ELECTRON ATTACHING PROPERTIES OF c-C_4F_8O DERIVED FROM SWARM PARAMETER MEASUREMENTS IN BUFFER GASES

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ABSTRACT

Using the pulsed Townsend method the electron swarm parameters have been measured for c-C_4F_8O in buffer gases Ar, N_2 or CO_2 with mixing ratios $\leq 1.2\%$. The measurements were performed in a novel Pulsed Townsend experiment [1] that can operate with a high degree of automation. The evaluated parameters presented here are the effective ionization rate, the critical field strength and the electron attachment parameters of c-C_4F_8O. A linear dependence between mixing ratio and the swarm parameters was found. This linear response has been used to derive a preliminary set of attachment cross sections for c-C_4F_8O.

1. INTRODUCTION

Octafluorotetrahydrofuran (c-C_4F_8O) became commercially available recently with the designated application as cleaning agent for chemical vapour deposition chambers. c-C_4F_8O was considered for substituting widely used plasma processing gases with high global warming potential [2]. It has been demonstrated that c-C_4F_8O can replace C_4F_{10} as radiating medium in Cherenkov detectors [3]. No reports of electron transport coefficients or electron collision cross sections of c-C_4F_8O are known to the authors.

For high voltage insulation applications, gas mixtures containing oxygenated fluorocarbons are considered as SF_6 substitutes [4, 5, 6]. c-C_4F_8O can be regarded as a test case for such gas mixtures, even though it is not considered a replacement candidate itself. It has a boiling point $T_b = -0.8$ °C, and vapour pressure ~200 kPa at 20 °C. High voltage technical equipment is typically operated at ~0.5…0.7 MPa gas pressure at ambient temperatures down to $-20 \cdots -30$°C. In consequence, gases with a high boiling point (like c-C_4F_8O) can only be used as electron-attaching admixture in a buffer gas.

In the present contribution we aim to characterize and quantify the electron attaching properties of c-C_4F_8O. The electron swarm parameters of c-C_4F_8O are measured with low mixing ratios $\leq 1.2\%$ in binary mixtures with Ar, N_2 or CO_2. It is shown that the effective ionization rate changes linearly with the mixing ratio, which greatly simplifies the evaluation of electron swarm parameters [7].

Finally, it is attempted to estimate attachment cross sections consistent with our experimental results of effective ionization rates. Processes resulting from collisions of negative ions with the neutral background such as collisional stabilization or detachment, and thus pressure dependency, are not the subject of the present investigation.

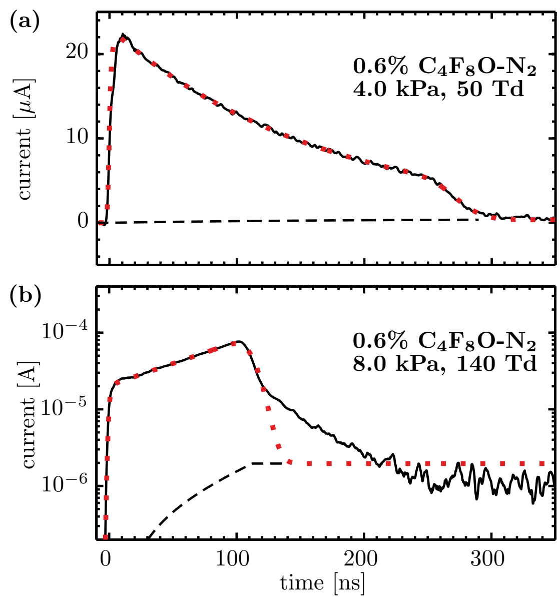

Fig. 1: Measured swarm drift currents (solid line), and a fit of the swarm current model (dotted line) including ion currents (dashed line) for 0.6% c-C_4F_8O in N_2.

2. METHODS

The experimental procedures and evaluation techniques applied in the present study have been comprehensively described previously [1, 7]. The sample gas c-C_4F_8O has been obtained from Linde with a quoted purity $2.5 \equiv 99.5\%$.

Swarm parameters: The swarm parameter measurements were made at room temperature 293 to 300 K. Measured swarm currents have been evaluated on the basis of an electron swarm model [1], in order to obtain the swarm drift velocity w, the effective ionization rate $\nu_{\rm eff}$ and the diffusion time constant $\tau_{\rm D}$. These transport parameters depend on the reduced field strength E/N, given in Townsend (1 Td $=10^{-21}$Vm^2). Here, E is the electrical field strength and N is the number density of the gas. The dependency of the swarm parameters on the mixing ratio k is investigated by means of the linear response technique [7].

Attachment cross sections: There are well known procedures for extracting cross sections from swarm parameters [8, 9]. In contrast to these methods, we have used a direct inverse method [10] to unfold the effective ionization rate of a gas mixture, which is given by the integral [7]:

$$\frac{\nu_{\rm eff}}{N}=\sqrt{\frac{2}{m_{\rm e}}}\int_0^\infty[(1-k)\sigma_{\rm B}+k(\sigma_{\rm i}-\sigma_{\rm a})]\varepsilon f\,{\rm d}\varepsilon\,. \quad (1)$$

Here $m_{\rm e}$ is the electron mass, $\sigma_{\rm B}(\varepsilon)$ is the ionization minus the attachment cross section of the buffer gas, $\sigma_{\rm i}(\varepsilon)$ and $\sigma_{\rm a}(\varepsilon)$ are the ionization and attachment cross sections of the sample gas, and $f(\varepsilon, E/N)$ is the electron energy distribution function (eedf) of the gas mixture. The eedf's for pure N_2 and CO_2 are calculated with the Boltzmann solver Bolsig+ [11] using two slightly different electron cross section sets from the Phelps as well as the SIGLO database (www.lxcat.net, both retrieved on December 9, 2013). For $\sigma_{\rm i}(\varepsilon)$ of c-C_4F_8O, we assume a threshold energy of 12 eV [12], and we adopt the shape and magnitude of the ionization cross section of C_3F_8 [13]. In the case of small concentrations of the attaching gas in N_2 or CO_2, and for $E/N \lesssim 80$ Td, the eedf of the mixtures is well-described by the eedf of the pure buffer gas. However, in Ar the change of the eedf due to adding c-C_4F_8O strongly effects $\nu_{\rm eff}/N$. We therefore exclude the measurements in Ar from the unfolding procedure. It is then possible to unfold equation (1) by means of well defined algorithms for discrete linear inversion problems. Here, we use truncated singular value decomposition (TSVD), which is a regularization method included in the Regularization Tools package [14].

buffer gas	experimental conditions	mixing ratio %	$(E/N)_{\rm crit}$ (Td)
Ar	2 - 8 kPa	0.21	30.0
(6.0)	24 - 54 Td	0.40	32.6
	11 - 17 mm	0.60	36.7
		1.01	41.0
N_2	2 - 4 kPa	0.15	104
(5.0)	20 - 130 Td	0.20	109
	11 - 17 mm	0.30	113
		0.40	119
		0.60	121
CO_2	2 - 4 kPa	0.15	86.0
(5.0)	20 - 116 Td	0.30	90.5
	11 - 17 mm	0.40	92.5
		0.60	97.2
		0.81	100
		0.99	102
		1.21	106

Tab. 1: Investigated mixing ratios of c-C_4F_8O in buffer gases (gas purity in brackets), and the measured critical field strength $\pm1.5\%$ uncertainty. The experimental conditions are specified by stating the ranges of total gas pressure, E/N and electrode spacing.

3. RESULTS

Table 1 summarizes the investigated gas mixtures. Example measurements of 0.6 % c-C_4F_8O in N_2 are shown in figure 1. The electron swarm model (dotted line) was fully consistent with the measured waveforms (solid line) for 4.0 kPa at 50 Td figure 1(a). However, at 8.0 kPa and 140 Td the occurrence of processes which are not included in the model can be seen figure 1(b). Consequently, it was not possible to evaluate these waveforms and they were not used for the evaluation in this contribution. Only measurements inside the experimental range indicated in table 1 have been used.

Figure 2 presents the measured $\nu_{\rm eff}/N$-results in Ar/, N_2/ and CO_2/c-C_4F_8O mixtures. Furthermore, it shows $\nu_{\rm eff}/N$ calculated by equation (1) with the obtained attachment cross section $\sigma_{\rm a}$ of c-C_4F_8O. From the $\nu_{\rm eff}/N$-data, the critical field strength $(E/N)_{\rm crit}$ was determined where $\nu_{\rm eff}/N = 0$ m^{3}s^{-1}. The results of $(E/N)_{\rm crit}$ are given in table 1.

The linear response technique yields a linear relation between mixing ratio k and $\nu_{\rm eff}/N$ in a range of $\nu_{\rm eff}/N$ and k for $k \leq 0.6\%$ in Ar, for $k \leq 0.4\%$ in N_2, and for $k \leq 1.0\%$ in CO_2. Figure 3 shows the attachment cross section $\sigma_{\rm a}$ of c-C_4F_8O, calculated from the response data.

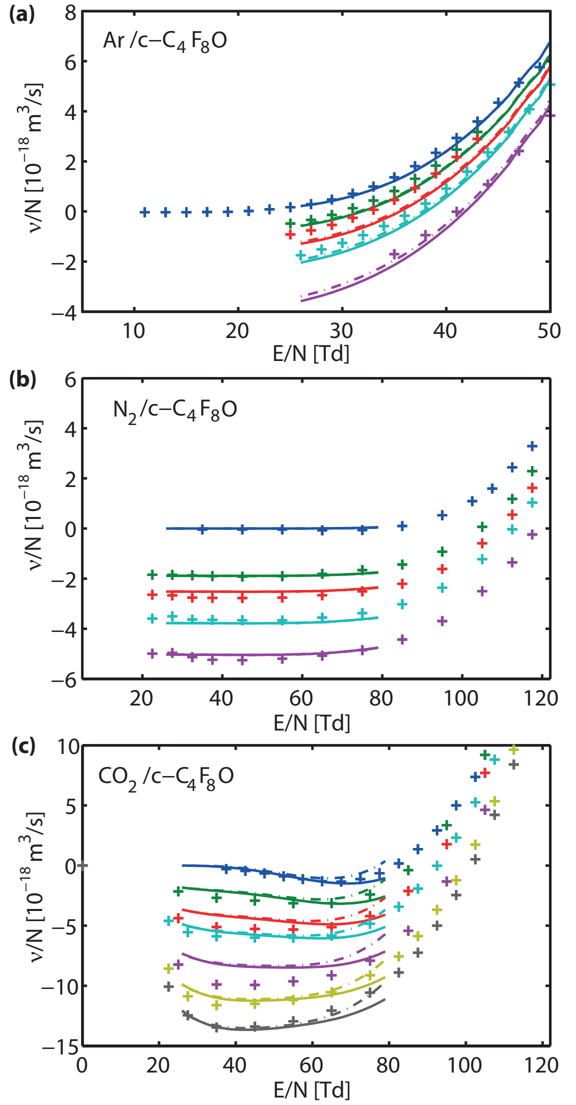

Fig. 2: Measured (+) effective ionization rate constants in **(a)** *Ar/c-C_4F_8O mixtures,* **(b)** *N_2/c-C_4F_8O mixtures and* **(c)** *CO_2/c-C_4F_8O mixtures, given in table 1. In each panel, the mixing ratio increases from the upper to the lower curve. The calculated rates using the two derived attachment cross sections on the basis of Phelps- and Siglo- cross section sets (for references see text) are indicated as solid and dashed-dotted lines, respectively.*

4. DISCUSSION

Electron attachment to c-C_4F_8O: One can note from figure 2 that the electron attachment rates are relatively small for $E/N < 30$ Td in CO_2. The largest attachment rates, which corresponds to the minimum in the $\nu_{\rm eff}/N$-curve, were observed around 40 Td. These findings indicate that $\sigma_{\rm a}(\varepsilon)$ is small for electron energies $\varepsilon \leq 1$ eV compared to other strongly attaching gases. Indeed, towards lower energies, $\sigma_{\rm a}$ is lower by several orders of magnitude compared to c-C_4F_8 or SF_6, as shown in figure 3.

It is evident that c-C_4F_8O has relatively large $\sigma_{\rm a}$ for electrons between 2 and 3 eV. It can be assumed that the peak of the cross section at 2.5 eV is caused by dissociative attachment processes.

We want to point out that it is particularly instructive to use CO_2 as a buffer gas to monitor the attachment cross section of a strongly attaching gas at energies below 1 eV. For our lower limit $E/N = 25$ Td the mean electron energy in CO_2 is around 1 eV. However, the function $f(\varepsilon, 25\,\text{Td})$ of CO_2 has a sharp peak around 0.1 eV, which gives rise to a good resolution of $\sigma_{\rm a}$ towards energies below 1 eV.

In general, the calculated reaction rates based on the $\sigma_{\rm a}$ agree well with the measured ones, see figure 2. The reaction rates in Ar, which were excluded from the unfolding procedure, were reproduced qualitatively.

Effects in N_2 buffer gas: A current waveform, see figure 1(b), was recorded with experimental parameters outside of the range specified in table 1: Larger $E/N = 140$ Td, and higher total pressure 8 kPa. Under these conditions the photocathode was coated by a dusty white layer, which probably has been formed of c-C_4F_8O dissociation products. It looks like the occurrence of swarm electrons with high ε led to large dissociation rates of c-C_4F_8O.

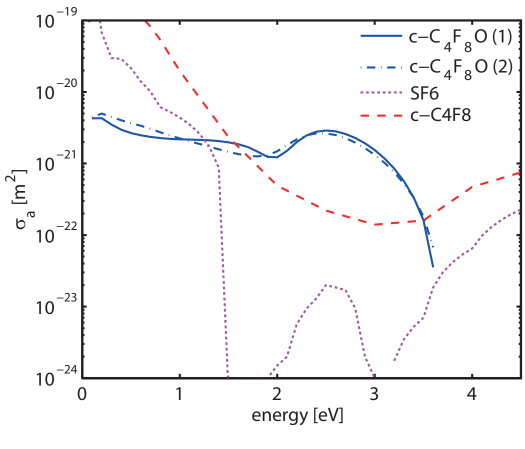

Fig. 3: Calculated attachment cross of c-C_4F_8O (solid and dashed-dotted line) derived from eedf's calculated on the basis of cross section sets from (1) Phelps and (2) Siglo (for references see text). Shown for comparison is the attachment cross sections for SF_6 [15] (dotted line) and c-C_4F_8 [16] (dashed line).

Figure 1(b) shows the observation of substantial currents after the swarm bulk has traversed the electrode gap. Such currents can arise from delayed electron production, probably due to electron detachment.

5. CONCLUSIONS AND OUTLOOK

Focus of this contribution is on the attachment processes in c-C_4F_8O, thus electron swarm parameters have been measured in a Pulsed-Townsend experiment for c-C_4F_8O with mixing ratios $\leq 1.2\%$ in buffer gases Ar, N_2 or CO_2. Shown here are the the effective ionization rate and the critical electric field strength.

Electron attachment parameters of c-C_4F_8O as a function of E/N have been obtained using an unfolding procedure. From this it is evident that c-C_4F_8O has relatively large attachment cross sections. Qualitatively, the results show that attachment of low energy electrons plays a minor role compared to the attachment of electrons with energies of a few eV.

Preliminary attachment cross sections have been estimated, which are consistent with the present experimental results of attachment rates in mixtures with Ar, N_2 and CO_2. Future studies will focus on measurements in an E/N-range extended towards lower values to be able to make a more precise estimation of σ_a at lower energies. Measurements were performed in a small pressure range only. Thus, no statement can be made about pressure dependency of attachment.

Generation of delayed electrons was presumed to occur in N_2/c-C_4F_8O at high E/N with concurrent dissociation processes. These processes should be subjects of future studies.

Similar studies are in preparation for gases with yet unknown characteristics that are potential replacement candidates for SF_6 to be used in high voltage gas insulated equipment.

Acknowledgement

The project is financially supported by Alstom (Schweiz) AG.

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