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# Motion of $SF_x{}^+$ $(x=1-3,5)$ and ion conversion in $SF_6$-$N_2$ mixtures

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This paper reports on the mass-analyzed measurement of the drift velocity of the positive $SF_6$ daughter ions, $SF_x{}^+$ $(x=1-3,5)$ in the mixture of $SF_6$ with $N_2$ for $SF_6$ concentrations of 10% and 50%. A double mass spectrometer-drift tube was used for these measurements. The density-normalized electric field intensity $E/N$, was varied from 30 to 360 Td $(1\ \mathrm{Td}=10^{-17}\ \mathrm{V\,cm^2})$. We have found an increasingly monotonic dependence of the drift velocity with $E/N$, and an inverse dependence of the above parameter with the decrease of the $SF_6$ content in the mixture. A test of Blanc's law for the zero-field reduced mobilities of the above ions shows a fair qualitative agreement. No drift velocities of these ionic species could be measured in pure $N_2$, since we found that these ions reacted strongly with the nitrogen molecules. The cases for $SF_3{}^+$ and $SF_5{}^+$ are discussed. A similar behavior was observed for the nitrogen ions drifting in pure $SF_6$.

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## I. INTRODUCTION

Sulfur hexafluoride is an outstanding high-voltage insulator, but it is also a powerful green house gas [1]. Efforts to reduce its environmental impact are focused on short-term solutions consisting of mixing it with gases with much less greenhouse effects, or even none, like nitrogen. It has been found, for instance, that mixtures containing between 40–50 % $SF_6$ in $N_2$ (by volume) are the optimum composition of an $SF_6$-$N_2$ mixture for use as a gaseous dielectric in place of pure $SF_6$ for both high-voltage insulation, and possibly for arc extinction and current interruption purposes [1,2]. Also, if the concentration of $SF_6$ in this mixture is around 10%, their dielectric characteristics for very fast transient voltages are very similar to those of pure $SF_6$, and can be used for gas-insulated transmission lines [3,4].

$SF_6$-$N_2$ mixture has been the most widely studied among a fairly long list of gaseous substitutes to pure $SF_6$. A fairly recent and accurate review on the extent of our knowledge on electron and ion swarm and transport properties is available [5]. It appears from this study, and also from the more recent literature published on this subject that, in contrast to pure $SF_6$, for which research on the ion transport and chemistry has recently become available, [6–10], no ion transport data are available on this mixture. Rao and Olthoff [10], who measured the kinetic energy distributions for positive and negative ions sampled from an $SF_6$ discharge at elevated $E/N$, found that the ion-molecule reaction scheme was difficult to understand, especially that of the positive ions. The studies concerning the chemical decomposition induced by subjecting the gas to an electrical discharge have been focused mostly on the measurement of reaction rates for the formation of neutral oxidation by products from corona discharges [4,5,11]. Only a few studies have been carried out on the detection of ions formed by sparking the $SF_6$ mixed with $N_2$ at impurity levels between 20–500 ppm [12]. Even at such small $N_2$ concentrations, ion molecule nitrogen-containing compounds such as $S_2F_8N^+$ exceed in intensity the peaks of those derived from $SF_6$ alone.

Knowledge of the ion drift velocity, for instance, is essential for evaluating mean ion energies and reaction rates, and also for plasma modeling, where this parameter sometimes influences sensitively the macroscopic discharge properties, like ion and current density. Whenever possible, mass-analyzed transport data are looked for, since complex molecules like $SF_6$ and $N_2$ bear a fairly complex reaction scheme, in which processes like dissociation and charge transfer play an important role. Moreover, a knowledge of the variation of the drift velocity with the density-normalized electric field intensity $E/N$ is essential for situations in which the ions are far from thermal equilibirum with the neutral gas molecules.

This paper was motivated by the aim of providing the first set of ion transport data of $SF^+$, $SF_2{}^+$, $SF_3{}^+$, and $SF_5{}^+$ in $SF_6$-$N_2$ mixtures over a relatively wide range of $E/N$ between 30 and 360 Td $(1\ \mathrm{Townsend}=10^{-17}\ \mathrm{V\,cm^2})$, so as to assist the extent of our knowledge on the basic mechanisms prevailing in the gas discharge, and also to fulfill some of the needs for discharge modelling. $SF_6$ concentrations in the gas mixture of 10% and 50% were used.

## II. APPARATUS

The drift tube with double mass spectrometry [13] used for this research is an improved version of the drift tube-mass spectrometer that was previously described in Ref. [7]. Briefly, a second quadrupole mass spectrometer (QMS) was attached to the exit of the original ion source. Primary ions, produced by electron impact in the hot-filament source, are focused electrostatically into the entrance of this new QMS having a mass range of 200 amu, and typical mass resolution of 0.1 amu. The ion source chamber can be moved over a distance from 0–38.70±0.05 cm at 13 discrete positions, defined by a set of 3.1-cm-wide guard rings. After mass analysis, the ions are focused through an orifice of 0.2 mm

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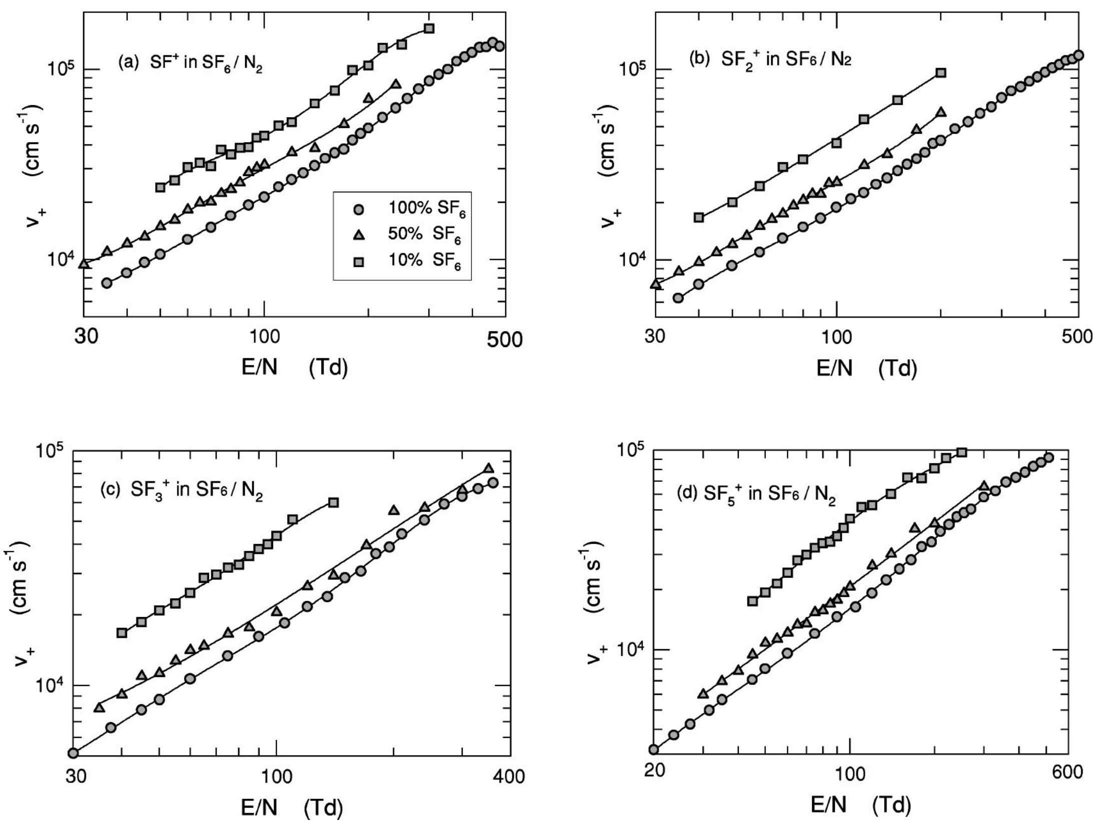

FIG. 1. Variation of the drift velocity of (a) $SF^+$, (b) $SF_2{}^+$, (c) $SF_3{}^+$, and (d) $SF_5{}^+$ in $SF_6/N_2$ mixtures. The present data correspond to mixtures with 10% and 50% $SF_6$, while the 100% $SF_6$ data were taken from Ref. [4].

into the drift space. Upon entrance into this region, the excess ion energy is relaxed by collisions with the gas neutrals over the first 3.1 cm of drift space, which is subjected to the same $E/N$ conditions that prevail in the drift region. This process was found to be very efficient for many ion-neutral systems, since only a few mean free paths would suffice to achieve whole energy relaxation. This region is terminated by a pair of flat, parallel, copper meshes that serve as ion shutters, intended for mobility measurements.

After traversing the drift space, a sample of the drifting ions enters the ion detection chamber through a central orifice of 0.2 mm diameter, where a second QMS, followed by a continuous dynode multiplier, generates the output pulses that are routed into a multichannel scaler, where an time-of-arrival spectrum (TAS) is formed.

It has been shown [14] that for long drift distances (>5 cm) and relatively low gas pressures, (<50 Pa), the calculated mean, $\langle t\rangle$, of the TAS can very closely approximated to

$$\langle t\rangle = \frac{z}{v_+}, \tag{1}$$

where $z$ is the drift distance, and $v_+$ is the ion drift velocity. Thus, a plot of $\langle t\rangle$ as a function of $z$ would give a straight line, the slope of which is the inverse of $v_+$. Normally, four consecutive ion source positions were used to obtain each $v_+$.

The gas pressure in the drift chamber was controlled to within 0.3% of its set value by a servo valve coupled to a Baratron gauge with 0.05% full range accuracy. Drift distances could be read from a graduated scale to an accuracy of $\pm 0.5$ mm. Two multichannel scalers were used for the present measurement. The time uncertainty was $\pm 1$ $\mu$s. Thus, for typical ion transit times in the range 0.5–10 ms, the instrumental errors in the drift velocity ranged typically between 0.5–1.3 %.

High purity grade (99.9%) $SF_6$ gas was used, while the purity of $N_2$ was 99.999%. Both gases were premixed in a separate cylinder, and its mixture was injected into the drift chamber without further purification. All measurements were taken over the ambient temperature range 293–310 K, for pressures between 0.66 and 13.3 Pa.

## III. RESULTS AND DISCUSSION

### A. Ion drift velocities in $SF_6$-$N_2$ mixtures

At least four different drift distances were used for each drift velocity measurement and, with the exception of a few points at the highest $E/N$ values attained in this experiment, at least two pressures were used for each drift velocity measurement. The final uncertainties, resulting from averaging these $v_+$ values, are in the range 2–4 %.

The drift velocities of $SF^+$, $SF_2{}^+$, $SF_3{}^+$, and $SF_5{}^+$ in the $SF_6$-$N_2$ mixtures are shown plotted in Figs. 1(a) to 1(d), respectively, for $SF_6$ concentrations of 10% and 50%. Also

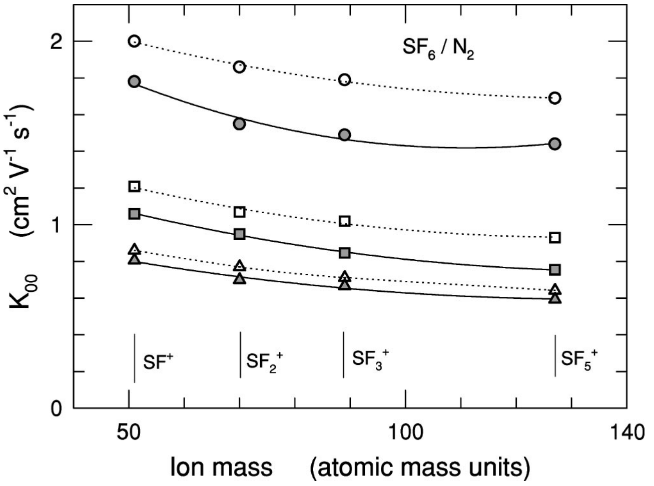

FIG. 2. Plot of the zero-field reduced mobility of SF$^+$, SF$_2^+$, SF$_3^+$, and SF$_5^+$ in SF$_6$/N$_2$ mixtures as a function of the mass of the above ions (closed symbols joined by solid lines), and the calculated values from, Blanc's law (Open symbos joined by dotted lines) for the two gas mixtures. The zero–field reduced mobility of the above ions for pure SF$_6$ [7,9], and its calculated values from Eq. (4) are also shown.

displayed for comparison are the mass-analyzed drift velocities of the same ions in pure SF$_6$ [7,9]. In all cases, for a given $E/N$ value, a marked increase in $v_+$ with a corresponding decrease in the SF$_6$ content in the mixture is observed. This behavior may be understood on the grounds of a stronger ion-neutral interaction with SF$_6$ than with N$_2$, since the mass ratio between SF$_6$ and N$_2$ is more than 5.2, and also because SF$_6$ has a larger dipole polarizability (6.55 Å$^3$) [15] than N$_2$ (1.74 Å$^3$) [16,17].

### B. Test of Blanc's law for vanishingly small fields

It is known that at low $E/N$ the ion drift velocity is proportional to $E/N$ [16,17]. The proportionality constant $K_{00}$, referred as the zero-field reduced mobility, is given by

$$K_{00}=\frac{v_+}{N_0(E/N)}, \tag{2}$$

where $N_0=2.69\times10^{19}\ \mathrm{cm}^{-3}$ is gas density at STP. We have evaluated $K_{00}$ from the first points of the above drift velocity curves, where the relation between $v_+$ and $E/N$ is very approximately linear, with a slope close to unity, indicative of the point charge-induced dipole type of interaction. The resulting $K_{00}$ values are displayed in Fig. 2 by the closed symbols for the 10% and 50% SF$_6$ concentrations, where a well-defined, smooth decrease of $K_{00}$ with the increase in ion mass is clearly seen. For the sake of comparison, the zero-field reduced mobilities of the same ionic species drifting in pure SF$_6$ [7,9] have been plotted. In order to enhance the discussion, also displayed in this figure are the calculated zero-field reduced mobilities from Blanc's law [16,17] which, for a binary gas mixture is given as

$$\frac{1}{K_{mix,\mathrm{SF}_x^+}}=\frac{[\mathrm{SF}_6]/([\mathrm{SF}_6]+[\mathrm{N}_2])}{K(\mathrm{SF}_x^+\ \text{in}\ \mathrm{SF}_6)}+\frac{[\mathrm{N}_2]/([\mathrm{SF}_6]+[\mathrm{N}_2])}{K(\mathrm{SF}_x^+\ \text{in}\ \mathrm{N}_2)} \tag{3}$$

where [SF$_6$] and [N$_2$] represent their respective concentrations in the mixture, and $x=1$–3,5. The first term in Eq. (3) can be readily calculated from the measured mobility; however, the mobility value needed for the second term could not be measured, since the injected SF$_x^+$ ions reacted strongly with the nitrogen molecules, giving rise to several fragment species by fast ion-molecule reactions that hindered the measurement of SF$_x^+$ in N$_2$. These findings will be discussed in the next paragraph. However, we partially circumvented the absence of these values by calculating them with the polarization-limit formula for the zero-field mobility of an ion drifting in a pure gas [16,17]

$$K_{00}=\frac{13.56}{\sqrt{\mu_r\alpha_d}}, \tag{4}$$

where $\mu_r$ is the reduced mass of the ion and neutral, and $\alpha_d$ is the dipole polarizability of the neutral molecule or atom. The results are shown in Fig. 2 for the 10% and 50% SF$_6$ concentrations, showing that, in spite of the expected quantitative difference between calculated and measured values, the trends of the experimental curves are similar to those calculated, whereas the former are systematically higher than the latter by 10–25 %. Obviously, a closer agreement would not have to be necessarily expected, since these theories are in principle based for monoatomic systems, and vanishingly small gas temperatures.

Also plotted in Fig. 2 are the calculated values of $K_{00}$ with Eq. (4) for the SF$_6$ fragment ions, showing also the same qualitative agreement as that observed for the corresponding ionic species in the gas mixtures.

### C. Interaction of the positive ions with N$_2$

Attempts to measure the drift velocity of SF$_x^+$ ($x=1$–3,5) in N$_2$ failed, since we found a rich and complex ion-molecule reaction scheme between these positive ions and nitrogen. The above is herein exemplified by Figs. 3 and 4, displaying the measured relative abundance of the fragment ions produced by the interaction of SF$_3^+$ and SF$_5^+$ in N$_2$. Two extreme N$_2$ pressures were chosen, well over the $E/N$ range covered for the drift velocity measurements.

Looking at Fig. 3(a) that, for $p=25$ mtorr (1 torr $=133.3$ Pa), one observes that the injected SF$_3^+$ breaks up into substantial amounts of S$^+$, followed by SF$^+$, and a steady increase of N$_2^+$ that would certainly arise by charge transfer, and becomes predominant above $E/N=700$ Td. At the other pressure extreme of 125 mtorr, shown in Fig. 3(b), S$^+$ and SF$^+$ still predominate, together with significant amounts F$^+$ and SF$_2^+$. Notice also that formation of N$_2^+$ has become relatively insignificant at this pressure. In view of the fairly complex scheme and of the amount of product ions formed, one could only speculate in qualitative terms to

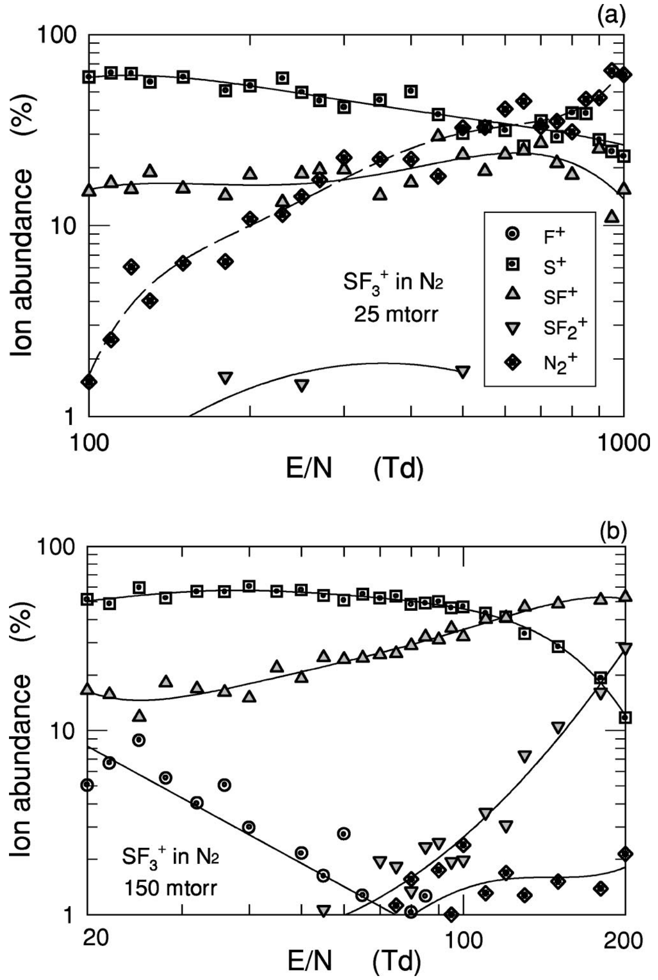

FIG. 3. The relative abundance of the ions formed by injecting $SF_3^+$ from the ion source into $N_2$ in the drift space, for pressures of (a) 25 mtorr and (b) 50 mtorr. Symbols are the same for both plots.

suggest the possible secondary and tertiary ion-molecule reactions

$$SF_3^+ + N_2 \rightarrow SF^+ + F_2 + N_2, \tag{5a}$$

$$SF^+ + N_2 \rightarrow S^+ + F + N_2, \tag{5b}$$

$$SF_3^+ + N_2 \rightarrow N_2^+ + SF_3, \tag{5c}$$

$$SF_3^+ + N_2 \rightarrow SF_2^+ + F + N_2. \tag{5d}$$

An equally interesting ion abundance pattern is observed in Fig. 4 for $SF_5^+$ injected into $N_2$. It seems from Fig. 4(a), for $p = 25$ mtorr that, the predominant resulting fragment ion is $SF^+$, followed by almost equal amounts of $S^+$ and $SF_2^+$, the latter increasing smoothly with a corresponding decrease of $S^+$ for $E/N > 200$ Td. $N_2^+$ is produced in smaller amounts, as compared with the previous $SF_3^+$-$N_2$ case, only reaching a maximum abundance value of nearly 5% at $E/N = 600$ Td. Although under these relatively low pressure conditions very little $SF_3^+$ is formed from $SF_5^+$, the situation reverses for $p = 150$ mtorr, as is shown in Fig. 4(b), where the abundance of the $SF_3^+$ ion increases strongly with $E/N$, becoming close 50% at $E/N = 200$ Td. In contrast with the predominance of $S^+$ and $SF^+$ at $p = 25$ mtorr, the abundances of $S^+$ and $SF^+$ decrease sharply for $E/N > 50$ Td, with a corresponding steady increase of $SF_2^+$ and $SF_3^+$, the latter probably arising from the collisional breakup of $SF_5^+$. Thus we attemp to speculate that the ion-molecule processes responsible for the formation of the fragment ions are

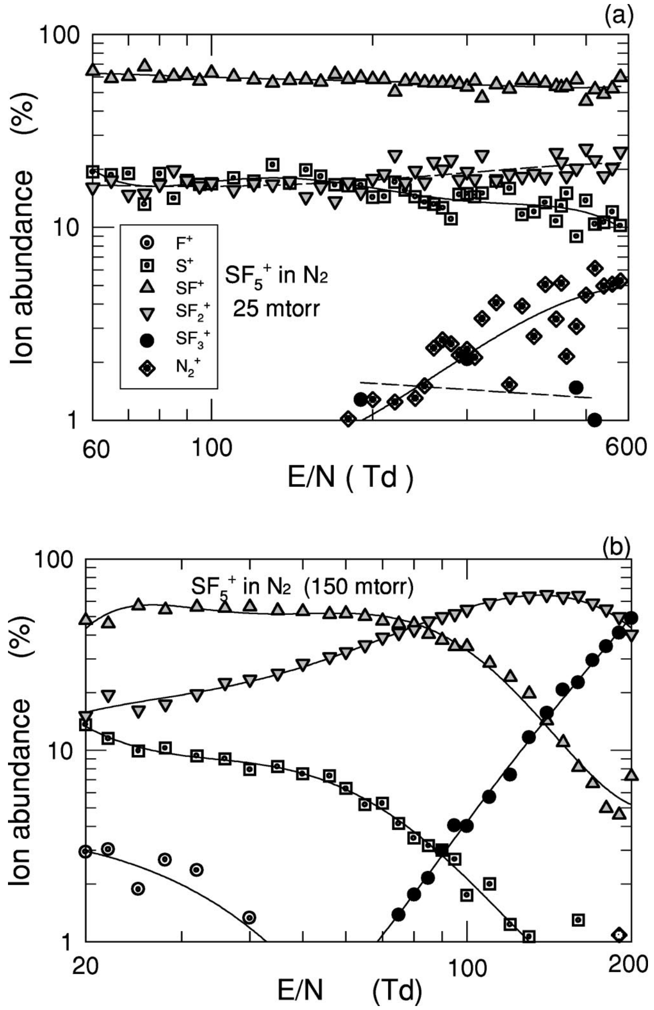

FIG. 4. The relative abundance of the ions formed by injecting $SF_5^+$ from the ion source into $N_2$ in the drift space, for pressures of (a) 25 mtorr and (b) 50 mtorr. Symbols are the same for both plots.

$$SF_5^+ + N_2 \rightarrow SF_2^+ + F_2 + F + N_2 \tag{6a}$$

$$\rightarrow SF_3^+ + F_2 + N_2, \tag{6b}$$

with $S^+$ and $SF^+$ being possibly formed by the tertiary reactions

$$SF_2^+ + N_2 \rightarrow S^+ + F_2 + N_2, \tag{7a}$$

$$SF_3{}^+ + N_2 \rightarrow SF^+ + F_2 + N_2 . \tag{7b}$$

Finally, attempts to measure the mobility of $N^+$ and $N_2{}^+$ in pure $SF_6$ failed because their measured signals at the end of the drift space were either very weak or absent, thereby suggesting the presence of very fast reactions leading to the formation of $SF_x{}^+$ ($x = 1–3,5$) species. Indeed, this observation is congruent with the very high thermal reaction rate (at 300 K) reported by Fehsenfeld [18] of $4 \times 10^{-9}$ cm$^3$ s$^{-1}$ for the reaction

$$N^+ + SF_6 \rightarrow SF_5{}^+ + NF. \tag{8}$$

No similar data were found for the reaction of $N_2{}^+$ with $SF_6$.

## IV. CONCLUSIONS

Although partially fulfilled, the original aims of the present work, rendered a fairly complete set of the drift velocities for the most abundant ions produced in the drift tube, either by the ion source, or by ion-molecule reactions. The abundance studies reveal an interesting and complex reaction scheme, in which the breakup of $SF_3{}^+$ and $SF_5{}^+$ into lighter species, and the charge transfer reaction to form $N_2{}^+$ are the outstanding features. The above results could be useful for building more realistic models of gas discharges in the $SF_6$-$N_2$ mixtures. Concerning the ion transport, the present set of data could be used to probe numerical procedures for the calculation of these drift velocities, using either interaction potentials or cross sections. Finally, under more fundamental grounds, it would be very advantageous to gain more insight into the very rich and complex ion-molecule reaction scheme that was observed.

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