

Ion–Molecule Reactions and Mobilities of SF_3^+ and SF_5^+ Ions in SF_6 Gas

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Abstract

Positive ion–molecule reactions in SF_6 were studied in a static drift-tube mass spectrometer using electron impact at 100 eV as the ion source. The ratio of electric field strength to gas number density, E/N , was typically varied from 40–282 Td and pressure ranged from 0.1 to 0.8 Torr. The most important processes were found to be $\text{SF}_5^+ + \text{SF}_6 \rightarrow \text{SF}_3^+ + \text{SF}_6 + \text{F}_2$ and $\text{SF}_3^+ + \text{SF}_6 \rightarrow (\text{S}_2\text{F}_9)^{+*} \rightarrow \text{S}_2\text{F}_7^+ + \text{F}_2$. The interaction potentials for the SF_5^+ and SF_3^+ ions in SF_6 were also found by using the measured mobility data which were obtained using a pulsed-ion transit-time method. We found that the (12,4, $\alpha^* = 0.1$) core model was adequate to describe the mobility over the range of E/N studied. The zero-field reduced mobilities for SF_3^+ and SF_5^+ were determined to be 0.68 and 0.55 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ respectively.

1. Introduction

Transport properties of ions in gases are of intrinsic, fundamental and applied interest (McDaniel and Mason 1973). They are directly needed in a number of problems that arise in gaseous electronics and magnetohydrodynamics, as well as gas lasers. With the aid of theory they yield derived results on ion transport and ion–molecule reactions as a function of temperature up to very high temperatures, which are needed for understanding phenomena in the upper atmosphere, in flames and elsewhere. Combined with theory, these data prove useful in providing fundamental information on ion–molecule interaction potentials. Finally, transport properties can also be used to describe quantitatively the behaviour of ions moving in a neutral buffer gas and related charge-transport phenomena, and are required together with ionisation cross-sections (Mark and Dunn 1984) for a quantitative understanding of electrical discharges.

Sulfur hexafluoride is well known as a gas with exceptionally good electrical insulating properties due to its high dielectric strength. The earliest published data on the mobility of positive ions in SF_6 gas were reported by Fleming and Rees (1969). In their experiments, which used a time-of-flight drift-tube, only one species of positive ions was observed and the zero-field mobilities were found to be 0.59 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. In the work of Jowko and Armstrong (1982), two species of positive ions with mobilities K_0 of 0.53 and 0.37 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were observed. The ions were not identified and it was suggested that they were probably due to the ion family SF_2^+ (SF_6)_x and/or SF_3^+ (SF_6)_x for the species with the higher mobility value, and S_2F_7^+ (SF_6)_x as a tentative explanation for the other species

observed. In an extensive review of all available data concerning the mobility of SF_6 ions in SF_6 gas, Brand and Jungblut (1983) reported that they were able to reproduce the mobility data of the positive ions in terms of a standard (9, 6, 4) potential. In the absence of mass spectrometry of positive ions, they assigned this set of data to SF_5^+ since it agreed well with the SF_5^+ ions of Patterson (1970). In a more recent work, Blair *et al.* (1989) measured the drift velocities for ions of both polarities at pressures ranging from 50 to 700 Torr (1 Torr \equiv 133 Pa). Their result for positive ions over the energy range $40 < E/P < 120$ is given by $v_d = 0.70E/P - 9.0$.

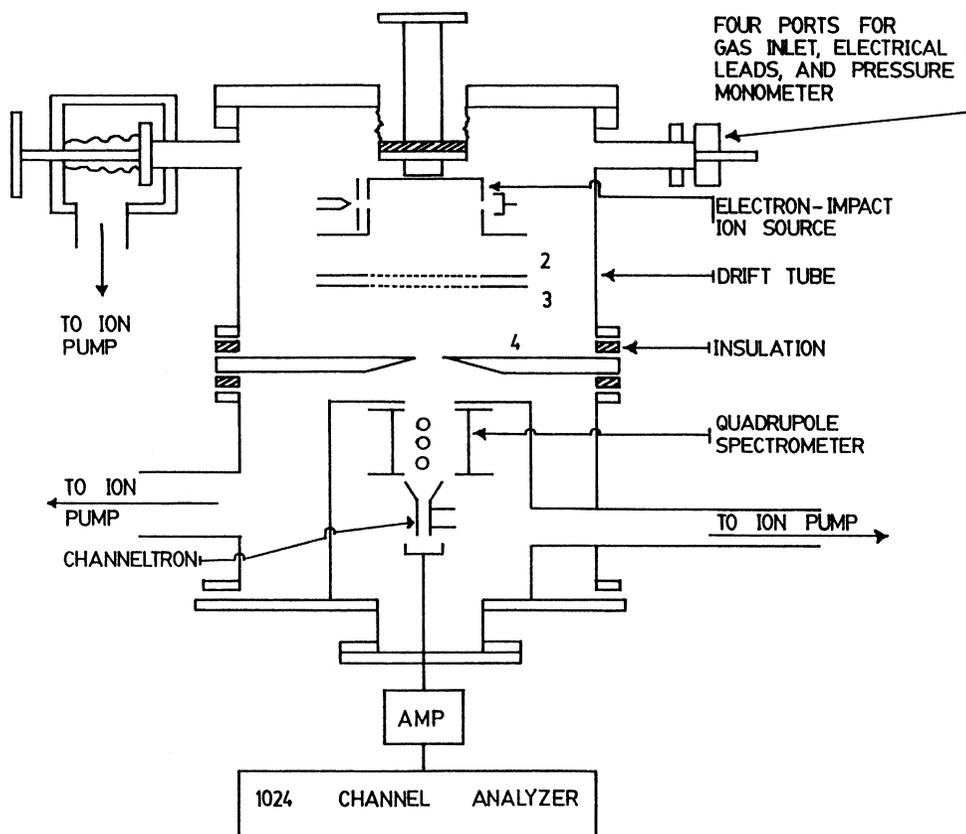


Fig. 1. Schematic diagram of the drift-tube mass spectrometer.

2. Experimental Methods

The ion-tube mass spectrometer used in this experiment is shown in Fig. 1 and has been described elsewhere (Talib and Saporoschenko 1992). Briefly summarised, the apparatus consists of an electron-impact ion source, a 1 cm ion-molecule reaction region, a shutter device for measuring drift velocity, a 0.013 cm diameter ion exit aperture, and a quadrupole mass spectrometer with an electron-multiplier ion detector. The drift velocities of the ions were measured using the variable drift distance method. The mobilities were then calculated using the equation

$$K_0 = \frac{v_d}{E} \frac{1}{760} \frac{p}{T} 273 \cdot 16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad (1)$$

where E is the magnitude of the applied electric field, p the gas pressure and T the temperature in Kelvin. In the limit of zero electric field and zero temperature, the experimental values are usually compared with the Langevin polarisation limit of the mobility, given by (McDaniel and Mason 1973)

$$K_{\text{pol}} \equiv K_0(E/N \rightarrow 0, T \rightarrow 0) = \frac{13 \cdot 853}{(\alpha_d \mu)^{1/2}} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad (2)$$

where α_d is the dipole polarisability of the neutral (in \AA^3) and μ is the reduced mass (in amu).

3. Results and Discussion

(3a) Ion-Molecule Reactions

The sulfur hexafluoride gas (electronic grade of stated purity 99.95%) was supplied by the Linde Division of Union Carbide Corporation (USA) and used without further purification. The electron-impact ion source was used throughout the experiment. An electron energy of 100 eV was used for the primary ionisation.

Mass spectra were obtained by scanning molecular masses in the range 1–300 amu using a quadrupole analyser. In all, nine positive ions were obtained in the spectrum of sulfur hexafluoride for $40 < E/N < 282$ Td ($1 \text{ Td} \equiv 10^{-17} \text{ V cm}^2$) and the pressure range $0.1 < p < 0.8$ Torr. Temperatures measured ranged from 299 to 344 K. The predominant ions were found to be SF_3^+ , SF_5^+ and S_2F_7^+ , accounting for more than 80% of the spectra formed under all experimental conditions. Other ions observed in small abundance were SF_2^+ , SF_4^+ and S_2F_6^+ , while S^+ , SF^+ and S_2F_5^+ always contributed to less than 1% of the mass spectra.

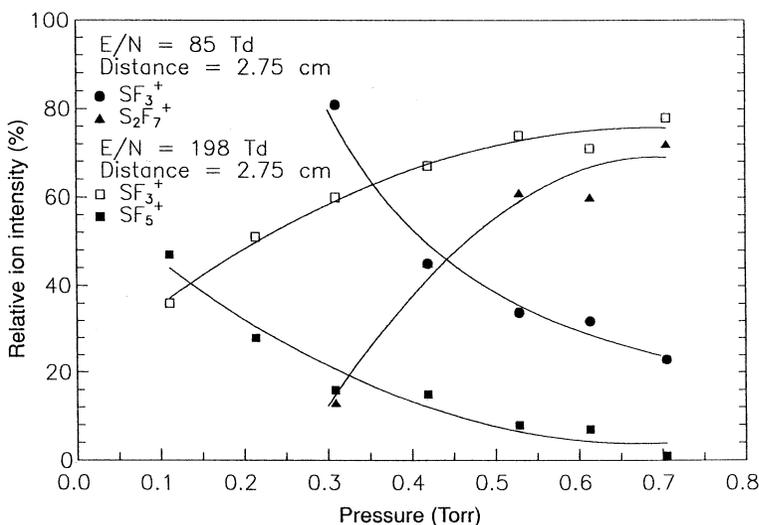


Fig. 2. Variation of relative ion intensity as a function of pressure at $E/N = 85$ and 198 Td with a drift distance of 2.75 cm.

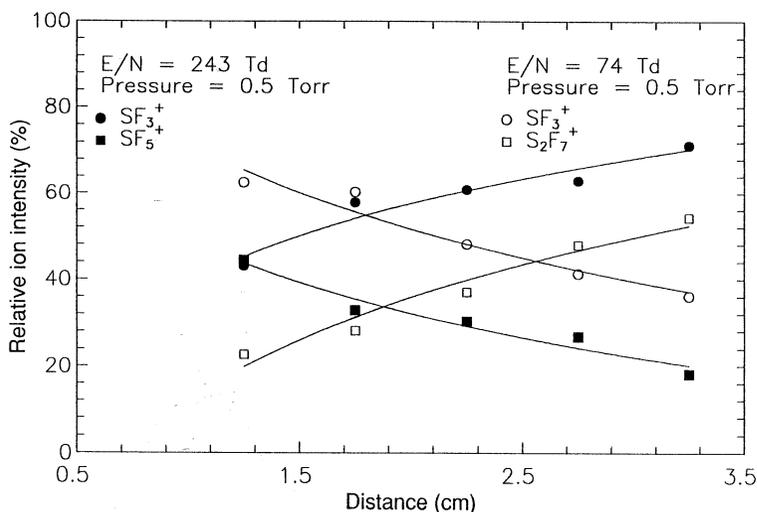


Fig. 3. Variation of relative ion intensity as a function of drift distance at $E/N = 74$ and 243 Td with $p = 0.5$ Torr.

As can be seen in Figs 2 and 3, an increase and decrease in the intensity of the SF_3^+ ions affected both the intensities of the SF_5^+ and $S_2F_7^+$ ions. An increase in the intensity of SF_3^+ ions resulted in a decrease of SF_5^+ intensity, while a decrease in the intensity of SF_3^+ ions led to an increase in $S_2F_7^+$ ions. From this observation, it is then possible to match the reduction in intensity of the primary ions with the increased intensity of the secondary ions sufficiently well to identify the reactions that took place. Therefore, a reasonable sequence of reactions that can be deduced from Figs 2 and 3 after the primary ionisation, $SF_6 + e \rightarrow SF_5^+ + F + 2e$, is

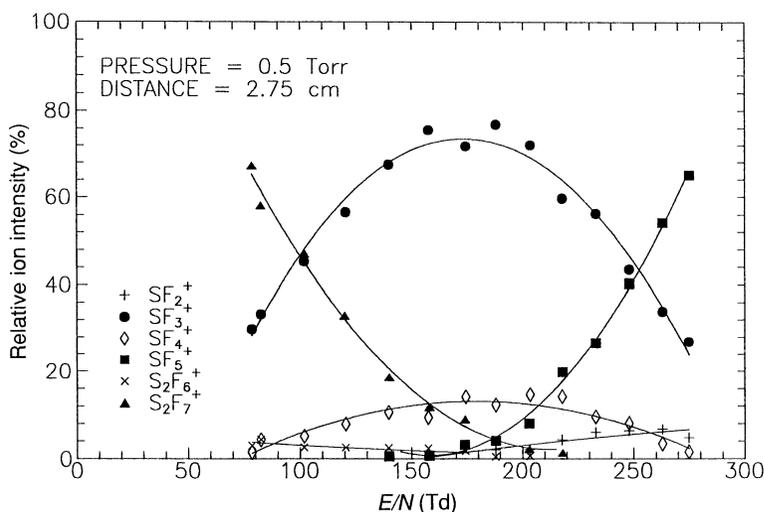


Fig. 4. Variation of relative ion intensity as a function of E/N at $p = 0.5$ Torr and drift distance 2.75 cm.

and as the pressure is increased



From Figs 2 to 4 we can also conclude that high pressure, low E/N and an increased drift distance (from the repeller to the ion exit aperture) favour the reaction



(3b) Ion Transport Coefficients

Measurements of the drift velocities of the ions were made in the pressure range 0.2 to 0.6 Torr and over the range $80 < E/N < 650$ Td. The gas temperature

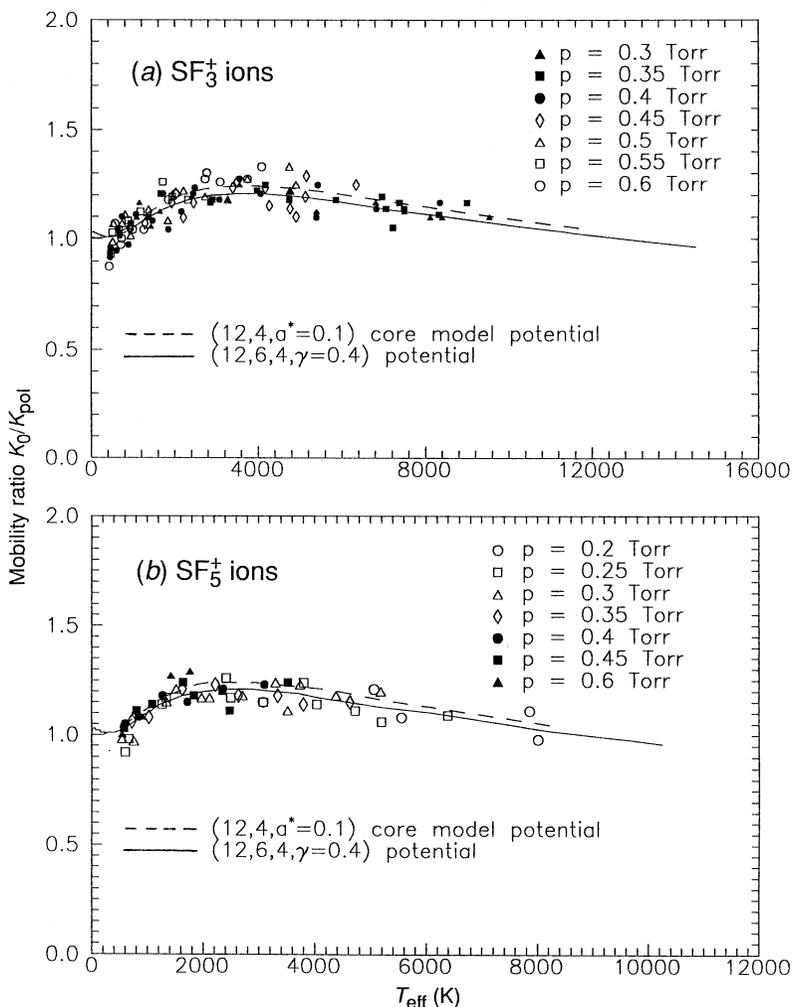


Fig. 5. Mobility ratio K_0/K_{pol} for (a) SF_3^+ ions in SF_6 and (b) SF_5^+ ions in SF_6 , as a function of the effective temperature T_{eff} at various pressures. The dashed curves represent the (12, 4, $a^* = 0.1$) core model potential.

measured inside the drift tube varied between 299 and 363 K. The mobility ratio K_0/K_{pol} , where K_0 is the reduced mobility and K_{pol} is the mobility in the limit of zero electric field and zero temperature, of SF_3^+ and SF_5^+ ions is given in Fig. 5 as a function of T_{eff} , where T_{eff} is given by

$$\frac{3}{2}k_{\text{B}} T_{\text{eff}} = \frac{3}{2}k_{\text{B}} T + \frac{1}{2}Mv_{\text{d}}^2. \quad (6)$$

A model used before for negative SF_6 ions in SF_6 represents the potential (Patterson 1972) as

$$V(r) = \frac{1}{2}\epsilon \left[(1 + \gamma) \left(\frac{r_{\text{m}}}{r} \right)^{12} - 4\gamma \left(\frac{r_{\text{m}}}{r} \right)^6 - 3(1 - \gamma) \left(\frac{r_{\text{m}}}{r} \right)^4 \right], \quad (7)$$

where ϵ is the depth of the potential minimum, r_{m} its position and γ , ranging between 0 and 1, is a parameter that describes the relative importance of the r^{-6} term compared with the r^{-4} term. For the limiting case $\gamma = 1$, equation (7) yields the well known Lennard-Jones (12, 6) potential. Values of γ , ϵ and r_{m} are then determined directly from the mobility data through the following procedure. The experimental mobility data, K_0 , are first normalised by dividing them by the calculated polarisation limit K_{pol} of equation (2) (which is for $E/N \rightarrow 0$ and $T \rightarrow 0$) and then plotted as a function of T_{eff} , which is obtained from equation (6). By matching the experimental values of K_0/K_{pol} at the extrema shown in Fig. 5 with values calculated for the (12, 6, 4) potential given by Viehland and Mason (1977), values of ϵ and γ can then be determined. The position of the potential minimum is then obtained by matching the coefficient of the r^{-4} term in equation (7) with the coefficient of the polarisation potential, $V = -e^2\alpha/2r^4$, which arises from the interaction of the ion charge with the dipole it induces in the neutral molecule, i.e.

$$\frac{3}{2}\epsilon(1 - \gamma)r_{\text{m}}^4 = \frac{1}{2}e^2\alpha. \quad (8)$$

Knowing the values of ϵ and γ , we can then calculate the mobility using the two-temperature theory. In the first approximation, we find that for the (12, 6, 4) potential (Viehland *et al.* 1975)

$$\frac{K_0}{K_{\text{pol}}} = \frac{1.4714}{(T^*)^{\frac{1}{2}}\Omega^{(1,1)*}(T^*)} \left(\frac{3n(1 - \gamma)}{n(3 + \gamma) - 12(1 + \gamma)} \right)^{\frac{1}{2}}, \quad (9)$$

where

$$T^* = \frac{k_{\text{B}}}{\epsilon} T_{\text{eff}}, \quad (10)$$

and where the dimensionless collision integral $\Omega^{(1,1)*}(T_{\text{eff}}^*)$ can be obtained from tables given by Viehland *et al.* (1975). Mobilities calculated using the (12, 6, 4) potential are represented by the solid curves in Fig. 5 and the potential parameters obtained by this method are given in Table 1.

Table 1. Potential parameters for the (12, 6, 4) potential

Ion	γ	r_m (Å)	ϵ/k_B (K)
SF ₃ ⁺	0.4	3.80	2898
SF ₅ ⁺	0.4	4.13	2050

Another model that has been suggested as a representation of polyatomic ions with neutral molecules uses a potential of the form

$$V(r) = \frac{\epsilon}{2} \left[\left(\frac{r_m - a}{r - a} \right)^{12} - 3 \left(\frac{r_m - a}{r - a} \right)^4 \right], \quad (11)$$

where ϵ is the depth of the potential well, the ion-neutral separation r is measured from the geometric centres, r_m is the position of the potential minimum, and a is the rigid core diameter.

Table 2. Potential parameters for the (12, 4) core model

Ion	a^*	r_m (Å)	ϵ/k_B (K)
SF ₃ ⁺	0.1	3.68	2968
SF ₅ ⁺	0.1	4.04	2100

Utilising the procedure outlined above yields values of ϵ and a^* . Again, by matching the r^{-4} coefficient with the accurately known polarisation potential, the position of the potential minimum can be calculated from

$$3\epsilon(r_m - a)^4 = e^2\alpha. \quad (12)$$

These values are given in Table 2. The ratio K_0/K_{pol} for the (12, 4) potential can then be calculated from (Mason *et al.* 1972)

$$\frac{K_0}{K_{\text{pol}}} = \frac{1.799(1 - a^*)^2}{(T^*)^{1/2} \Omega^{(1,1)*}(T^*)}, \quad (13)$$

where $a^* = a/r_m$ and $\Omega^{(1,1)*} = \Omega^{(1,1)}/\pi r_m^2$. This ratio is represented by the dashed curves in Fig. 5. Values of the collision integral were obtained from Mason *et al.* (1972).

Comparing the calculated mobilities obtained from both the (12, 6, 4) potential and (12, 4) core potential with the measured mobilities, we see that both potentials give quite an accurate fit to the data, with both potentials producing almost identical curves. However, we suspect the (12, 4) core model to be closer to the real potential since it is formulated for large molecular ions and large polyatomic neutral molecules such as those studied in this paper, whereas the (12, 6, 4) potential is based on the assumption of small ions and neutral molecules. A best fit to the experimental data using a polynomial of order 4 for the SF₃⁺ ions and a polynomial of order 5 for the SF₅⁺ ions gives the zero-field mobility for both ions as tabulated in Table 3.

Table 3. Theoretical and experimental zero-field mobilities ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) of ions in SF_6 gas

Ion	Langevin polarisation limit	Present work
SF_3^+	0.73	0.68
SF_5^+	0.66	0.55

In the absence of mass spectrometry, Brand and Jungblut (1983) reported measured mobility values of SF_5^+ ions in SF_6 over a wide range of E/N and were able to describe the mobility data in terms of a standard (9, 6, 4) potential, that is,

$$V(\text{SF}_5^+ + \text{SF}_6) = \frac{2.1 \times 10^5}{r^9} - \frac{2480}{r^6} - \frac{44.9}{r^4} \text{ eV}, \quad (14)$$

for r in Å. However, this result yielded an unreasonably large value for the r^{-6} term.

Therefore, in view of the discussion above, we conclude that of the two potentials, the one that can best describe the interaction potential for the SF_5^+ and SF_3^+ ions moving in SF_6 is the (12, 4) core model potential.

4. Conclusion

Nine positive ions were observed in the spectrum of SF_6 and the most abundant found to be SF_3^+ , SF_5^+ and S_2F_7^+ . The major reactions that take place were found to be those given by equations (2) and (3). The interaction potentials for the SF_3^+ and SF_5^+ ions were found by using the measured mobility data. We found that the (12, 4, $a^* = 0.1$) core model was adequate to describe the mobility over a wide range of field energy.

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