Is CF₃I a good gaseous dielectric? A comparative swarm study of CF₃I and SF₆

J. de Urquijo
Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, P.O. Box 48-3, 62251 Cuernavaca, Mor., México

jdu@fis.unam.mx

Abstract. This paper deals with the measurement of the electron drift velocity, the longitudinal diffusion coefficient and the effective ionisation coefficient in pure CF₃I and CF₃I mixtures. The E/N range covered was 100-850 Td (1 Td=10⁻¹⁷ V cm²). The present results were derived from a pulsed Townsend experiment. For pure CF₃I, the values of the electron drift velocity and of the effective ionisation coefficient were found to increase steadily with E/N. The E/N value at which ionisation equals attachment, commonly referred to as the limiting field strength, was found to be E/Nₘₚₜ=437 Td, which is higher than that of SF₆ (360 Td), a widely used insulating gas. Moreover, the curve for the mixture of 70% CF₃I with N₂ is very similar to that of SF₆ in the neighbourhood of E/Nₘₚₜ. Thus, from the point of view of these coefficients, CF₃I would seem to be superior in dielectric behaviour to SF₆. Besides, CF₃I is an environmentally friendly gas as opposed to SF₆. Certainly, many more tests should be performed to regard CF₃I as a good dielectric and possible substitute to SF₆.

1. Introduction

Sulphur hexafluoride is probably one of the most extensively used gases because of its many industrial and scientific applications. SF₆ is chemically inert, non-toxic, non-flammable, non-explosive, and thermally stable at temperatures less than 500 C. The outstanding properties of SF₆ make it suitable as an insulating medium in the equipment used for the transmission and distribution of electric power. SF₆ is strongly electronegative, with a high dielectric strength, and a breakdown voltage nearly three times higher than that of air at atmospheric pressure. On the other hand, SF₆ forms highly toxic and corrosive compounds (e.g., S₃F₁₀, SOF₂) when it is subjected to electrical discharges. Sulphur hexafluoride is an efficient infrared (IR) absorber and, due to its chemical inertness, it is not readily removed from the earth's atmosphere. Both these latter properties make SF₆ a potent greenhouse gas, although benign with regard to stratospheric ozone depletion, since it is chemically inert [1]. Since the very first measurements in 1970 [0.03 pptv (1 ppt=1 part in 10⁻¹² per volume of atmospheric air)], the purely anthropogenic greenhouse gas SF₆ increased by two orders of magnitude to a global mean value of 2.8 pptv in 1992. While the uncertainties in these numbers make extrapolations difficult, it is clear that the atmospheric concentration of SF₆ is increasing and could reach 10 pptv by the year 2010 and 65 pptv by the year 2100, depending upon the assumptions of release rates [2]. SF₆ has a global warming potential (GWP) of nearly 24,000 times greater than that of CO₂, the predominant contributor to the greenhouse effect, and its atmospheric lifetime in the environment has been estimated around 3,200 years.
The above concerns have moved scientists and engineers into finding possible substitutes for this otherwise formidable gas. Mixtures of SF$_6$ with fluorocarbon gases, rare gases and atmospheric gases have been tried. Of these, the SF$_6$-N$_2$ mixture has been found industrially useful for some high voltage applications. Other fluorocarbons, such as c-C$_4$F$_8$ have a higher dielectric strength than that of SF$_6$, although a GWP of 11,200 and a residence time in the atmosphere of 3,200 years of the former would discard it as a viable substitute gas.

Trifluoriodomethane (CF$_3$I), currently used as an etching gas [3], has been found very recently to be a potential high voltage insulator, both on its own and mixed with N$_2$ and CO$_2$ [4,5]. In contrast to SF$_6$, the global warming potential of CF$_3$I is less than that of CO$_2$ (GWP=1), and its lifetime in the atmosphere is very short, estimated to be less than two days, thereby ensuring that CF$_3$I does not deplete the ozone layer [6]. CF$_3$I has also found applications as an alternative refrigerant to commonly used fluorocarbons such as CF$_4$, for example [7]. In spite of the potential importance of CF$_3$I, there is still a substantial lack of information regarding this molecule. Recent reviews on electron interactions with CF$_3$I [8,10] indicate that even the cross sections for total electron scattering, attachment and ionization are scarce, and that further research on these matters is called for to either confirm or revise the available data, and also to extend the energy ranges thus far studied. Moreover, one of these recent review [8] states that no data for electron transport, ionization and attachment coefficients are available for this molecule.

This paper presents previously published measurements [11] on the electron drift velocity $v_e$, the density-normalized longitudinal diffusion coefficient $ND_e$, and the density-normalized effective ionization coefficient $(\alpha-\eta)/N$ for pure CF$_3$I and its mixtures (1%-70%) with N$_2$ ($\alpha$ and $\eta$ are the electron impact ionization and attachment coefficients, respectively). From the point of view of a possible application of CF$_3$I as a gaseous dielectric, we compare the above swarm coefficients with those of SF$_6$, including their limiting field strength.

2. Experimental

The pulsed Townsend apparatus that was used to measure the above parameters has been described in detail elsewhere [12]. A schematic of the apparatus is shown in Fig. 1a. Briefly, the method relies on the time-resolved observation of the total displacement current (electrons, positive and negative ions) moving through a parallel-plate capacitor (12 cm in diameter) filled with the research gas, to which a voltage has been applied to produce a very homogeneous electric field over a central portion of 2 cm diameter. The initial photoelectrons are released by a UV flash from the third harmonic (355 nm) of a Nd-YAG laser. In this experiment the gap distance was kept fixed at 3.1 cm, set to within an accuracy of 0.025 mm.

Prior to filling it with the gas or its mixture, the vacuum vessel was evacuated down to $10^{-6}$ torr. The range of working pressures was 0.2-20 torr. The gas pressure and mixture composition was measured with an absolute capacitance manometer to an accuracy of 0.01%, while the gas temperature was measured to an accuracy of 0.2% over the range 293-300 K. The CF$_3$I and N$_2$ samples both had a quoted purity of 99.9% and 99.999%, respectively, and were introduced into the discharge vessel without further purification. The displacement current was measured with a 40 MHz transimpedance amplifier, and recorded on a 100 MHz digital oscilloscope.

In the presence of electron drift, longitudinal diffusion, ionization and attachment, the temporal development of the electron current within the gap is described by the expression [11]

$$i_e(t) = \frac{n_0 q_e}{2T_e} \exp(\alpha_e v_e t) \left[ 1 - \phi \left( \frac{(v_e + \alpha_e D_e) t - d}{4D_e t} \right) \right] + \exp \left( \frac{v_e + \alpha_e D_e}{D_e} t \right) \phi \left( \frac{(v_e + \alpha_e D_e) t + d}{4D_e t} \right) - 1 \right]$$  \hspace{1cm} (1)

where $n_0$ is the initial photoelectron number, $q_e$ is the electron charge, $d$ is gap spacing, $T_e$=d/$v_e$ is the electron transit time, $\alpha_e=\alpha-\eta$, and
\[ \phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} \, du. \] (2)

is the error function of argument \( u \). Equation (1) was derived on the assumption of a simultaneous release of the photoelectrons from the cathode at time \( t=0 \). Because of the finite laser pulse duration and of the instrumental bandwidth, the rise of the measured electron avalanche is not sharp, yet it displays a Gaussian-like shape resembling that of the laser pulse. On the other hand, the fall is affected by longitudinal diffusion effects which, for fixed \( E/N \), become more apparent as the gas pressure is reduced.

Figure 1. A schematic of the pulsed Townsend apparatus. HV, high voltage Supply; L, laser; A, anode; K, cathode; AMP, transimpedance amplifier; OSC, Digital oscilloscope.

Figure 2. A sample electronic transient of CF₃I. Conditions are indicated at the inset. \( T_e \) is the electron transit time and \( I_{\text{excess}} \) is the current due to the ions (see the text).

When diffusion is either negligible or absent, equation (1) reduces to

\[
i_e(t) = \begin{cases} 
\frac{n_0 q_o}{T_e} \exp(\alpha_e v_e t) & 0 \leq t \leq T_e \\
0 & t > T_e
\end{cases}
\] (3)

A result that had been quoted previously [14].

Initial values of \( v_e \) and \( (\alpha-\eta)/N \) were derived from equation (3) to fit the electron transients. Briefly, the electron transit time \( T_e \) is that elapsed between the midpoints of the rising and falling edges of the pulse, from which \( v_e=d/T_e \) is calculated, and the density normalized effective ionization coefficient \( (\alpha-\eta)/N \) is obtained from a least-squares fitting procedure applied to the rising \( (\alpha > \eta) \) or falling \( (\alpha < \eta) \) exponential part of the avalanche. At this point, we would like to note that both \( v_e \) and of \( (\alpha-\eta)/N \) are obtained simultaneously from the same electron transient. Under some conditions of \( E/N \) and \( N \), when \( \alpha \) and \( \eta \) are large, the ionic currents during the electron transit may contribute to the
total, measurable current; even though its contribution is relatively small, this can be readily subtracted from the total current by approximating their exponential rise to a straight line, thereby obtaining an even closer measurement of the electron current (see Fig. 2, \(I_{\text{excess}}\)).

When the above procedure was completed, then full use of equation (1) was made to obtain the longitudinal diffusion coefficient. Usually, corrections to the drift velocity rendered values slightly larger (1-2%), although the effective ionization coefficient remained essentially unchanged. These final values are the ones to be reported below.

3. Measurement of electron swarm coefficients in CF₃I

The swarm coefficients reported in this section correspond to the measurements of electron avalanches over the pressure range 0.4-20 torr, and room temperatures between 293 and 301 K. The uncertainties reported here are the result of averaging a series of measured coefficients for the same \(E/N\) value and different pressures. Normally, we used two to five different pressures. The average uncertainties are 1% for the electron drift velocity, 8% for the longitudinal diffusion coefficients, 9% for the ratio \(D_L/K_e\), where \(K_e\) is the electron mobility, and 5% for the effective ionization coefficient, respectively.

3.1 Electron drift velocities

The electron drift velocities, \(v_e\), for CF₃I, CF₃I-N₂ and N₂ are shown plotted in Figure 3 over the range of \(E/N\) from 100 to 850 Td. The CF₃I-N₂ mixtures correspond to CF₃I shares of 5%, 10%, 20%, 50% and 70%. The \(E/N\) range covered for each CF₃I-N₂ mixture was limited, on the lower part, by the strong attachment of this gas, which precluded the observation of the falling portion of the electron avalanche, while the upper part of the \(E/N\) range was limited by the very low pressures used (<0.5 torr), which produced avalanches with substantial contributions from longitudinal diffusion. The drift velocity curves for the 1% and 2% CF₃I-N₂ mixtures have also been measured, but their values over the \(E/N\) range used were very similar to those of pure N₂, and thus were omitted for the sake of clarity in the figures presented.

![Graph](image)

Figure 3. The electron drift velocity in CF₃I and in the CF₃I-N₂ mixtures with 5%, 10%, 20%, 50% and 70% CF₃I as a function of \(E/N\) [11]. The crosses are the recommended electron drift velocities for SF₆ [9,15]. The SF₆ data are shown only for order-of-magnitude comparison and trend with those of CF₃I and the CF₃I-N₂ mixtures.
For the purpose of comparison with another potent gaseous dielectric, we have also plotted Aswchwanen’s values for the drift velocity of electrons in SF$_6$ [9,15]. It is noted that the values of $v_e$ for SF$_6$ are higher than those for CF$_3$I for E/N<700 Td. The calculated momentum transfer cross section for CF$_3$I [8] is approximately an order of magnitude smaller than the measured cross section of SF$_6$ over a wide electron energy range [15]. This means that, even considering the larger relative mass of CF$_3$I (194 Da) with respect to that of SF$_6$ (146 Da), the electron drift velocity in CF$_3$I should still be greater than that in SF$_6$. In view of this, we suggest that the relatively small values of the electron drift velocities in CF$_3$I with respect to those in SF$_6$ for E/N<700 Td may be due, additionally, to the stronger polar character of CF$_3$I as compared to that of SF$_6$, with dipole polarizabilities of 9.36 Å$^3$ and 6.54 Å$^3$, respectively [16,17].

The electron drift velocities in N$_2$ were also measured in this study, and found to be in good agreement with previously published data [18]. It is important to note that the 5% and 10% CF$_3$I-N$_2$ curves deviate from the N$_2$ curve, and also that their $v_e$ values become systematically smaller than those of N$_2$, due to the influence of CF$_3$I. For CF$_3$I contents greater than 10%, the $v_e$ curves bear a round curvature over their initial region of E/N, departing from the N$_2$ curve, and resembling the typical curves of negative differential conductivity [19,20].

To the best of our knowledge, no previous data for the electron drift velocities in either CF$_3$I or the CF$_3$I-N$_2$ mixture have been published before.

3.2 Longitudinal diffusion coefficients for electrons and the ratio $D_L/K_e$

The values of the density-normalized longitudinal diffusion coefficient, ND$_L$, for electrons in pure CF$_3$I and in the 5%, 10%, 20%, 50% and 70% CF$_3$I-N$_2$ mixtures, have been plotted in Figure 4 as a function of E/N. The ND$_L$ values for the 1% and 2% CF$_3$I-N$_2$ mixtures, since these are very close to that of N$_2$.

![Figure 4](image_url)

Figure 4. The density-normalized longitudinal diffusion coefficients ND$_L$ for electrons in CF$_3$I and in the CF$_3$I-N$_2$ mixtures with 5%, 10%, 20%, 50% and 70% CF$_3$I as a function of E/N. For the solid lines through the points, see the curve fittings in Ref. [11]. The crosses are the recommended ND$_L$ values for SF$_6$ [9,15]. These data are shown only for order-of-magnitude comparison and trend with those of CF$_3$I and the CF$_3$I- N$_2$ mixtures.
A comparison with the ND₆ values for SF₆, shows that those for pure CF₃I are smaller than the ones for SF₆ by a factor of about two over the whole E/N range of overlap. Again, for the sake of comparison, the longitudinal diffusion coefficients of Aschwanden [9] for SF₆ are also plotted in this figure. The different mixtures of CF₃I-N₂ present a similar trend as in the pure case. Moreover, the percentages corresponding to 50% and 70% of CF₃I have values smaller that those for SF₆. To the best our knowledge, no previous values of ND₆ have been published.

A coefficient that provides a measure of the translational energy of the charge carriers as a function of E/N is the ratio between the density-normalized longitudinal diffusion coefficient and the electron mobility, D₇/Kₑ, with Kₑ=νₑ/E. This ratio is shown plotted in Figure 5, together with the corresponding values for the mixtures as a function of E/N. The D₇/Kₑ values for SF₆ shown in this figure for the purpose of comparison are, as in the case for ND₆, higher than those for CF₃I by a factor between 1.5 and 2.

![Figure 5](image_url)

**Figure 5.** The ratio between the longitudinal diffusion coefficient and the electron mobility, D₇/Kₑ, for electrons in CF₃I and in the CF₃I-N₂ mixtures. The solid lines through the points represent a curve fitting described in Ref. [11]. The crosses are the D₇/Kₑ values for SF₆ [9,15], shown here for the purpose of comparing the relative magnitudes of this parameter in SF₆ with those of CF₃I and the CF₃I-N₂ mixtures.

### 3.3 Effective ionization coefficients and rates

The effective ionization coefficients (α−η)/N in CF₃I and in the mixtures of this gas with N₂ are plotted in Figure 6 for the mixtures with low concentration of CF₃I in N₂, and in figure 7 for the 10%, 20%, 50%, 70% CF₃I-N₂ mixtures, all as a function of E/N. Again, the lower limit of our measurements of (α−η)/N was due to the impossibility of assessing the electron transit time and hence determine both νₑ and (α−η), since the strong attachment produced a fast decaying signal that precluded us from measuring the electron transit time. The values of (α−η)/N in N₂ and 1%, 2% and 5% CF₃I-N₂ have been plotted separately, in figure 6, to emphasize the increase in (α−η)/N for E/N>230 Td with respect to the values of α/N for pure N₂. This effect is mainly due to the fact that the ionization potential of CF₃I is lower (10.23 eV) than that of N₂ (15.58 eV). On the other hand, Figure 7 shows the values of (α−η)/N for pure CF₃I and for the 10%, 20%, 50%, 70% CF₃I-N₂ mixtures.
Interestingly, the trend of the \((\alpha-\eta)/N\) values for CF\textsubscript{3}I runs almost parallel to that of SF\textsubscript{6}. An interesting feature of this curve is the value of the limiting (or critical) field strength, \(E/N_{lim}\), which is defined as that value of \(E/N\) at which ionization equals attachment, that is, \((\alpha-\eta)/N=0\). A value of \(E/N_{lim}=437\) Td is measured for CF\textsubscript{3}I, which turns out to be significantly higher than that of \(E/N_{lim}=361\) Td for SF\textsubscript{6}, an important and widely used high voltage gas insulator [15]. From this point of view, it would then be likely that CF\textsubscript{3}I be considered as a viable substitute for SF\textsubscript{6}, since it bears the good insulating properties of the latter, besides its non-ozone-depleting effects and significantly low global warming potential, in contrast to those of SF\textsubscript{6}. Moreover, note that the 70% CF\textsubscript{3}I-N\textsubscript{2} curve is essentially the same as that for SF\textsubscript{6} over the whole \(E/N\) range of overlap, up to \(E/N=550\) Td.

Our experiment could only render effective ionization coefficients. At this stage, we have not been able to assess any particular ionization or attachment coefficients. However, we would like to mention that the only measurements of Jiao et al on the electron impact ionization of CF\textsubscript{3}I [21] indicate that the ions formed are CF\textsubscript{3}I\(^+\), CF\textsubscript{2}I\(^+\), CF\textsubscript{2}I\(^+\), CF\textsubscript{3}I\(^+\), and I\(^-\), with CF\textsubscript{3}I\(^+\) as the predominant positive ion species for electron energies up to 70 eV, followed by I\(^-\), CF\textsubscript{3}I\(^+\), CF\textsubscript{2}I\(^+\), CF\textsubscript{2}I\(^+\), CF\textsubscript{3}I\(^+\), and CF\textsubscript{3}I, the cross sections of these latter two being a factor of ten smaller than the former three.

As regards negative ions from CF\textsubscript{3}I, the strongly electronegative character of this gas stems from the fact that electron attachment to CF\textsubscript{3}I proceeds dissociatively via the formation of I\(^-\), F\(^-\) and CF\textsubscript{3} and F\(^+\) via two dissociating negative ion states at \(-0\) eV and 3.8 eV [8]. According to our \(D_e/K_e\) data, which provide a rough measure of the average energy of the electron swarm, it is likely that in our experiment both I\(^-\) and F\(^-\) are formed. It is known that I\(^-\) is formed by the zero-eV process via the reaction [8]

\[ e + CF_3 I \rightarrow I^- + CF_3 \]  

(4)

while F\(^-\) and CF\textsubscript{3}I\(^+\) are formed by the 3.8 eV process via the reactions
Very recently, using several variants of the laser photoelectron attachment method, Marienfeld et al [22] have measured and calculated the dissociative electron impact attachment cross sections to CF$_3$I molecules leading to I$^-$ formation over the energy range 0.5–500 meV.

Moreover, the mixture with 70% of CF$_3$I in N$_2$ runs almost over the corresponding values of SF$_6$. The practical value of this situation is that an environmentally friendly mixture of CF$_3$I in N$_2$ may have the same efficiency as an insulating gas mixture as compared to that of the much less environmentally friendly case of SF$_6$. To the best of our knowledge, no measurements of the effective ionization coefficient have been published previously.

3.4 Limiting values of E/N

Figure 6 presents the so called *limiting* or *critical* field strength values of E/N$_{lim}$ at which $\alpha=\eta$ for all the CF$_3$I-N$_2$ mixtures studied, including that of pure CF$_3$I. A comparison with the well known E/N$_{lim}$ values for the SF$_6$-N$_2$ mixture reveals that for CF$_3$I concentrations in CF$_3$I-N$_2$ the mixture lower than 60%, the SF$_6$-N$_2$ mixture is superior, although this limit the CF$_3$I-N$_2$ mixture is superior to that of SF$_6$-N$_2$. In fact, as judged from these swarm properties, the 70% CF$_3$I-N$_2$ mixture is even superior to that of pure SF$_6$.
4. Conclusion

We have used previously published data [11] of the electron transport and ionisation coefficients in CF$_3$I and CF$_3$I-N$_2$ mixtures, covering a wide range of E/N. In this paper we have presented a comparison of such coefficients with those of SF$_6$, in the aim to evaluate them from the point of view of assessing CF$_3$I as a possible substitute of SF$_6$. In particular, we have found that the limiting field strength of pure CF$_3$I ($E/N_{\text{lim}} = 437$ Td) is higher than that of SF$_6$ ($E/N_{\text{lim}} = 361$ Td). An encouraging aspect of the measurements for the mixtures of CF$_3$I in N$_2$ presented here is that CF$_3$I or its mixture with N$_2$ both have the good properties to be regarded as viable gaseous dielectrics, in consonance with recent research in this direction indicating that CF$_3$I or its mixture with N$_2$ would be viable gaseous dielectrics since the mixture with 70% CF$_3$I presents a very similar behaviour to that of pure SF$_6$. Admittedly, many other chemical, thermal and economical studies are needed to consider CF$_3$I or its mixtures with N$_2$ as real substitutes for SF$_6$ in high voltage and switchgear applications.

In view of the scarcity of data on the interaction of these gases with electrons, we hope the present data will be useful for testing the available relevant cross sections, or even to attempt deriving the first sets.

Acknowledgements

This work was supported by Project PAPIIT IN102305. Thanks are due to A. Bustos and R. Bustos for their technical assistance.

References

[1] Christophorou L G and Olthoff J K and Green D S 1997 *NIST Technical Note 1425*
Washington: U.S. Government Printing Office

[2] Hope C 2003 *The marginal impacts of CO2, CH4 and SF6 emissions;*
www.ofgem.gov.uk/sustainability/Environmnt/Policy/Documents/3281-hope_report.pdf
Judge Institute of Management, University of Cambridge

[3] Misra A, Sees J, Hall L, Levy RA, Zaitsev VB, Aryusook K, Ravindranath C, Sigal V, Kesari S, Rufin D 1998, Materials Letters 34, 415

[4] Nakauchi S, Tosu D, Matsuoka S, Kumada A, Hidaka K 2006 Proc. XVI Int. Conf. Gas Disch. and Appl. Vol 1 pp 365-369 Xi’an, China

[5] Taki M, Hiromi O, Maekawa D, Mizoguchi H, Yanabu S 2006 Proc. XVI Int. Conf. Gas Disch. and Appl. Vol 2 pp 793-796 Xi’an, China

[6] Solomon S, Burkholder J B, Ravishankra A R, and. García R R 1994 J. Geophys. Res. D 99 20929

[7] Duan Y Y, Shi L, Sun L Q, Zhu M S and Han L Z 2000 Int. J. Thermophys. 21 393

[8] Christophorou L G and Olthoff JK 2000 J. Phys. Chem. Ref. Data, 29 553

[9] Aschwanden Th 1985, in Gaseous Dielectrics IV, ed L G Christophorou et al (New York: Pergamon) p 24

[10] Rozum I, Limão-Vieira P, Eden S, Tennyson J, and Mason N J 2006 J. Phys. Chem. Ref. Data 35, 267

[11] de Urquijo J, Juárez A M, Basurto E and Hernández-Ávila J L 2007 J. Phys. D 40 2205

[12] Hernández-Ávila J L, Basurto E, and de Urquijo J 2002 J. Phys. D 35 2264

[13] Brambring J 1964 Z Physik 179 532

[14] Raether H 1964 Electron Avalanches and Breakdown in Gases (London: Butterworths)

[15] Christophorou LG, and Olthoff JK 2000 J. Phys. Chem. Ref. Data 29, 267

[16] Glen RC 1994 J. Comp.-Aided Mol. Design, 8 457

[17] Lide, DR 2001 (Ed.) Handbook of Chemistry and Physics, 73rd ed., CRC Press

[18] Dutton J 1975 J. Phys. Chem. Ref. Data 4, 577

[19] Petrović, Z Lj, Crompton R W; Haddad G N 1984 Australian Journal of Physics, 37, 23

[20] Vrhovac, Slobodan B, Petrović Z Lj 1996 Physical Review E, 53, 4012-4025

[21] Jiao CQ, Garscadden A, Ganguly B, Dejoseph CA 2000 American Physical Society, 53rd Annual Gaseous Electronics Conference October 24-27 Houston, Texas Meeting abstract KR1.006

[22] Marienfeld S, Fabrikant I I, Braun M, Ruf M-W and Hotop H, J. Phys. B 39, 105 (2006)