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Measurement of the electron attachment properties of SF$_5$CF$_3$ and comparison to SF$_6$

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Abstract.

The electron attachment properties of SF$_5$CF$_3$ are experimentally investigated using a pulsed Townsend setup. Different SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/CO$_2$ mixtures, with SF$_5$CF$_3$ mole fractions ranging from $2 \times 10^{-4}$ to 1, are characterized. The effective ionization rate coefficient, electron drift velocity and reduced longitudinal electron diffusion coefficient in these mixtures are obtained. For low mole fractions of SF$_5$CF$_3$, 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$_5$CF$_3$. For pure SF$_5$CF$_3$, 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$_5$CF$_3$ and SF$_6$ and their significance for gaseous electrical insulation.

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Keywords: CF$_8$S, trifluoromethylsulfur pentafluoride, electron attachment, electrical insulation.
Introduction

When trifluoromethylsulphur pentafluoride (SF$_5$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$_5$CF$_3$ was found to be superior to that of SF$_6$ [3], SF$_5$CF$_3$ is therefore an excellent insulating gas. However, in the same work SF$_5$CF$_3$ 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$_5$CF$_3$. Therefore, SF$_5$CF$_3$ is hardly recommended for use in switching applications, where arcing is frequent. Further applications were envisioned for SF$_5$CF$_3$, such as refrigerant gas [2] and hydrologic tracer [4]. However, the environmental impact of SF$_5$CF$_3$ regarding global warming has been lately intensely discussed [5, 6, 7, 8], as it was found that SF$_5$CF$_3$ 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$_5$CF$_3$ 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$_5$CF$_3$ can hardly be considered as a low-GWP alternative to SF$_6$ in electrical insulation, the comparative study of SF$_5$CF$_3$ 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$_5$CF$_3$ are experimentally characterized in this work. The electron swarm parameters in pure SF$_5$CF$_3$ and in SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/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$_5$CF$_3$ and SF$_6$, such as measurements of the electron attachment and ionization cross sections of SF$_5$CF$_3$ [18, 19] and SF$_6$ [20, 21] in electron beam experiments and measurements of the attachment and ionization rate coefficients of SF$_5$CF$_3$ 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$_5$CF$_3$ in N$_2$ and CO$_2$ are presented. These results are compared to calculations based on SF$_5$CF$_3$ cross sections from other works. An estimation of the attachment cross section of SF$_5$CF$_3$ calculated from the present data is also presented. In the third part of this work, measurement results for mixtures with higher SF$_5$CF$_3$ content in N$_2$ and CO$_2$ are presented, including measurements in pure SF$_5$CF$_3$, and the latter are compared to early measurements in pure SF$_5$CF$_3$ from a steady-state Townsend setup. In the last part of this work, the properties of SF$_5$CF$_3$ 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$_5$CF$_3$ 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 10^9 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 \( I_{\text{exp}} \) 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 30 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 analysed.

1.2. Electron current analysis

Assuming a gaussian spatial distribution of the electrons, the electron current \( I_e \) can be expressed analytically for \( t \geq 0 \) as [23, 24]

\[
I_e(t) = \frac{I_0}{2} \exp(k_{\text{eff}} N t) \left(1 - \text{erf} \left(\frac{t - T_0}{\sqrt{2} T_L} \right)\right),
\]

where \( I_0 \) is the electron current at time \( t = 0 \), \( k_{\text{eff}} \) is the effective ionization rate coefficient, \( N \) is the number density of the gas, \( T_0 \) is the electron drift time, which relates to the electron drift velocity \( w_e \) via \( T_0 = d/w_e \), \( \tau_0 \) is the characteristic time for longitudinal electron diffusion, which relates to the longitudinal diffusion coefficient \( D_L \) via \( 2D_L = w_e^2 \tau_0 \), \( N_e(0) \) is the initial number of electrons and \( q_0 \) is the elementary charge. The determination of the effective ionization rate coefficient \( k_{\text{eff}} \), the electron drift velocity \( w_e \) and the longitudinal electron diffusion coefficient \( N D_L \) using this model was described in detail previously [24]. The quantities \( k_{\text{eff}}, w_e, \) and \( N D_L \) depend on the density-reduced electric field \( E/N \), given in Townsend (1 Td = 10^-21 V m^2).

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 \( k_{\text{eff}} \) is defined as the difference between the ionization and attachment rate coefficients \( k_i \) and \( k_a \). The relation between \( k_{\text{eff}} \) of a gas mixture and the attachment and ionization cross sections of its components is given by (see for instance equation (10) of reference [26])

\[
k_{\text{eff}} = k_i - k_a,
\]

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

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

where \( x_n \) is the mole fraction of species \( n \) in the mixture, \( \sigma_i^{(n)} \) is the total attachment cross section of species \( n \), \( \sigma_a^{(n)} \) 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

\[
\int_0^\infty \sqrt{\varepsilon} f d\varepsilon = 1.
\]

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

\[
k_{\text{eff}} = (1 - x) k_{\text{eff}}^b + x \sqrt{\frac{2}{m_e}} \int_0^\infty \left(\sigma_i - \sigma_a\right) \varepsilon f d\varepsilon,
\]

where \( k_{\text{eff}}^b \) is the effective ionization rate coefficient in the pure buffer gas, \( \sigma_i \) and \( \sigma_a \) 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 \( \text{N}_2 \) and \( \text{CO}_2 \), complete sets of electron scattering cross sections are available, for instance via the LXcat project [27, 30]. In the present work, Biagi’s cross section set [28] is used for \( \text{N}_2 \) and the one of Phelps [29] for \( \text{CO}_2 \). The effective ionization rate coefficient

\[
\sigma_i \text{ att.} = \int \sigma_i \varepsilon f d\varepsilon.
\]
rate coefficient $k_{\text{eff}}$ and EEDF for these gases are obtained by solving the Boltzmann equation in the two-term approximation, using the solver Bolsig+ [26].

Using equation (7), only the ionization and attachment cross sections of SF$_5$CF$_3$ (and not a complete cross section set of SF$_5$CF$_3$) are required for calculating $k_{\text{eff}}$ in diluted SF$_5$CF$_3$ mixtures. In this work, the ionization cross section of SF$_5$CF$_3$ from reference [18] and the attachment cross section from reference [19] are used to calculate $k_{\text{eff}}$ for comparison with the present measurement results.

The attachment cross section $\sigma_a$ may be estimated through equation (7) using measurements of $k_{\text{eff}}$. This constitutes an ill-posed problem since $\sigma_a$ needs to be deconvoluted from the electron energy distribution function. We use in this work a linear inversion method and a gaussian expansion method, which have been described previously [25].

### 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 initiated in a gas. 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 that the sum of the $(E/N)_{\text{crit}}$ of its components weighted by their mole fractions in the mixture [31].

### 2. Diluted SF$_5$CF$_3$ mixtures in N$_2$ and CO$_2$

An overview of the present measurements in diluted SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/CO$_2$ mixtures is given in table 1.

<table>
<thead>
<tr>
<th>Buffer SF$_5$CF$_3$</th>
<th>$(E/N)_{\text{crit}}$ (Td)</th>
<th>(kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>5-130</td>
<td>2, 10</td>
</tr>
<tr>
<td>0.02</td>
<td>15-130</td>
<td>2, 6, 10</td>
</tr>
<tr>
<td>0.09</td>
<td>40-135</td>
<td>2, 6, 10</td>
</tr>
<tr>
<td>0.51</td>
<td>140-163</td>
<td>10</td>
</tr>
</tbody>
</table>

| CO$_2$            | 5-120               | 2, 10  |
| 0.02              | 20-105              | 10     |
| 0.09              | 30-110              | 2, 6, 10|

**Table 1.** Overview of the measurements in diluted SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/CO$_2$ mixtures.

2.1. Sample measurements

Figures 2(a) and (b) show sample measurements of the current versus time in the mixture of 0.51% SF$_5$CF$_3$ 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.

![Figure 2](image-url)  
**Figure 2.** Currents versus time in the mixture of 0.51% SF$_5$CF$_3$ 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.
2.2. Results of the electron current analysis

The electron current analysis described in section 1.2 yields the effective ionization rate coefficient $k_{\text{eff}}$, the electron drift velocity $w_e$, and the longitudinal electron diffusion coefficient $N_{D_L}$. These quantities in the considered SF$_5$CF$_3$/N$_2$ mixtures are shown in figure 3(a), (b) and (c) respectively, and in figure 4(a), (b) and (c) for the SF$_5$CF$_3$/CO$_2$ mixtures, and can also be downloaded from LXcat [17].

The measured quantities $k_{\text{eff}}$, $w_e$ and $N_{D_L}$ in pure N$_2$ and CO$_2$ are compared to the same quantities calculated with Bolsig+ using the cross section sets of Biagi [28] and Phelps [29] 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 [32].

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

The effective ionization rate coefficient $k_{\text{eff}}$ shown in figures 3(a) and 4(a) is increasingly negative with increasing mole fraction of SF$_5$CF$_3$, due to electron attachment to SF$_5$CF$_3$. Accordingly, a large increase of the density-reduced critical electric field ($E/N$)$_{\text{crit}}$ with increasing mole fraction of SF$_5$CF$_3$ can be observed. The electron drift velocity and diffusion coefficient in the diluted SF$_5$CF$_3$ mixtures are identical to the same quantities in the pure buffer gases. It was expected that adding a small amount of SF$_5$CF$_3$ would not affect the electron transport (drift and diffusion). The measured quantities $k_{\text{eff}}$, $w_e$ and $N_{D_L}$ show no dependence on the gas pressure in the investigated pressure range of 2 to 10 kPa.

![Figure 3](image_url)

Figure 3. (a) Effective ionization rate coefficient, (b) electron drift velocity and (c) density normalized longitudinal electron diffusion coefficient versus $E/N$ in diluted SF$_5$CF$_3$/N$_2$ mixtures. The gas mixtures are color-coded: the percentages of SF$_5$CF$_3$ 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 ([2 kPa, △ 6 kPa, ○ 10 kPa]). The lines are calculated as indicated in section 1.3: --- Bolsig+ calc. using data from ref. [28], — — calc. with equation (7) using data from refs. [18, 19, 28].
2.3. Electron attachment cross section of SF$_5$CF$_3$

The measured values of $k_{\text{eff}}$ in the diluted SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/CO$_2$ mixtures are used to estimate the electron attachment cross section $\sigma_a$ of SF$_5$CF$_3$ using the linear inversion and gaussian expansion methods mentioned in section 1.3. The resulting $\sigma_a$ are shown in figure 5(a), and compared to the total attachment cross section of SF$_5$CF$_3$ 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$_5$CF$_3$ [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$_5$CF$_3$, but in the range below 0.1 eV, the present results are too low compared to the beam measurement. 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 due to the absence of electrons with these low energies at the minimum $E/N$ value that was measured, and has been previously discussed for the similar case of SF$_6$ [25]. 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. Despite this, the present results show that reasonable estimations of the total attachment cross section of gases can be obtained by these methods, when no direct measurement of the attachment cross section is available.

3. Mixtures with higher SF$_5$CF$_3$ content and pure SF$_5$CF$_3$

An overview of the present measurements in SF$_5$CF$_3$/$N_2$ and SF$_5$CF$_3$/$CO_2$ mixtures with higher SF$_5$CF$_3$ content is given in table 2.

3.1. Sample measurements

Figures 6(a) and (b) show sample current transients in pure SF$_5$CF$_3$. In contrast to the currents measured in mixtures with low SF$_5$CF$_3$ 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 $k_{e}$ = $k_{i}$ - $k_{a}$ is small in absolute value (the electron number varies comparatively less).

3.2. Results of the electron current analysis

The effective ionization rate coefficient $k_{e}$, the electron drift velocity $w_e$ and the longitudinal electron diffusion coefficient $N D_L$ obtained in the considered SF$_5$CF$_3$/$N_2$ mixtures are shown in figure 7(a),(b) and (c) respectively, and in figure 8(a),(b) and (c) for the SF$_5$CF$_3$/$CO_2$ mixtures, and can also be downloaded.

**Table 2.** Overview of the measurements in the SF$_5$CF$_3$/$N_2$ and SF$_5$CF$_3$/$CO_2$ mixtures with higher SF$_5$CF$_3$ content.

<table>
<thead>
<tr>
<th>Buffer SF$_5$CF$_3$ gas mol%</th>
<th>[E/N]-range pressures (Td)</th>
<th>(kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>5-180</td>
</tr>
<tr>
<td></td>
<td>4.96</td>
<td>212-232</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>261-271</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>310-318</td>
</tr>
<tr>
<td></td>
<td>40.2</td>
<td>396-401</td>
</tr>
<tr>
<td></td>
<td>59.1</td>
<td>453-458</td>
</tr>
<tr>
<td></td>
<td>74.6</td>
<td>500-505</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>545-577</td>
</tr>
</tbody>
</table>

| 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$_5$CF$_3$, at a pressure of 4kPa, for an electrode spacing of 15 mm, and for a reduced electric field $E/N$ of (a) 573 Td and (b) 577 Td.
The quantities $k_{\text{eff}}$, $w_e$ and $N_{D_L}$ show no dependence on the gas pressure for the investigated pressures. The decrease of $k_{\text{eff}}$ with increasing mole fraction of SF$_5$CF$_3$ is clearly visible for the SF$_5$CF$_3$/N$_2$ and SF$_5$CF$_3$/CO$_2$ mixtures. The values of $w_e$ in the SF$_5$CF$_3$/N$_2$ mixture show a smooth transition from pure N$_2$ to pure SF$_5$CF$_3$, whereas the values of $N_{D_L}$ are much more erratic. The electron diffusion coefficient $N_{D_L}$ is the quantity with the largest 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 and limited signal bandwidth.

The present measurements can also be presented in the form of the reduced effective ionization coefficient $\alpha_{\text{eff}}/N$ which relates to the effective ionization rate coefficient $k_{\text{eff}}$ and the electron drift velocity $w_e$ as $\alpha_{\text{eff}}/N = k_{\text{eff}}/w_e$. The present values of $\alpha_{\text{eff}}/N$ are shown in figure 9 and compared to values measured by Harrison in 1953 [22]. An excellent agreement is observed in the values of $\alpha_{\text{eff}}/N$, despite the differences in the experimental and analysis techniques.

**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$_5$CF$_3$ 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 (a) 2 kPa, (b) 3 kPa, (c) 4 kPa, (d) 5 kPa, (e) 7 kPa, (f) 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. [28].
The reduced effective ionization coefficient in SF$_5$CF$_3$ as a function of $E/N$. Present results: $\bullet$ 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.

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$_5$CF$_3$ 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$_5$CF$_3$ 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$_5$CF$_3$ resulting from all these aspects.

**Attachment properties** In contrast to SF$_6$, the electron attachment to SF$_5$CF$_3$ is exclusively dissociative, even at thermal electron energies ($\sim 0.03 \text{ eV}$) [19, 16]. The main anion formed by electron attachment to SF$_5$CF$_3$ is SF$_5^-$. At thermal energies and up to 0.15 eV, the attachment cross section of SF$_5$CF$_3$ 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$_5$CF$_3$ is 8.0 $\times 10^{-14} \text{ m}^{-3} \text{s}^{-1}$ [33]. However, from 0.15 eV to 2 eV, the attachment cross section of SF$_5$CF$_3$ 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$_5$CF$_3$ is higher than that of SF$_6$ for $E/N$ values larger than a few Townsend. At $E/N = 570 \text{Td}$ the attachment rate coefficient in pure SF$_5$CF$_3$ can be estimated using the attachment coefficient $\eta/N = 4 \times 10^{-21} \text{ m}^2$ from ref. [22] and the electron drift velocity $w_e = 2.5 \times 10^5 \text{ m} \text{s}^{-1}$ 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 $k = 4.6 \times 10^{-16}$ m$^3$s$^{-1}$, obtained by a Bornsgren calculation using the cross section set from Biagi [28].

**Ionization properties** The ionization of SF$_5$CF$_3$ 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 [34]. 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$_5$CF$_3$ than for SF$_6$ and the total ionization cross section of SF$_5$CF$_3$ is larger, see figure 5(b). Despite this, assumedly due to the different electron energy distributions in SF$_6$ and SF$_5$CF$_3$, the ionization rate coefficient in SF$_5$CF$_3$ at $E/N = 570$ Td is $k \approx w_s \alpha/N = 1 \times 10^{-15}$ m$^3$s$^{-1}$, twice smaller than the calculated value for SF$_6$ at the same $E/N$, namely $2.2 \times 10^{-15}$ m$^3$s$^{-1}$.

**Density reduced critical electric field** As a result of the larger attachment rate coefficient and the smaller ionization rate coefficient of SF$_5$CF$_3$, the effective ionization rate coefficient of SF$_5$CF$_3$ is lower than that of SF$_6$. The density-reduced critical electric field of SF$_5$CF$_3$ is 570 Td, 1.6 times higher than that of SF$_6$, namely 359 Td. The density reduced critical electric field of SF$_5$CF$_3$/N$_2$, SF$_5$CF$_3$/CO$_2$, SF$_6$/N$_2$, and SF$_6$/CO$_2$ mixtures as a function of the mole fraction of SF$_5$CF$_3$ or SF$_6$ is shown in figure 10. A synergy is observed in all these mixtures. A mixture of about 30% SF$_5$CF$_3$ 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$_5$CF$_3$ were reported in [2]. The boiling point of SF$_5$CF$_3$ is $-20 ^\circ$C, which is relatively high compared to the boiling point of SF$_6$, namely $-64 ^\circ$C. The vapor pressures of SF$_5$CF$_3$ and SF$_6$ [37] are shown in figure 11. The vapor pressure of SF$_5$CF$_3$ is lower than that of SF$_6$ by about one order of magnitude.

**Critical electric field** Since the critical electric field $E_{\text{crit}}$ 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$_5$CF$_3$, it has to be mixed with another gas to be used in medium or high voltage equipment. Figure 12(a) shows the critical electric field of different SF$_5$CF$_3$/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$_5$CF$_3$ 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 $E_{\text{crit}}$ in figure 12 are relative to the critical field of SF$_6$ at 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
Global warming potential The radiative efficiency of SF₅CF₃ is of 0.59 Wm⁻²ppb⁻¹, slightly higher than that of SF₆, namely 0.57 Wm⁻²ppb⁻¹ [9]. However, due to the shorter estimated lifetime of SF₅CF₃ compared to SF₆, 800 years and 3200 years respectively, the GWP of SF₅CF₃ on a 100 year time horizon is 17 400, slightly lower than that of SF₆, namely 23 500. The difference is accentuated when one considers that SF₅CF₃ would 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 SF₅CF₃, which are in good agreement with existing data from previous beam and swarm measurements. It extends previous data to mixtures of SF₅CF₃ with N₂ and CO₂, in particular a synergy is observed for the reduced critical electric field of SF₅CF₃ mixtures with N₂ and CO₂. In pure SF₅CF₃, 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 SF₆ with those of SF₅CF₃, it appears that the substitution of F by CF₃ has manyfold repercussions on the insulating properties. The substitution leads to an increased electric strength of SF₅CF₃, but as well to a higher boiling point. Consequently, SF₅CF₃ has to be used in a gas mixture, and the electric strength of that mixture depends largely on the synergism between SF₅CF₃ 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 SF₅CF₃ 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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