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Ionızation, Attachment and Positive Synergism in CF_3I+CF_4+Ar Gas Mixtures with Dilute CF_3I Components

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Abstract

The purpose of the present paper is to evaluate the swarm parameters in CF_3I+CF_4+Ar ternary gas mixtures with dilute CF_3I components. The swarm parameters reported are namely, ionization, attachment, effective ionization, excitation rates and electron mean energies. We present the swarm data of the ternary mixture for various CF_4+Ar base mixtures with dilute CF_3I concentrations and analyze positive synergism in terms of attachment, ionization and excitation rates in the E/N range of 50–700 Td (1 Td = 10^{-21} Vm^2). In the ternary mixture, Ar component of the ternary mixture is kept constant at concentrations in the range of 40% - 90% and the CF_3I component is increased from 0.5% to 55%. In the dilute CF_3I mixtures, there is a marked increase in the electronegativity together with increased total excitation rates while the CF_3I component is increased. The mean energy of electrons is also reduced with increasing CF_3I content at given E/N accordingly. The limiting E/N values are obtained at the E/N values where the rate of ionization is equal to the rate of attachment. The limiting E/N increases in the ternary mixture as the CF_3I ratio is increased in the present study. The synergism is calculated using the Boltzmann solution results of the limiting E/N fields. Positive synergism is observed within the parameter range of this study. The degree of synergy is very high with dilute CF_3I components.

1. INTRODUCTION

Recently, we have shown that with the addition of CF_3I (Trifluoroiodomethane) component, the electronegativity increases [1]. In an $Ar+CF_4+CF_3I$ gas mixture, Prohina et al have also shown before that the electronegativity of the $Ar+CF_4$ increases with the CF_4 ratio is decreased [2].

It is known that the residence time of CF_3I in the atmosphere is very short and CF_3I with its low GWP (global warming potential) and ozone depletion is considered as a low environmental impact gas [3].

CF_3I is used in plasma etching [4-6], and because of its dielectric properties it can be a good insulant for high voltage applications [7, 8]. However, although its GWP is less than unity, practical application of pure CF_3I is limited due to its high boiling point and furthermore, it's decomposed by products may be dangerous for humans. An effective way of reducing its inherent disadvantages would be to reduce the partial pressure of CF_3I in a gas mixture [9-11].

In this paper we present the swarm data of the ternary mixture for various CF_4+Ar base mixtures with dilute CF_3I concentrations and analyze positive synergism in terms of attachment, ionization and excitation rates with dilute CF_3I concentration in the E/N range of 50–700 Td (1 Td = 10^{-21} Vm^2). The swarm parameters in the proposed gas mixture with dilute CF_3I is deficient in the literature. The main contribution of the present paper is to evaluate and report the swarm parameters in CF_3I+CF_4+Ar ternary mixtures together with electron mean energies and electron energy distributions. Furthermore, with the increasing dilute content of CF_3I, synergism in ternary mixtures is evaluated by means of the liming number density electric

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fields of the component gases directly calculated form the Boltzmann solution rather than employing semi-empirical methods.

2. CALCULATION METHOD

We present a brief description of the calculation method here, since we have made a comprehensive solution of the Boltzmann equation employed in gas mixtures [12, 13]. Rate coefficients are defined as,

$$k_\alpha = \left(\frac{2e}{m}\right)^{0.5} \int_0^\infty \varepsilon Q_i(\varepsilon) d\varepsilon \tag{1}$$

$$k_\eta = \left(\frac{2e}{m}\right)^{0.5} \int_0^\infty \varepsilon Q_a(\varepsilon) d\varepsilon \tag{2}$$

In the above equations, k_α gives rate of ionization and k_η is the rate of attachment. e, m and ε are the electron charge, the electron mass and the kinetic energy of an electron, respectively. Similarly, we can define rate of electronic excitation k_{ex} with the following equations,

$$k_{ex} = \left(\frac{2e}{m}\right)^{0.5} \int_0^\infty \varepsilon Q_{ex}(\varepsilon) d\varepsilon \tag{3}$$

In the above equations, Q_i, Q_a, Q_v, Q_{ex} is ionization, attachment, vibrational excitation, and electronic excitation cross sections, respectively. f is the distribution function of electron energy (EEDF) evaluated from the Boltzmann equation defined as,

$$\begin{aligned}\left(\frac{E}{N}\right)^2 \frac{d}{d\varepsilon}\left(\frac{\varepsilon}{3Q_m^e}\frac{df}{d\varepsilon}\right) + \left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\frac{d}{d\varepsilon}\left(\frac{\varepsilon}{3Q_m^e}f\right) + \left(\frac{eE}{N}\right)\left(\frac{\alpha-\eta}{N}\right)\frac{\varepsilon}{3Q_m^e}\frac{df}{d\varepsilon} + \left(\frac{\alpha-\eta}{N}\right)^2\frac{\varepsilon}{3Q_m^e}f \\ + \frac{2m}{M}\frac{d}{d\varepsilon}(\varepsilon^2 Q_m f) + (\varepsilon+\varepsilon_v)Q_v(\varepsilon+\varepsilon_v)f(\varepsilon+\varepsilon_v) - \varepsilon Q_v(\varepsilon)f(\varepsilon) \\ + (\varepsilon+\varepsilon_{ex})Q_{ex}(\varepsilon+\varepsilon_{ex})f(\varepsilon+\varepsilon_{ex}) - \varepsilon Q_{ex}(\varepsilon)f(\varepsilon) + \frac{1}{\Delta}\left(\frac{\varepsilon}{\Delta}+\varepsilon_i\right)Q_i\left(\frac{\varepsilon}{\Delta}+\varepsilon_i\right)f\left(\frac{\varepsilon}{\Delta}+\varepsilon_i\right) \\ + \frac{1}{1-\Delta}\left(\frac{\varepsilon}{1-\Delta}+\varepsilon_i\right)Q_i\left(\frac{\varepsilon}{1-\Delta}+\varepsilon_i\right)f\left(\frac{\varepsilon}{1-\Delta}+\varepsilon_i\right) - \varepsilon Q_i(\varepsilon)f(\varepsilon) - \varepsilon Q_a(\varepsilon)f(\varepsilon) = 0\end{aligned} \tag{4}$$

where, N, E and M are the density of the gas, the applied electric field and the molecular mass, η and α are the coefficients of attachment and Townsend's first ionization, respectively. In the Boltzmann equation, Δ gives the share of energy between the electrons after an ionization collision. ε_v defines threshold energies of the inelastic collisions for vibrational excitation, ε_{ex} defines threshold energies of the inelastic collisions for electronic excitation, ε_i defines threshold energies of the inelastic collisions for ionization. Q_m is the momentum transfer collision cross section and,

$$Q_m^e = Q_m + Q_v + Q_{ex} + Q_a + Q_i \tag{5}$$

Q_m^e is the effective collision cross section for momentum transfer. The Boltzmann equation is solved by finite difference [14, 15]. The cross sections of Argon are by Hayashi [16] and Yanguas-Gil et al [17] and for CF_4 the data of Kurihera et al [18] is employed. The authors have used these cross sections and a well agreement is obtained with the theoretical and experimental results [17, 19, 20]. The cross section set of Kawaguchi et al is used for CF_3I [21].

Equation 6 represents positive synergism in a gas mixture of m components in terms of the limiting number density reduced fields with x_i being the mole fraction of the i_{th} component,

$$\left(\frac{E}{N}\right)_{lim_M} > \sum_{i=1}^{m} x_i \left(\frac{E}{N}\right)_{lim_i} \tag{6}$$

where $\sum_{i=1}^{m} x_i = 1$ and $(E/N)_{lim_M}$ is the limiting value of the number density reduced field of the gas mixture with m components.

In order to define degree of synergy in a gas mixture with respect to dielectric strength, we should consider Equation 7,

$$D_M = M/L - 1 \tag{7}$$

where $L = \sum_{i=1}^{m} x_i (E/N)_{lim_i}$ and $M = (E/N)_{lim_M}$, M is the limit electric field from the Boltzmann equation and L is the limit electric field from the combination of the contribution of gases with $m = 3$ for the ternary mixture. These values are of 440 Td, 143.5 Td and 29.33 Td for CF_3I, CF_4 and Ar respectively [1]. To attain positive synergism the ratio *M/L* should be greater than unity.

3. RESULTS and DISCUSSIONS

The ionization rate constants in 5% CF_4 + 95% Ar mixture is shown in Figure 1 and Figure 2 attachment rates for the same mixture is displayed. In figure 3, effective ionization rate which is the difference between the ionization and attachment rates in CF_3I is given as a function of number density reduced field, E/N.

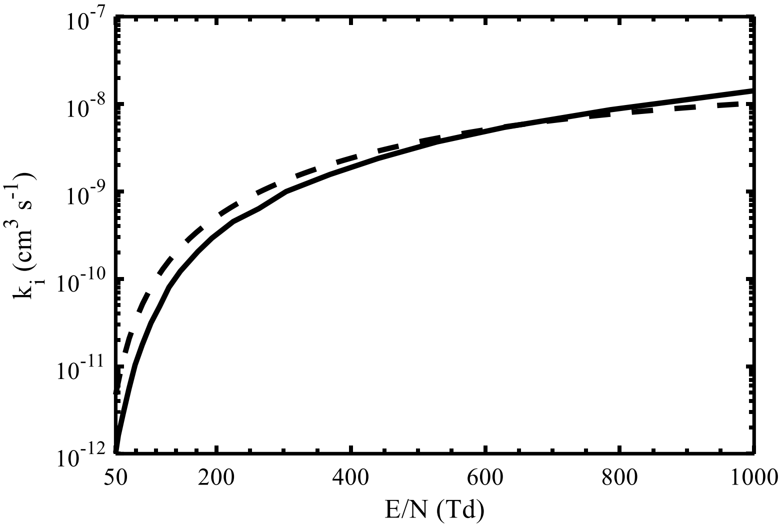

Figure 1. *Ionization rates in 5% CF_4 + 95% Ar mixture, full curve [16], dashed curve present results*

The ionization and attachment rates calculated in the present paper agree very well with the rate coefficients calculated in [16] for the 5% CF_4 + 95% Ar mixture which is the only available Boltzmann data for this binary mixture. In Figure 3, the effective ionization rate evaluated which is the difference between the ionization and attachment rates in CF_3I is given as a function of number density reduced field, E/N. The present results agree very well with the experimental effective ionization rate of Ref. 22 which is calculated using the experimental electron drift velocities and effective ionization coefficients reported in Table 1 of [22].

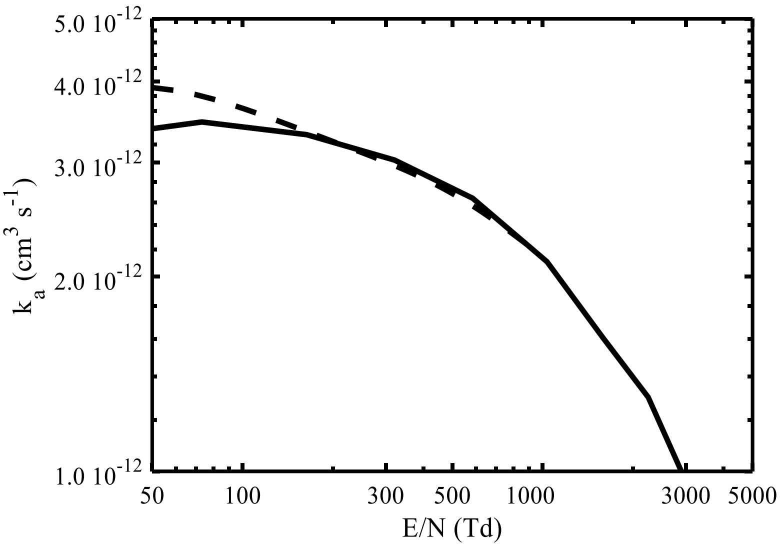

Figure 2. *Attachment rates in 5% CF_4 + 95% Ar mixture, full curve [16], dashed curve present results*

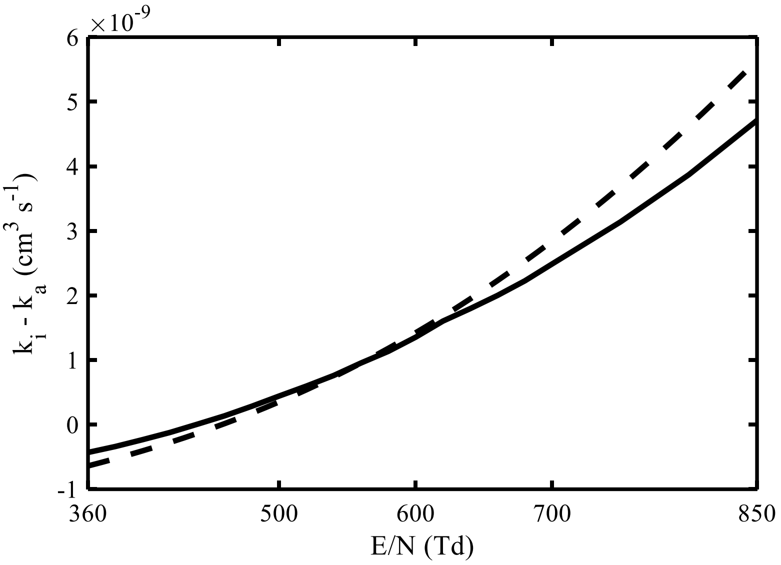

Figure 3. *Effective ionization rates in CF_3I, full curve [22], dashed curve present results*

Figure 4 gives the ionization rates of the present study in 90% Ar ternary mixtures for 0.5% and 5% CF_3I contents. Since the ionization rates evaluated for 3% and 1% CF_3I components are very close to each other and lie within range 0.5% and 5% CF_3I content mixtures the related data is not shown.

Figure 5 shows the attachment rates evaluated in 90% Ar for dilute CF_3I contents. The attachment rates increase as the CF_3I content is increased at constant E/N value. The marked increase of electronegativity in the ternary mixture is particularly significant in the lower E/N range of the present study.

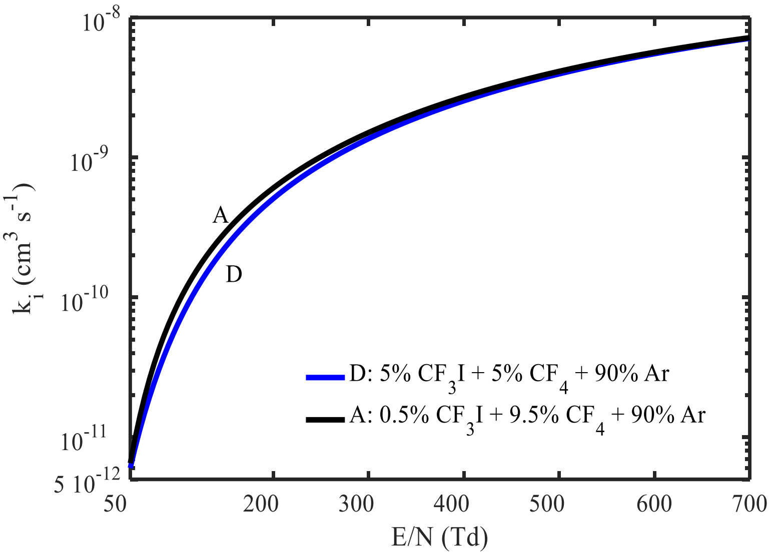

Figure 4. *Ionization rates in 90% Ar ternary mixtures, A: 0.5% CF_3I + 9.5% CF_4 + 90% Ar, D: 5% CF_3I + 5% CF_4 + 90% Ar*

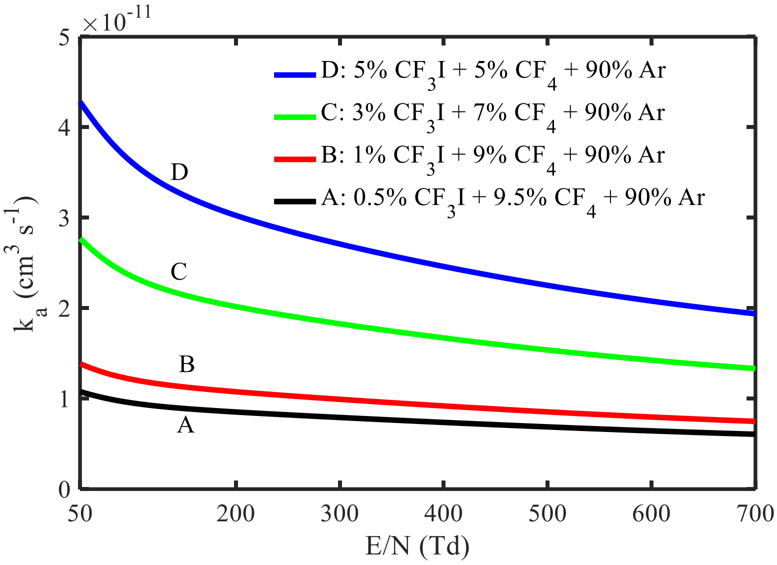

Figure 5. *Attachment Rates in 90% Ar ternary mixture, A: 0.5% CF_3I + 9.5% CF_4 + 90% Ar, B: 1% CF_3I + 9% CF_4 + 90% Ar, C: 3% CF_3I + 7% CF_4 + 90% Ar, D: 5% CF_3I + 5% CF_4 + 90% Ar*

The electronic excitation rates in the 90% Ar ternary mixture is shown in Figure 6. For a mixture, the excitation rate increases as E/N increases. Additionally, at a constant E/N the excitation rate coefficients increase as the CF_3I increases. The observed response in the excitation rate coefficients as the CF_3I content increased indicates an effective energy loss mechanism slowing down the electrons and such slowed down electrons can be captured with attachment collisions due to the stronger electronegativity of the ternary mixture as given in Figure 5.

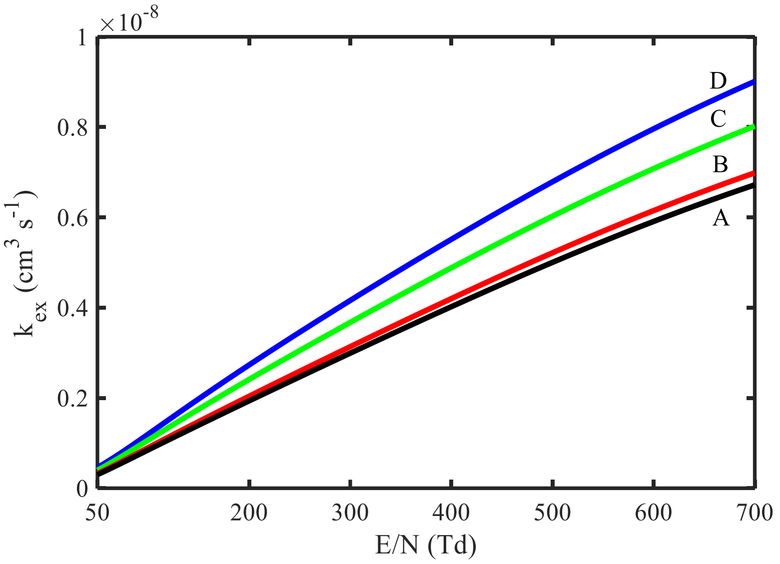

Figure 6. *Electronic excitation rates in 90% Ar ternary mixture, A: 0.5% CF_3I + 9.5% CF_4 + 90% Ar, B: 1% CF_3I + 9% CF_4 + 90% Ar, C: 3% CF_3I + 7% CF_4 + 90% Ar, D: 5% CF_3I + 5% CF_4 + 90% Ar*

The distribution functions of electron energy for dilute CF_3I components is shown in Figure 7. The addition of CF_3I, increases the maximum value of the EEDF in the lower energy range indicating increased number of slow electrons while the tail of the distribution drops in the higher energy range as a result of decreased number of higher energy electrons. Such response of EEDF with increasing dilute CF_3I contents is consistent with the increased attachment and excitation rates observed as the dilute CF_3I component is increased as can be seen from figures 5 and 6. Hence, as given in Figure 8 the mean energy of electrons is reduced with increasing dilute CF_3I content at given E/N accordingly.

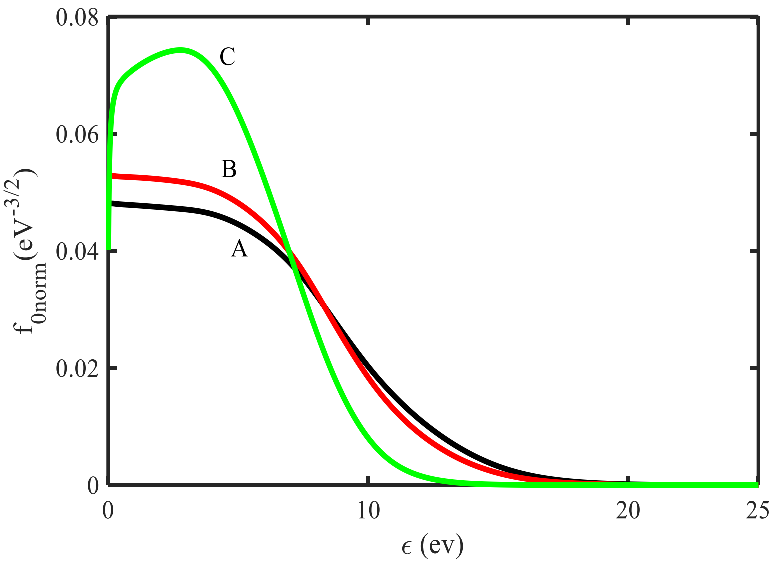

Figure 7. *The distributions of electron energy in 60 % Ar ternary mixture at 100 Td, A: 0.5% CF_3I + 39.5% CF_4 + 60% Ar, B: 1% CF_3I + 39% CF_4 + 60% Ar, C: 3% CF_3I + 37% CF_4 + 60% Ar*

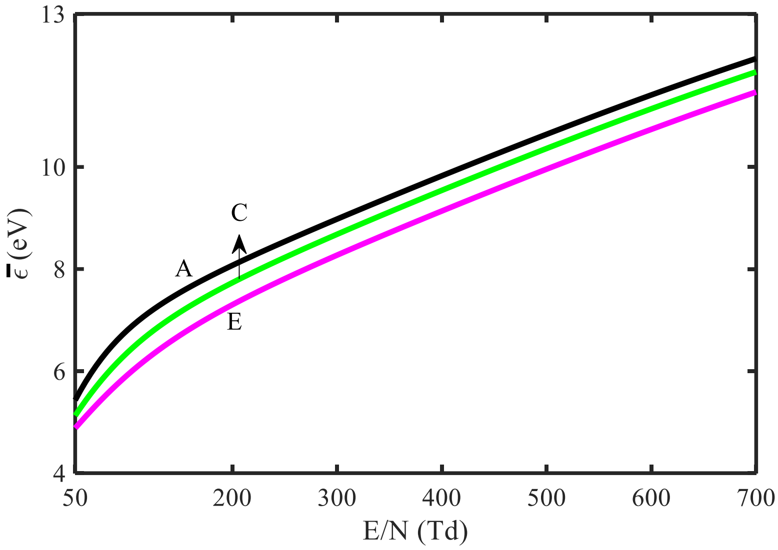

Figure 8. *Mean electron energies in 60 % Ar ternary mixture, A: 0.5% CF_3I + 39.5% CF_4 + 60% Ar, C: 3% CF_3I + 37% CF_4 + 60% Ar, E: 7% CF_3I + 33% CF_4 + 60% Ar*

In Figure 9, the limiting number density reduced electric field is displaced. The limiting E/N is an important parameter for insulation design of high voltage apparatus since at the E/N value corresponding to the limiting field, attachment rate is equal to the ionization rate and for E/N values lower than the critical E/N value an avalanche will not develop. Figure 9 shows limiting fields in ternary mixture at various Ar contents as a function of CF_3I together with a detailed display for the dilute CF_3I admixtures. The limiting E/N increases in a ternary mixture as the CF_3I ratio is increased in the parameter range of the present study.

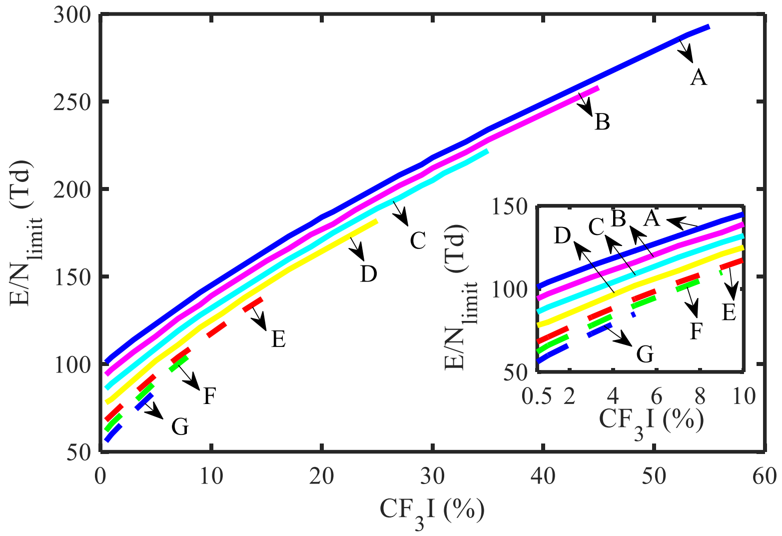

Figure 9. *Limiting E/N in CF_3I + CF_4 + Ar ternary mixtures, A: 40% Ar, B: 50% Ar, C: 60% Ar, D: 70% Ar, E: 80% Ar, F: 85% Ar, G: 90% Ar*

Figure 10, displays the synergy calculated by employing Equation 6. From this figure, it can be observed that the degree of synergism is higher for dilute CF_3I contents in the ternary mixtures investigated. The synergism has certain maximum values at certain CF_3I contents for a given ternary mixture with fixed Ar contents.

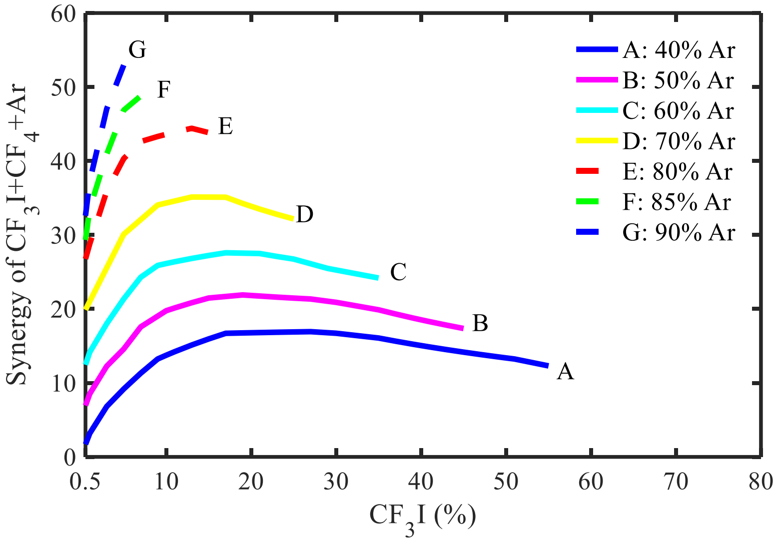

Figure 10. *Degree of synergy as a function of CF_3I contents in CF_3I+CF_4+Ar mixtures, A: 40% Ar, B: 50% Ar, C: 60% Ar, D: 70% Ar, E: 80% Ar, F: 85% Ar, G: 90% Ar*

4. CONCLUSIONS

With dilute CF_3I concentrations, in $CF_3I + CF_4 + Ar$ at various constant Ar contents, synergism in terms of attachment, ionization and excitation rates in the E/N range of 50–700Td is investigated.

It is observed that, at a constant E/N, the excitation rate coefficients increase as the CF_3I component in the mixture increases while the CF_4 component is decreased accordingly. This response in the excitation rate coefficients as the CF_3I content is increased indicates an effective energy loss mechanism slowing down the electrons and such slowed down electrons can be captured with attachment collisions due to the stronger electronegativity of the ternary mixture as a result of CF_3I admixture. Limiting number density reduced electric fields evaluated in the ternary mixtures also increases with the increasing dilute CF_3I contents. Synergism in ternary mixtures is evaluated by means of the liming number density electric fields calculated form the Boltzmann solution. Positive synergism is observed within the parameter range of the present study. The degree of synergism is high at dilute CF_3I contents in the ternary mixtures.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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