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 SF$_3^+$ + SF$_6$ → SF$_5^+$ + SF$_6$ + F$_2$ and SF$_3^+$ + SF$_6$ → ($S_2F_9$)$^{+*}$ → $S_2F_7^+$ + F$_2$. The interaction potentials for the SF$_3^+$ and SF$_5^+$ 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, $a^* = 0·1$) 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 cm$^2$ V$^{-1}$ 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 described 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 cm$^2$ V$^{-1}$ 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 cm$^2$ V$^{-1}$ 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 \( \text{SF}_6 \) ions in \( \text{SF}_6 \) 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 \( \text{SF}_6^+ \) since it agreed well with the \( \text{SF}_6^+ \) 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 \( v_d = 0.70E/P - 9.0 \).

\[
\text{Fig. 1. Schematic diagram of the drift-tube mass spectrometer.}
\]

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
\[ K_0 = \frac{v_d}{E} \frac{1}{760} \frac{p}{T} 273 \cdot 16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \]  

(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)

\[ K_{\text{pol}} \equiv K_0(E/N \to 0, \ T \to 0) = \frac{13.853}{(\alpha_d \mu)^{1/2}} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \]  

(2)

where \( \alpha_d \) is the dipole polarisability of the neutral (in \( \text{Å}^3 \)) and \( \mu \) 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 Td \( \equiv 10^{-17} \) 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 \( \text{SF}_3^+, \text{SF}_5^+ \) and \( \text{S}_2\text{F}_7^+ \), accounting for more than 80% of the spectra formed under all experimental conditions. Other ions observed in small abundance were \( \text{SF}_2^+, \text{SF}_4^+ \) and \( \text{S}_2\text{F}_6^+ \), while \( \text{S}^+, \text{SF}^+ \) and \( \text{S}_2\text{F}_5^+ \) always contributed to less than 1% of the mass spectra.

![Fig. 2](image-url)  

**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.
As can be seen in Figs 2 and 3, an increase and decrease in the intensity of the SF₃⁺ ions affected both the intensities of the SF₅⁺ and S₂F₇⁺ ions. An increase in the intensity of SF₃⁺ ions resulted in a decrease of SF₅⁺ intensity, while a decrease in the intensity of SF₅⁺ ions led to an increase in S₂F₇⁺ 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, SF₆ + e → SF₅⁺ + F + 2e, is

![Figure 3](image_url)  
**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.

![Figure 4](image_url)  
**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

$$\text{SF}_3^+ + \text{SF}_6 \rightarrow \text{S}_2\text{F}_7^+ + \text{F}_2.$$  \hfill (4)

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

$$\text{SF}_3^+ + \text{SF}_6 \rightarrow \text{S}_2\text{F}_7^+ + \text{F}_2.$$  \hfill (5)

(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

![Graph](image)

**Fig. 5.** Mobility ratio $K_0/K_{\text{pol}}$ for (a) $\text{SF}_3^+$ ions in SF$_6$ and (b) $\text{SF}_4^+$ ions in SF$_6$, as a function of the effective temperature $T_{\text{eff}}$ at various pressures. The dashed curves represent the (12, 4, $\alpha^* = 0.1$) core model potential.
measured inside the drift tube varied between 299 and 363 K. The mobility ratio $K_0/K_{\text{pol}}$, where $K_0$ is the reduced mobility and $K_{\text{pol}}$ 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 $T_{\text{eff}}$, where $T_{\text{eff}}$ is given by

$$\frac{3}{2} k_B T_{\text{eff}} = \frac{3}{2} k_B T + \frac{1}{2} M v_d^2.$$  

A model used before for negative SF$_6$ ions in SF$_6$ represents the potential (Patterson 1972) as

$$V(r) = \frac{1}{2} \varepsilon \left[ (1 + \gamma) \left( \frac{r_m}{r} \right)^{12} - 4 \gamma \left( \frac{r_m}{r} \right)^6 - 3(1 - \gamma) \left( \frac{r_m}{r} \right)^4 \right],$$  

where $\varepsilon$ is the depth of the potential minimum, $r_m$ its position and $\gamma$, 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 $\gamma$, $\varepsilon$ 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 $K_{\text{pol}}$ of equation (2) (which is for $E/N \rightarrow 0$ and $T \rightarrow 0$) and then plotted as a function of $T_{\text{eff}}$, which is obtained from equation (6). By matching the experimental values of $K_0/K_{\text{pol}}$ at the extrema shown in Fig. 5 with values calculated for the (12, 6, 4) potential given by Viehland and Mason (1977), values of $\varepsilon$ and $\gamma$ 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.

$$\frac{3}{2} \varepsilon (1 - \gamma) r_m^4 = \frac{1}{2} e^2 \alpha.$$  

Knowing the values of $\varepsilon$ and $\gamma$, 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)

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

where

$$T^* = \frac{k_B}{\varepsilon} T_{\text{eff}},$$  

and where the dimensionless collision integral $\Omega^{(1,1)*}(T^*)$ 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.
Another model that has been suggested as a representation of polyatomic ions with neutral molecules uses a potential of the form

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

(11)

where \( \epsilon \) 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.

Utilising the procedure outlined above yields values of \( \epsilon \) 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

\[ 3\epsilon(r_m - a)^4 = e^2 \alpha. \]  

(12)

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

\[ \frac{K_0}{K_{\text{pol}}} = \frac{1.799(1 - a^*)^2}{(T^*)^{\frac{1}{2}} \Omega^{(1,1)*}(T^*)^{\frac{1}{2}}}, \]  

(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 \( \text{SF}_3^+ \) ions and a polynomial of order 5 for the \( \text{SF}_5^+ \) ions gives the zero-field mobility for both ions as tabulated in Table 3.
Table 3. Theoretical and experimental zero-field mobilities (cm² V⁻¹ s⁻¹) of ions in SF₆ gas

<table>
<thead>
<tr>
<th>Ion</th>
<th>Langevin polarisation limit</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₃⁺</td>
<td>0.73</td>
<td>0.68</td>
</tr>
<tr>
<td>SF₅⁺</td>
<td>0.66</td>
<td>0.55</td>
</tr>
</tbody>
</table>

In the absence of mass spectrometry, Brand and Jungblut (1983) reported measured mobility values of SF₅⁺ ions in SF₆ 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,

\[ V(SF₅⁺ + SF₆) = \frac{2.1 \times 10^5}{r^9} - \frac{2480}{r^6} - \frac{44.9}{r^4} \text{ eV}, \quad (14) \]

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 SF₅⁺ and SF₃⁺ ions moving in SF₆ is the (12, 4) core model potential.

4. Conclusion

Nine positive ions were observed in the spectrum of SF₆ and the most abundant found to be SF₃⁺, SF₅⁺ and S₂F⁺. The major reactions that take place were found to be those given by equations (2) and (3). The interaction potentials for the SF₃⁺ and SF₅⁺ 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.

References