E/N values are also given error bars coming mainly from to the error $\pm 0.1 \text{ mm}$ in the electrode gap distance, which dominates over the errors from the temperature, pressure and voltage measurements.

The electron drift velocity w_e obtained in the present experiment, as mentioned in [23, 25, 26], is

Figure 1. Data flow between rate coefficients (top row) and electron scattering cross sections (bottom row). k_{eff} : effective ionization rate coefficient. EEDF: electron energy distribution function.

the bulk drift velocity, i.e. the velocity of the center of mass of the electron swarm. In the presence of non-conservative collisions, such as ionization and attachment, it may significantly differ from the flux drift velocity, which is the average velocity of all electrons in the swarm [27, 25, 28].

1.3. From electron scattering cross sections to rate coefficients and vice versa

The diagram of figure 1 gives an overview of the methods described in this section, and should as well help the reader to keep track of the data sources.

The effective ionization rate coefficient k_{eff} is defined as the difference between the ionization and attachment rate coefficients k_i and k_a . The relation between k_{eff} of a gas mixture and the attachment and ionization cross sections of its components is given by (see for instance equation (10) of reference [30])

$$k_{\text{eff}} = k_i - k_a, \quad (3)$$

$$k_i = \sqrt{\frac{2}{m_e}} \int_0^\infty \sum_n x_n \sigma_i^{(n)} \varepsilon f d\varepsilon, \quad (4)$$

$$k_a = \sqrt{\frac{2}{m_e}} \int_0^\infty \sum_n x_n \sigma_a^{(n)} \varepsilon f d\varepsilon, \quad (5)$$

where x_n is the mole fraction of species n in the mixture, $\sigma_a^{(n)}$ is the total attachment cross section of species n , $\sigma_i^{(n)}$ is the total ionization cross section of species n , m_e is the electron mass and $f(E/N, \varepsilon)$ is the electron energy distribution function (EEDF) in the mixture. The EEDF is normalized as follows

$$\int_0^\infty \sqrt{\varepsilon} f d\varepsilon = 1. \quad (6)$$

In the particular case where a sample gas is added with a small mole fraction $x \ll 1$ to a buffer gas, the EEDF

of the gas mixture can be assumed to be the same as that of the pure buffer gas and equations (3-5) simplify to

$$k_{\text{eff}} = (1 - x)k_{\text{eff}}^b + x\sqrt{\frac{2}{m_e}} \int_0^\infty (\sigma_i - \sigma_a)\varepsilon f d\varepsilon, \quad (7)$$

where k_{eff}^b is the effective ionization rate coefficient in the pure buffer gas, σ_i and σ_a are the total ionization and attachment cross sections of the sample gas, and f is the EEDF of the buffer gas.

For the buffer gases N_2 and CO_2 , complete sets of electron scattering cross sections are available, for instance via the LXcat project [31, 34]. In the present work, Biagi's cross section set [32] is used for N_2 and the one of Phelps [33] for CO_2 . The effective ionization rate coefficient k_{eff}^b and EEDF for these gases are obtained by solving the Boltzmann equation in the two-term approximation, using the solver Bolsig+ [30].

Using equation (7), only the ionization and attachment cross sections of SF_5CF_3 (and not a complete cross section set of SF_5CF_3) are required for calculating k_{eff} in diluted SF_5CF_3 mixtures. In this work, the ionization cross section of SF_5CF_3 from reference [18] and the attachment cross section from reference [19] are used to calculate k_{eff} for comparison with the present measurement results. The attachment cross section σ_a may be estimated through equation (7) using measurements of k_{eff} . Equation (7) can be discretized into a matrix problem of the form $A\sigma_a = b$, where A and b are known (in function of the quantities k_{eff} , k_{eff}^b , f and σ_i), and σ_a needs to be determined [29]. This constitutes a so-called discrete ill-posed problem. To obtain σ_a , we use in this work a linear inversion method and a two-term Gaussian expansion method, which have been described previously [29]. The linear inversion method consists in using the singular value decomposition and the Tikhonov regularization with the L-curve method for choosing the regularization parameter. This method has the advantage to yield a unique solution, since it requires no initial guess of the solution, in contrast to iterative methods [28]. For comparison, we also fit a two-term Gaussian expansion, i.e. we approximate the shape of the attachment cross section by two Gaussian functions. This latter method is useful to verify the energy range and magnitude of the attachment cross section.

1.4. Density-reduced critical electric field

The density-reduced critical electric field $(E/N)_{\text{crit}}$ of a gas is defined as the E/N ratio for which $k_{\text{eff}} = 0$, that is $k_i = k_a$. For $E/N < (E/N)_{\text{crit}}$, electron attachment is dominating over ionization. For $E/N > (E/N)_{\text{crit}}$, ionization dominates over electron attachment. Therefore, $(E/N)_{\text{crit}}$ is a figure of merit for electrical insulation, it is the minimum

E/N ratio for which an electrical discharge can be self-sustained. The $(E/N)_{\text{crit}}$ of a gas mixture cannot be predicted based solely on the $(E/N)_{\text{crit}}$ of the individual components since it depends largely on the electron energy distribution in the gas mixture. A gas mixture is said to have a synergy when its $(E/N)_{\text{crit}}$ is larger than the sum of the $(E/N)_{\text{crit}}$ of its components weighted by their mole fractions in the mixture [35].

2. Diluted SF_5CF_3 mixtures in N_2 and CO_2

An overview of the present measurements in diluted SF_5CF_3/N_2 and SF_5CF_3/CO_2 mixtures is given in table 1.

2.1. Sample measurements

Figures 2(a) and (b) show sample measurements of the current versus time in the mixture of 0.51% SF_5CF_3 in N_2 , along with the result of the iterative procedure [24] to separate the electron and ion components, and the fit of the electron current model (1) to the electron component. In figure 2(a) the current is exponentially decreasing due to dominating electron attachment, whereas in figure 2(b) the current is exponentially increasing due to dominating ionization. The peaks in the signal between 0 – 20 ns and 90 – 110 ns are overshoots due to underdamping of the measurement circuit.

2.2. Results of the electron current analysis

The electron current analysis described in section 1.2 yields the effective ionization rate coefficient k_{eff} , the electron drift velocity w_e and the longitudinal electron diffusion coefficient ND_L . These quantities in the considered SF_5CF_3/N_2 mixtures are shown in figure 3(a),(b) and (c) respectively, and in figure 4(a),(b) and (c) for the SF_5CF_3/CO_2 mixtures, and can also be downloaded from LXcat [17].

The measured quantities k_{eff} , w_e and ND_L in pure N_2 and CO_2 are compared to the same quantities calculated with Bolsig+ using the cross section sets

Table 1. Overview of the measurements in diluted SF_5CF_3/N_2 and SF_5CF_3/CO_2 mixtures.

buffer gas	SF_5CF_3 mol%	(E/N) -range (Td)	pressures (kPa)
N_2	0	5-130	2, 10
	0.02	15-130	2, 6, 10
	0.09	40-135	2, 6, 10
	0.51	140-163	10
CO_2	0	5-120	2, 10
	0.02	20-105	10
	0.09	30-110	2, 6, 10

Figure 2. Currents versus time in the mixture of 0.51% SF_5CF_3 in N_2 , at a pressure of 10 kPa, for an electrode spacing of 15 mm, and for a reduced electric field E/N of (a) 147 Td and (b) 163 Td.

of Biagi [32] and Phelps [33] respectively. There is a good overall agreement between our measurements and the calculations, except for the electron drift velocity in CO_2 at E/N ratios above 50 Td. For this E/N range, our measurements are rather in agreement with calculations using the cross section set Siglo [36].

The measured values of k_{eff} in $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures shown in figures 3(a) and 4(a) are compared to calculated values of k_{eff} in the same mixtures using the attachment and ionization cross sections of SF_5CF_3 [19, 18] as explained in section 1.3. There is an excellent agreement between the measured and calculated values.

The effective ionization rate coefficient k_{eff} shown in figures 3(a) and 4(a) is increasingly negative with

Figure 3. (a) Effective ionization rate coefficient, (b) electron drift velocity and (c) density normalized longitudinal electron diffusion coefficient versus E/N in diluted $\text{SF}_5\text{CF}_3/\text{N}_2$ mixtures. The gas mixtures are color-coded: the percentages of SF_5CF_3 are indicated in figure (a) and the same color code is used for figures (b) and (c). The markers are the present measured values at different gas pressures ($\square$ 2 kPa, $\triangle$ 6 kPa, $\circ$ 10 kPa). The lines are calculated as indicated in section 1.3: — Bolsig+ calc. using data from ref. [32], - - - calc. with equation (7) using data from refs. [18, 19, 32].

Figure 4. (a) Effective ionization rate coefficient, (b) electron drift velocity and (c) density normalized longitudinal electron diffusion coefficient versus E/N in diluted $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures. The gas mixtures are color-coded: the percentages of SF_5CF_3 are indicated in figure (a) and the same color code is used for figures (b) and (c). The markers are the present measured values at different gas pressures ($\square$ 2 kPa, $\triangle$ 6 kPa, $\circ$ 10 kPa). The lines are calculated as indicated in section 1.3: — Bolsig+ calc. using data from ref. [33], - - - calc. with equation (7) using data from refs. [18, 19, 33].

increasing mole fraction of SF_5CF_3 , due to electron attachment to SF_5CF_3 . Accordingly, a large increase of the density-reduced critical electric field $(E/N)_{\text{crit}}$ with increasing mole fraction of SF_5CF_3 can be observed. The electron drift velocity and diffusion coefficient in the diluted SF_5CF_3 mixtures are identical to the same quantities in the pure buffer gases. It was expected that adding a small amount of SF_5CF_3 would not affect the electron transport (drift and diffusion). The measured quantities k_{eff} , w_e and ND_L show no dependence on the gas pressure in the investigated pressure range of 2 to 10 kPa.

2.3. Electron attachment cross section of SF_5CF_3

The measured values of k_{eff} in the diluted $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures are used to estimate the electron attachment cross section σ_a of SF_5CF_3 using the linear inversion and gaussian expansion methods mentioned in section 1.3. The resulting σ_a are shown in figure 5(a), and compared to the total attachment cross section of SF_5CF_3 measured in an electron beam experiment [19]. The electron attachment cross section of SF_6 [20] is also plotted for comparison in the discussion section. The total ionization cross sections of SF_5CF_3 [18] and SF_6 [21] are shown in figure 5(b).

In the electron energy range of 0.1 to 0.8 eV, the present results (linear inversion and gaussian expansion) are in good agreement with the beam measurement of SF_5CF_3 . In the range below 0.1 eV the present results are not reliable, therefore they are depicted using dotted lines in figure 5(a). For the gaussian expansion cross section, this error is due to the imposed shape of the cross section. For the linear inversion cross section, this error is likely due to the insufficient amount of electrons with these low energies at the minimum E/N value that was measured, as has been previously discussed for the similar case of SF_6 [29]. The linear inversion cross section result displays a narrow peak at 3.4 eV, which barely comes above the sensitivity limit of the method (5% of maximal peak value), but contributes significantly to electron attachment at high E/N ratios, such as the range of 140 to 163 Td in the N_2 mixture. This peak is almost one order of magnitude higher than the peak at 3.5 eV measured in the beam experiment. Similarly, for the gaussian expansion cross section the second peak is shifted (to 5.4 eV) and has a too high amplitude compared to the beam cross section. Further errors in the present results could be due to non-negligible modification of the EEDF of N_2 and CO_2 by the SF_5CF_3 admixtures. Despite this, the present results show that reasonable estimations of the order of magnitude and energy range of the total attachment cross section of gases can be obtained by these methods, when no direct measurement of the

Figure 5. (a) Total attachment cross sections of SF_5CF_3 linear inversion, Gaussian expansion, — ref. [19] (Graupner), and total attachment cross section of SF_6 — ref. [20] (Braun). (b) Total ionization cross section of SF_5CF_3 — ref. [18] (Chen), and of SF_6 — ref. [21] (Christophorou).

attachment cross section is available.

3. Mixtures with higher SF_5CF_3 content and pure SF_5CF_3

An overview of the present measurements in $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures with higher SF_5CF_3 content is given in table 2.

3.1. Sample measurements

Figures 6(a) and (b) show sample current transients in pure SF_5CF_3 . In contrast to the currents measured in mixtures with low SF_5CF_3 mole fractions, the amplitude of the ion current is of the same order of magnitude as that of the electron current. Since the ions are much slower than the electrons, it requires much more ions to generate a current of the same order of magnitude as the electron current. This indicates that both the ionization and attachment rate coefficients are large (many ions are formed), whereas their difference $k_{\text{eff}} = k_i - k_a$ is small in absolute value (the electron number varies comparatively less).

3.2. Results of the electron current analysis

The effective ionization rate coefficient k_{eff} , the electron drift velocity w_e and the longitudinal electron diffusion coefficient ND_L obtained in the considered $\text{SF}_5\text{CF}_3/\text{N}_2$ mixtures are shown in figure 7(a),(b) and (c) respectively, and in figure 8(a),(b) and (c) for the $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures, and can also be downloaded from LXcat [17].

The quantities k_{eff} , w_e and ND_L show no dependence on the gas pressure for the investigated pressures. The decrease of k_{eff} with increasing mole fraction of SF_5CF_3 is clearly visible for the $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures. The values of w_e in the $\text{SF}_5\text{CF}_3/\text{N}_2$ mixture show a smooth transition from pure N_2 to pure SF_5CF_3 , whereas the values of ND_L are much more erratic. The electron diffusion coefficient ND_L is the quantity with the largest

Table 2. Overview of the measurements in the $\text{SF}_5\text{CF}_3/\text{N}_2$ and $\text{SF}_5\text{CF}_3/\text{CO}_2$ mixtures with higher SF_5CF_3 content.

buffer gas	SF_5CF_3 mol%	(E/N) -range (Td)	pressures (kPa)
N_2	0	5-180	2, 10
	4.96	212-232	3, 10
	10.4	261-271	2, 10
	20.1	310-318	10
	40.2	396-401	10
	59.1	453-458	7
	74.6	500-505	5
	100	545-577	2, 4
CO_2	0	5-140	2, 10
	5.96	166-184	10
	10.75	190-220	2, 6, 10

Figure 6. Current versus time in pure SF_5CF_3 , at a pressure of 4 kPa, for an electrode spacing of 15 mm, and for a reduced electric field E/N of (a) 573 Td and (b) 577 Td.

uncertainty in the present experiment. It is determined by the slope of the falling edge of the waveform (see equation (1)), which is not very well resolved due to noise, limited signal bandwidth, and overshoots on the measured signal.

The present measurements can also be presented in the form of the reduced effective ionization coefficient α_{eff}/N . Here, we derive α_{eff}/N simply as $\alpha_{\text{eff}}/N = k_{\text{eff}}/w_e$. In fact, a more rigorous way to derive α_{eff}/N from bulk coefficients is [27, 25, 37]

$$\alpha_{\text{eff}}/N = \frac{w_e}{2ND_L} - \sqrt{\left(\frac{w_e}{2ND_L}\right)^2 - \frac{k_{\text{eff}}}{ND_L}}, \quad (8)$$

but we dispensed from this correction in the present case because it amounts to less than 0.1% of α_{eff}/N , which is negligible in comparison to the measurement

Figure 7. (a) Effective ionization rate coefficient, (b) electron drift velocity and (c) density normalized longitudinal electron diffusion coefficient versus E/N . The gas mixtures are color-coded: the percentages of SF_5CF_3 are indicated in figure (a) and the same color code is used for figures (b) and (c). The markers are the present measured values at different gas pressures ($\square$ 2 kPa, $\triangle$ 3 kPa, ∇ 4 kPa, $\diamond$ 5 kPa, $\triangleright$ 7 kPa, $\circ$ 10 kPa). The lines are calculation results in pure N_2 , obtained with the solver Bolsig+ using the N_2 cross section set from ref. [32].

Figure 8. (a) Effective ionization rate coefficient, (b) electron drift velocity and (c) density normalized longitudinal electron diffusion coefficient versus E/N . The gas mixtures are color-coded: the percentages of SF_5CF_3 are indicated in figure (a) and the same color code is used for figures (b) and (c). The markers are the present measured values at different gas pressures ($\square$ 2 kPa, $\triangle$ 6 kPa, $\circ$ 10 kPa). The lines are calculation results in pure CO_2 , obtained with the solver Bolsig+ using the CO_2 cross section set from ref. [33].

Figure 9. Reduced effective ionization coefficient in SF_5CF_3 as a function of E/N . Present results: $\diamond$ 2 kPa, $\square$ 4 kPa (the error is represented by two solid lines). Values from ref. [22]: $\circ$ 0.6 kPa, $\triangle$ 0.8 kPa.

precision of around 10%. The present values of α_{eff}/N are shown in figure 9 and compared to values measured by Harrison in 1953 using a steady-state Townsend setup [22]. An excellent agreement is observed between the present values and the values of α_{eff}/N at 0.6 kPa from Harrison, despite the differences in the experimental and analysis techniques. The values from Harrison at 0.8 kPa are somewhat lower, but given the experimental spread, the agreement with the present values is still reasonable.

4. Discussion

Ideally, insulating gases could be synthesized by substituting functional groups from a basis molecule to obtain the desired properties [15, 16]. The comparison of SF_5CF_3 and SF_6 gives an insight into the effect of replacing an F atom by a CF_3 functional group. We discuss some properties of SF_5CF_3 and SF_6 which are relevant for electrical insulation, based on the present study and on multiple other results from the literature, and we conclude on the insulation capability of SF_5CF_3 resulting from all these aspects.

Attachment properties In contrast to SF_6 , the electron attachment to SF_5CF_3 is exclusively dissociative, even at thermal electron energies (~ 0.03 eV) [19, 16]. The main anion formed by electron attachment to SF_5CF_3 is SF_5^- . At thermal energies and up to 0.15 eV, the attachment cross section of SF_5CF_3 is smaller than that of SF_6 , see figure 5(a). The thermal attachment rate coefficient to SF_6 is $2.4 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$, three times larger than that of SF_5CF_3 $8.0 \times 10^{-14} \text{ m}^3 \text{ s}^{-1}$ [38]. However, from 0.15 eV to

2 eV, the attachment cross section of SF_5CF_3 is larger than that of SF_6 , and this energy range is more representative for the typical electron energies in electrical discharges. Therefore, the attachment rate coefficient to SF_5CF_3 is higher than that of SF_6 for E/N values larger than a few Townsend. At $E/N = 570$ Td the attachment rate coefficient in pure SF_5CF_3 can be estimated using the attachment coefficient $\eta/N = 4 \times 10^{-21} \text{ m}^2$ from ref. [22] and the electron drift velocity $w_e = 2.5 \times 10^5 \text{ ms}^{-1}$ from the present work. This yields the value $k_a = w_e \eta / N = 1 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$, twice larger than the attachment rate coefficient in pure SF_6 at the same E/N , namely $k_a = 4.6 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$, obtained by a Bolsig+ calculation using the cross section set from Biagi [32].

Ionization properties The ionization of SF_5CF_3 is, at least on the timescale of several microseconds, exclusively dissociative. The main cation formed is CF_3^+ with an appearance energy of 12.9 eV [39]. In contrast, the main cation formed by ionization of SF_6 is SF_5^+ [21] with an ionization energy of 15.7 eV. The ionization energy is smaller for SF_5CF_3 than for SF_6 and the total ionization cross section of SF_5CF_3 is larger, see figure 5(b). Despite this, assumedly due to the different electron energy distributions in SF_6 and SF_5CF_3 , the ionization rate coefficient in SF_5CF_3 at $E/N = 570$ Td is $k_i = w_e \alpha / N = 1 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$, twice smaller than the calculated value for SF_6 at the same E/N , namely $2.2 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$.

Density reduced critical electric field As a result of the larger attachment rate coefficient and the smaller ionization rate coefficient of SF_5CF_3 , the effective ionization rate coefficient of SF_5CF_3 is lower than that of SF_6 . The density-reduced critical electric field of SF_5CF_3 is 570 Td, 1.6 times higher than that of SF_6 , namely 359 Td. The density reduced critical electric field of $\text{SF}_5\text{CF}_3/\text{N}_2$, $\text{SF}_5\text{CF}_3/\text{CO}_2$, SF_6/N_2 and SF_6/CO_2 mixtures as a function of the mole fraction of SF_5CF_3 or SF_6 is shown in figure 10. A synergy is observed in all these mixtures. A mixture of about 30% SF_5CF_3 in N_2 has the same density-reduced critical electric field as SF_6 .

Vapor pressure The boiling point, vapor pressure and critical point of SF_5CF_3 were reported in [2]. The boiling point of SF_5CF_3 is -20°C , which is relatively high compared to the boiling point of SF_6 , namely -64°C . The vapor pressures of SF_5CF_3 and SF_6 [42] are shown in figure 11. The vapor pressure of SF_5CF_3 is lower than that of SF_6 by about one order of magnitude.

Figure 10. Density reduced critical electric field $(E/N)_{\text{crit}}$ as a function of the mole fraction of SF_5CF_3 or SF_6 in N_2 and CO_2 .

Figure 11. Vapor pressure curves of SF_5CF_3 and SF_6 .

Critical electric field Since the critical electric field E_{crit} scales linearly with the gas pressure, it is important that insulating gases have high vapor pressures. The filling pressure of high voltage equipment is typically of 0.6 MPa at 20°C , and the minimum operating temperatures can be in the range of -40°C to 0°C , typically -25°C . For medium voltage equipment the filling pressure is typically of 0.13 MPa at 20°C , and the minimum temperature is typically of -25°C . Considering the relatively low vapor pressure of SF_5CF_3 , it has to be mixed with another gas to be used in medium or high voltage equipment. Figure 12(a) shows the critical electric

Figure 12. Critical electric field of $\text{SF}_5\text{CF}_3/\text{N}_2$ mixtures relative to the critical electric field of SF_6 at $p = 0.1$ MPa.

field of different $\text{SF}_5\text{CF}_3/\text{N}_2$ mixtures as a function of the dew point of these mixtures, at the temperatures and pressures typical for high voltage applications. The mixtures contain 5 to 35% SF_5CF_3 and different filling pressures from 0.5 to 1 MPa are considered. For comparison, the critical electric field of pure SF_6 at different filling pressures is plotted as a function of the dew point of SF_6 . The values of E_{crit} in figure 12 are relative to the critical field of SF_6 at $p = 0.1$ MPa, and the pressures are the filling pressures at a temperature of 20 °C. From figure 12(a) can be read that a mixture of about 30% SF_5CF_3 at 0.6 MPa in N_2 has the same critical electric field as SF_6 at 0.6 MPa, but has a dew point (minimum temperature) of -9 °C, whereas that of SF_6 is -30 °C. Similarly, a mixture of about 10% SF_5CF_3 at 0.8 MPa in N_2 has the same critical electric field and minimum operating temperature as SF_6 at 0.6 MPa. Therefore, SF_5CF_3 could only replace SF_6 in high voltage equipment at the cost of increasing the filling pressure or the minimum operating temperature.

Figure 12(b) shows the critical electric field of different $\text{SF}_5\text{CF}_3/\text{N}_2$ mixtures as a function of the dew point of these mixtures, at the temperatures and pressures typical for medium voltage applications. The mixtures contain 20 to 100% SF_5CF_3 and different filling pressures from 0.10 to 0.15 MPa are considered. From figure 12(b) can be read that the mixture of about 30% SF_5CF_3 at 0.13 MPa performs as well as pure SF_6 at 0.13 MPa, and has still a low minimum temperature of -45 °C.

Global warming potential The radiative efficiency of SF_5CF_3 is of $0.59 \text{ Wm}^{-2}\text{ppb}^{-1}$, slightly higher than that of SF_6 , namely $0.57 \text{ Wm}^{-2}\text{ppb}^{-1}$ [9]. However, due to the shorter estimated lifetime of SF_5CF_3 compared to SF_6 , 800 years and 3200 years respectively, the GWP of SF_5CF_3 on a 100 year time horizon is 17 400, slightly lower than that of SF_6 , namely 23 500. The difference is accentuated when one considers that SF_5CF_3 would be not be used as a pure gas, but as part of a gas mixture, and therefore used in lesser amounts.

Conclusion

This work provides new experimental data of SF_5CF_3 , which are in good agreement with existing data from previous beam and swarm measurements. It extends previous data to mixtures of SF_5CF_3 with N_2 and CO_2 . In particular, a synergy is observed for the reduced critical electric field of SF_5CF_3 mixtures with N_2 and CO_2 . In pure SF_5CF_3 , the present data confirms and complements previous data by providing the electron drift velocity and diffusion in addition to the effective ionization rate coefficient. The possibility to estimate the attachment cross section using swarm measurements is demonstrated, and the obtained attachment cross sections are in reasonable agreement with existing beam cross sections.

By comparing the properties of SF_6 with those of SF_5CF_3 , it appears that the substitution of F by CF_3 has many fold repercussions on the insulating properties. The substitution leads to an increased electric strength of SF_5CF_3 , but as well to a higher boiling point. Consequently, SF_5CF_3 has to be used in a gas mixture, and the electric strength of that mixture depends largely on the synergism between SF_5CF_3 and the chosen buffer gas, an aspect which is not included in predictions of the electric strength. Considering all these aspects, it results that the superior electric strength of SF_5CF_3 is insufficient to compensate for its lower vapor pressure. This example highlights the importance of knowing with precision the boiling point of prospective replacement gases and their critical field in a gas mixture. The boiling point is an essential

parameter which affects strongly the end result, yet even recent predictions of the boiling point of gases are still very imprecise [14, 15]. Therefore, it is highly desirable to improve the prediction of the boiling point of gases, and to predict not only the electric strength of pure gases but as well possible synergy effect with buffer gases.

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