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Boltzmann analysis of electron swarm parameters in CHF_3+CF_4 mixtures

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Abstract: The electron drift velocity, mean energy, ionization, attachment, effective ionization coefficient, limit electrical field, and synergism of pure CHF_3 (fluoroform), pure CF_4 (tetrafluoromethane), and CHF_3+CF_4 gas mixtures are calculated by Boltzmann equation analysis in a wide range of density normalized electrical fields (E/N). The finite difference method is used to solve the two-term approximation of the Boltzmann equation under steady-state Townsend conditions. To our knowledge, no previous electron swarm parameters of these mixtures have been published. At constant E/N values, the electron mean energies and drift velocities increase with decreasing CHF_3 content. The addition of CF_4 into the mixture increases the attachment coefficient but reduces the ionization coefficient since CF_4 is more electronegative than CHF_3. Furthermore, the limit electrical fields increase with increasing CF_4 concentration.

Key words: Gas discharge characteristics, fluoroform, tetrafluoromethane, Boltzmann equations

1. Introduction

Tetrafluoromethane (CF_4) has been greatly used in pulsed-power switching, particle detectors, and plasma etching of semiconductor materials due to its relative strong dielectric characteristics and nonflammable, and nontoxic properties [1, 2]. It has a low critical temperature and high critical pressure [3]. On the other hand, the lifetime of CF_4 is 50,000 years, and it is a greenhouse gas with a global warming potential 6630 times that of CO_2 for a 100-year time scale [4, 5].

The electron swarm parameters of CF_4, which are the electron mean energy, drift velocity, ionization, attachment, and effective ionization coefficients, are widely investigated in the literature [6, 7]. These swarm parameters are also calculated in CF_4+argon gas mixtures [8, 9] and in CF_4+SF_6 gas mixtures [10, 11]. Furthermore, the ternary mixtures of CF_4 were also analyzed by the authors [12, 13].

On the other hand, CHF_3 is used in fire suppression, refrigeration blends, and semiconductor production [14]. It is a hydrofluorocarbon refrigerant gas with zero ozone depletion potential [15]. However, its global warming potential is nearly two times higher than that of CF_4 but its lifetime is significantly less than that of CF_4, so it is an ideal substitute for CF_4 in some industrial applications [5, 14]. The electron swarm parameters of CHF_3 are calculated using Boltzmann analysis [16]. Its mixtures with argon, SF_6, and N_2 are also investigated [10, 17, 18].

In this study, electron swarm parameters of CHF_3+CF_4 gas mixtures are calculated by using two-term Boltzmann equation analysis. Although multiterm Boltzmann equation analysis increases the accuracy of the

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solution [19, 20], within the scope of this study, two-term Boltzmann equation analysis is preferred for the numerical solution of Boltzmann's equation because most of the plasma modeling in the literature is based on two-term theory [21, 22]. The electron energy distribution function (EEDF) is calculated in steady-state Townsend experiments and then electron swarm parameters are calculated using this distribution function. The limit electrical field at which the ionization and attachment are in balance is found, and then the synergism is evaluated between 0% and 100% CF_4. CHF_3 is widely used for plasma applications in industry for etching and deposition. Furthermore, it has been considered as a polar buffer gas for electronegative gas mixtures [17, 18]. CF_4 is also used in plasma etching of semiconductor materials and for pulsed power switching applications. The aim of this paper is to investigate the swarm parameters of CHF_3+CF_4 mixtures to be used in plasma and switching applications in view of the lower residence time of CHF_3 in the atmosphere.

2. Calculation method

We previously reported a detailed explanation of the solution of the Boltzmann equation [8, 13], so a brief description of the calculation method is presented here. In the below equations, M is the molecular mass, E is the applied electric field intensity, N is the gas density, and α and η are Townsend's first ionization and attachment coefficients. m and e are the electron mass and charge. ϵ is the kinetic energy of an electron. Q is the electron collision cross-section with the subscripts being the threshold energies of the inelastic collisions, where subscripts i, a, v, and ex mean ionization, attachment, vibrational excitation, and electronic excitation, respectively. Q_m^e is the effective cross-section. f is the distribution function of electron energy. There are multiple vibration, ionization, and attachment cross-sections for CHF_3 and CF_4. Total cross-sections are taken as the summation of respective multiple collision cross-sections in order to set the corresponding cross-sets in Eq. (1).

$$\begin{aligned}\left(\frac{E}{N}\right)^2 \frac{d}{d\epsilon}\left(\frac{\epsilon}{3Q_m^e}\frac{df}{d\epsilon}\right) + \left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\frac{d}{d\epsilon}\left(\frac{\epsilon}{3Q_m^e}f\right) + \left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\frac{\epsilon}{3Q_m^e}\frac{df}{d\epsilon} \\ + \left(\frac{\alpha-\eta}{N}\right)^2 \frac{\epsilon}{3Q_m^e}f + \frac{2m}{M}\frac{d}{d\epsilon}\left(\epsilon^2 Q_m f\right) + (\epsilon+\epsilon_v)Q_v(\epsilon+\epsilon_v)f(\epsilon+\epsilon_v) - \epsilon Q_v(\epsilon)f(\epsilon) \\ +4(2\epsilon+\epsilon_i)Q_i(2\epsilon+\epsilon_i)f(2\epsilon+\epsilon_i) - \epsilon Q_i(\epsilon)f(\epsilon) - \epsilon Q_a(\epsilon)f(\epsilon) = 0\end{aligned} \tag{1}$$

Eq. (1) can be rewritten as a second order differential equation as in Eq. (2). Then the distribution function of electron energy distribution is calculated by solving this differential equation.

$$A\frac{d^2F}{d\epsilon^2} + B\frac{dF}{d\epsilon} + CF + D = 0 \tag{2}$$

The coefficients of the second order differential equation are:

$$A = e\left(\frac{E}{N}\right)^2 \frac{\epsilon}{3Q_m^e} \tag{3}$$

$$B = e\left(\frac{E}{N}\right)^2 \left(\frac{Q_m^e - \epsilon\frac{dQ_m^e}{d\epsilon}}{3(Q_m^e)^2}\right) + 2\left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\left(\frac{\epsilon}{3Q_m^e}\right) + 2\left(\frac{m}{M}\right)e\epsilon Q_m \tag{4}$$

$$C = \left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\left(\frac{Q_m^e - \epsilon\frac{dQ_m^e}{d\epsilon}}{3(Q_m^e)^2}\right) + \left(\frac{\alpha-\eta}{N}\right)^2 e\left(\frac{\epsilon}{3Q_m^e}\right) + 2\left(\frac{m}{M}\right) e\left(2\epsilon Q_m + \epsilon^2\frac{dQ_m}{d\epsilon}\right) - e\epsilon(Q_m^e - Q_m) \quad (5)$$

$$D = e(\epsilon+\epsilon_v)Q_v(\epsilon+\epsilon_v)F(\epsilon+\epsilon_v) + e(\epsilon+\epsilon_{ex})Q_{ex}(\epsilon+\epsilon_{ex})F(\epsilon+\epsilon_{ex}) + 4e(2\epsilon+\epsilon_i)Q_i(2\epsilon+\epsilon_i)F(2\epsilon+\epsilon_i) \quad (6)$$

First, a guess value of $\alpha-\eta$ (for argon $\eta=0$) is introduced into Eq. (2) and then, by solving the second order differential equation, the new value of $\alpha-\eta$ is found. In order to modify the EEDF, this new value is again introduced into the equation. This iterative procedure is stopped when a final convergence for $\alpha-\eta$ is obtained [8, 12].

The cross-sections for CHF_3 are by Kushner and Zhang [23] and those for CF_4 by Kurihara et al. [9] are employed.

3. Results and discussion

In this paper, the ionization, attachment, effective ionization coefficients, and limit electrical fields are determined for pure CHF_3, pure CF_4, and mixtures of CHF_3+CF_4 by solving Boltzmann's equation.

The density normalized effective ionization coefficients ($(\alpha-\eta)/N$) in pure CHF_3 and pure CF_4 are displayed in Figure 1. The results of pure CHF_3 are compared with the results of Christophorou and Olthoff [16] and the results of pure CF_4 are compared with the results of Christophorou et al. [6]. Furthermore, the density normalized effective ionization coefficients are also calculated by an electron Boltzmann equation solver, Bolsig+ [24], and reasonable agreement with our results is obtained.

The electron drift velocities (W) in pure CHF_3 and CF_4 are shown in Figure 2. Similar to the density normalized effective ionization coefficients, the results of pure CHF_3 are compared with the results of Christophorou and Olthoff [16] and the results of pure CF_4 are compared with the results of Nikitovic et al. [25]. The Bolsig+ calculation results are also plotted in this figure with good agreement.

The effect of addition of CF_4 into CHF_3 is observed by increasing the CF_4 concentration from 0% to 25% with an incremental step of 5%. In the CHF_3+CF_4 gas mixtures investigated, the CHF_3 concentrations are higher than those of CF_4, since the atmospheric lifetime of CHF_3 is much less than that of CF_4. The electron mean energies ($\bar{\epsilon}$) in CHF_3+CF_4 mixtures are shown in Figure 3. It can be seen from this figure that the electron mean energies increase with decreasing CHF_3 content, while at high E/N values the electron mean energy stays relatively constant with decreasing CHF_3 content.

The electron drift velocities in CHF_3+CF_4 mixtures are shown in Figure 4. The electron drift velocities increase with decreasing CHF_3 content but at high E/N values they stay relatively constant with the decreasing CHF_3 content. The electron drift velocities increase with increasing E/N values. As can be seen from the inset figure, the variations in electron drift velocities are more pronounced at lower E/N values. Since the magnitude of the momentum transfer cross-section of CHF_3 is larger than that of CF_4, as the CHF_3 concentration increases the drift velocities decrease in the lower E/N range.

Figure 5 represents the density normalized ionization coefficients (α/N) of CHF_3+CF_4 gas mixtures. At E/N values of less than 150 Td the addition of CF_4 into the mixture slightly reduces the ionization coefficient, but this change is relatively small. The ionization coefficient increases with increasing E/N values.

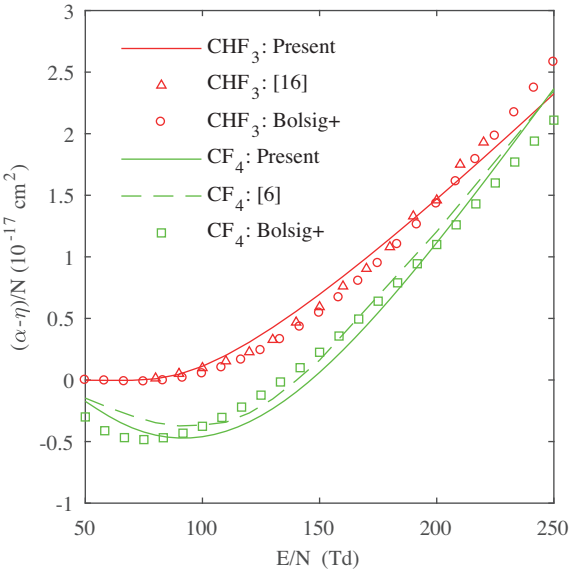

Figure 1. $(\alpha - \eta)/N$ in pure CHF_3 and CF_4.

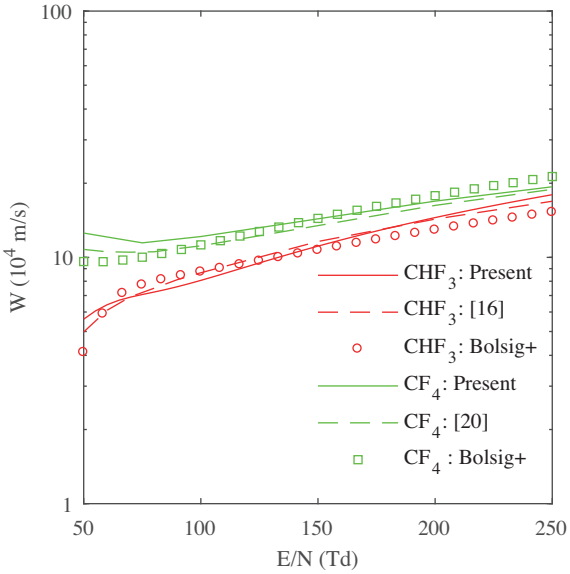

Figure 2. W in pure CHF_3 and CF_4.

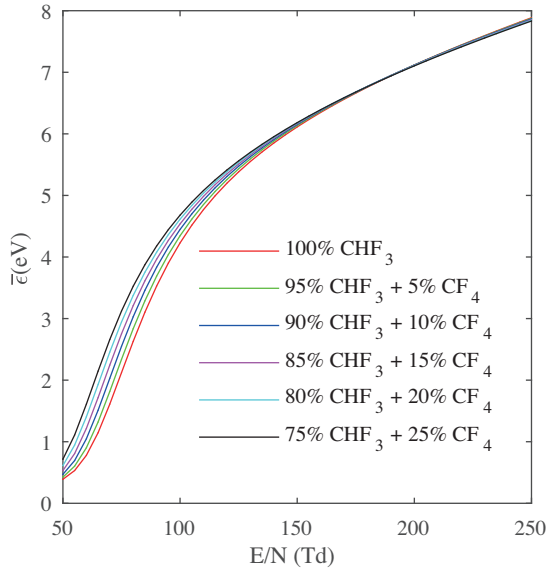

Figure 3. $\bar{\epsilon}$ in CHF_3+CF_4 gas mixtures.

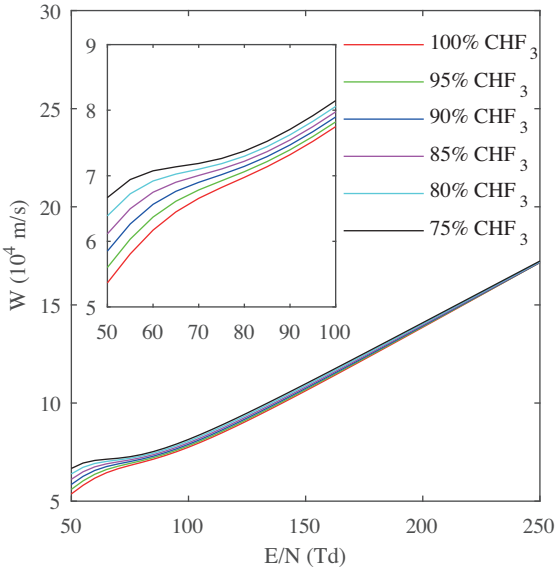

Figure 4. W in CHF_3+CF_4 gas mixtures.

The density normalized attachment coefficients (η/N) of CHF_3+CF_4 gas mixtures are shown in Figure 6. The addition of CF_4 into the mixture increases the attachment coefficient. CF_4 is a more electronegative gas than CHF_3, so by increasing the CF_4 content, the binary mixture becomes more electronegative.

Figure 7 displays $(\alpha - \eta)/N$ of CHF_3+CF_4 gas mixtures. At E/N values of less than 150 Td the addition of CF_4 to the mixture reduces the effective ionization coefficient, while at E/N values of more than 150 Td the density normalized effective ionization coefficients saturate with increasing CF_4 content. By adding CF_4 to CHF_3, the ionization, attachment coefficient, and ionization minus attachment coefficient (effective ionization coefficient) are changed. The change in the attachment coefficient is more pronounced than the change in the

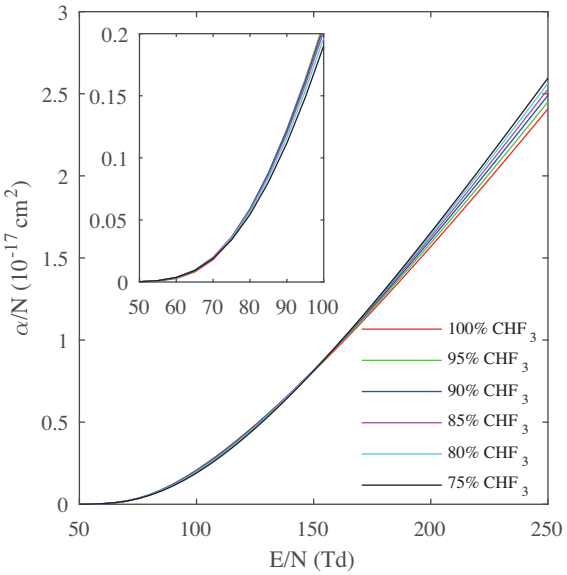

Figure 5. α/N in CHF_3+CF_4 gas mixtures.

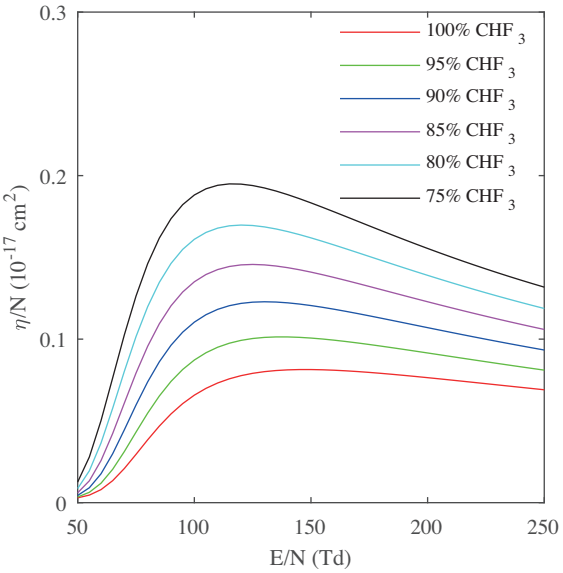

Figure 6. η/N in CHF_3+CF_4 gas mixtures.

ionization coefficient, so the change of the effective ionization coefficient is more dependent on the change in the attachment coefficient.

The density normalized limit electrical fields (E/N_{limit}) of CHF_3+CF_4 gas mixtures are shown in Figure 8. It can be observed from this figure that as CF_4 content increases, the electronegative character of the mixture increases and so the limit electrical field increases. The present limit electrical field of pure CHF_3 is calculated as 72 Td, which matches the value reported by Dengming and Yunkun [26], where they found E/N_{limit} = 74.8 Td. There is good agreement of the present result of the limit electrical field of pure CF_4 (144 Td) with the experimental results of Lakshminarasimha et al. [27] (143 Td) and Datskos et al. [28] (142 Td).

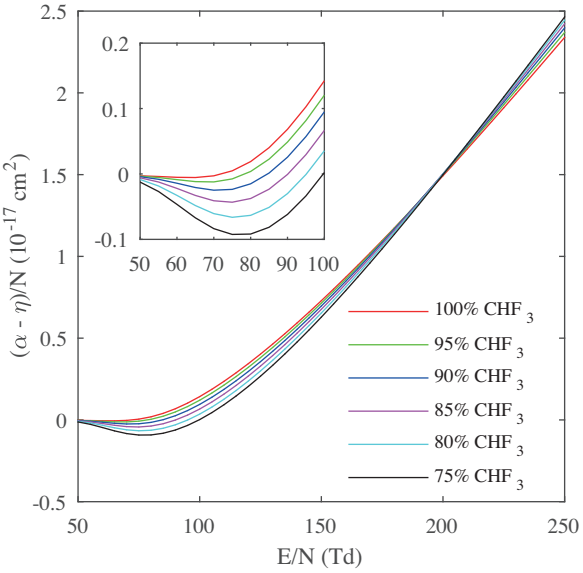

Figure 7. $(\alpha - \eta)/N$ in CHF_3+CF_4 mixture.

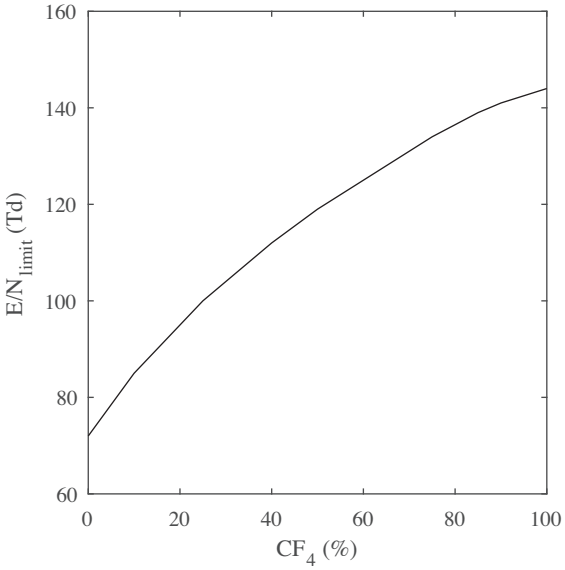

Figure 8. E/N_{limit} in CHF_3+CF_4 mixture.

The dielectric strength of the gas mixtures is divided by the sum of the dielectric strength of each gas in the gas mixtures. Then the result is subtracted by 1 and multiplied by 100, so the synergism [12, 13] results are found for the gas mixtures, which are shown in Figure 9.

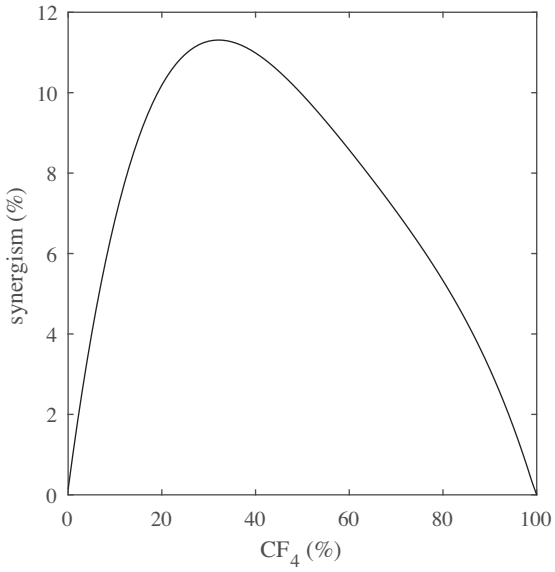

Figure 9. The synergism in CHF_3+CF_4 mixture.

4. Conclusions

CHF_3 and CF_4 are both electronegative and greenhouse gases, but the atmospheric lifetime of CHF_3 is much less than that CF_4 and so CHF_3 is a substitute gas for CF_4. In this study, dielectric properties of CHF_3, CF_4, and their binary mixtures are investigated by Boltzmann equation analysis.

The effective ionization coefficients and drift velocities of pure CHF_3 and pure CF_4 are calculated by using Boltzmann equation analysis. Then the results are compared with the ones in the literature and good agreement is observed. After the accuracy of the calculation method is proven, the electron swarm parameters of CHF_3+CF_4 gas mixtures are calculated in a wide range of E/N.

The limit electrical fields in pure CHF_3, pure CF_4, and CHF_3+CF_4 gas mixtures are obtained by determining the E/N at which the effective ionization coefficients are zero. The synergism is obtained by calculation and linear combinations of the limit electrical field. At constant E/N values, the electron mean energies increase with decreasing CHF_3 content, but at high E/N this change becomes stable. A similar response is observed in electron drift velocities, which increase with decreasing CHF_3 content.

CF_4 is more electronegative than CHF_3 so the addition of CF_4 into the mixture increases the attachment coefficient but reduces the ionization coefficient. However, the change of ionization coefficient is lower than the change of attachment coefficient. Total change in effective ionization coefficient depends on the change in attachment coefficient and ionization coefficient and it decreases with increasing CF_4 content. The limit electrical fields increase with increasing electronegativity and so increase with increasing CF_4 content and the synergism is obtained with these results.

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