Mass Spectrometric Studies of Positive Ion/Molecule Reactions in NH₃ and SF₆ Gases

ZAINAL ABIDIN TALIB¹ & M. SAPOROSCHENKO²

¹Department of Physics
Faculty of Science & Environmental Studies
Universiti Pertanian Malaysia
43400 UPM, Serdang, Selangor Darul Ehsan, Malaysia

²Department of Physics
Southern Illinois University
Carbondale, 62901, USA

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ABSTRACT

Positive ion-molecule reactions in NH₃ and SF₆ gas were studied in a static ion drift-tube mass spectrometer. E/N (the ratio of electric field strength to gas number density) varied typically from 20-400 Td and pressure ranged from 0.1 to 0.8 Torr. The most important process was found to be

\[
\begin{align*}
\text{NH}_3^+ + \text{NH}_3 &\leftrightarrow \text{NH}_4^+ + \text{NH}_3 \\
\text{SF}_6^+ + \text{SF}_6 &\rightarrow \text{SF}_7^+ + \text{SF}_6 + \text{F}_2 \\
\text{SF}_4^+ + \text{SF}_6 &\rightarrow \text{SF}_7^+ + \text{F}_2
\end{align*}
\]

INTRODUCTION

This paper will attempt to show the relationship between mass spectroscopy and the reactions of ions with neutral molecules by using an apparatus called static ion drift tube mass spectrometer. Drift-tube experiments constitute a class of low energy ion-molecule collision experiments, where the kinetic energies of the ions are varied typically in the range of 0.01 to 10 eV by varying the ratio E/N between an applied electrostatic field E and the number density N of the gas molecules. In such an experiment, a swarm of ions moves through a neutral gas under the influence of a uniform electrostatic field. The ions undergo elastic, inelastic, and reactive collisions with many atoms or molecules during their passage through the drift-tube but there are so few ions present that ion-ion interactions may be neglected. The motion of the swarm of ions through the neutral gas in the drift-tube is influenced by the gas temperature, T, by the ratio, E/N, and by the details of the ion-neu-
neutral collisions. In this paper, we report measurements of the reactions of positive ammonia ions and positive sulphur hexafluoride ions in their parent gas, respectively.

Sulfur hexafluoride, SF$_6$, is well-known as a gas with exceptionally good electrical insulating properties due to its high dielectric strength. Of interest in this paper is the mechanism(s) by which products are formed since only a relatively few experiments (Frees et al. 1981) have dealt with the study of the basic processes occurring in the electrical breakdown of SF$_6$, and the majority of these experiments have been mainly directed to the reactions of negative SF$_6$ ions$^{2,3}$ (McGeethan et al. 1975, Fehsenfeld 1971) in SF$_6$ gas.

In contrast, much work has been done on the ammonia system especially in the study of ion-molecule reactions (Dorfman and Noble 1959; Derwish et al. 1963; Dawson and Tickner 1965; Hogg and Kebarle 1965; Hogg et al. 1966; Searles and Kebarle 1968; Long and Franklin 1973). Thus this gas would provide an excellent source of reference.

**MATERIALS AND METHODS**

The static ion drift-tube mass spectrometer which was constructed by the authors at Southern Illinois University at Carbondale, U.S.A. is shown in Figure 1. The main ultrahigh-vacuum system is constructed of stainless steel and is evacuated by ion pumps (400 l/s, 200 l/s and 100 l/s). The upper part of Figure 1 shows the drift-tube with the ion source and the electrical shutter (electrode 2-3) with the drift space defined as the distance between electrodes 3-4 and the lower part shows the ion detection system with the quadrupole mass spectrometer and channeltron electron multiplier. The drift-tube is separated from the mass spectrometer by an insulated metal plate which has an ion exit aperture of diameter 0.013 cm.

The position of the ion source in the drift-tube is adjustable externally by means of a linear-motion feedthrough. The gases used in this experiment are research grade with a stated purity of 99.995%.
RESULTS AND DISCUSSION

Ammonia

Mass spectra were obtained by scanning the molecular masses in the range 2-127 amu using a quadrupole analyzer. Thirteen positive ion mass species in all were observed in the spectrum at 14<D/N<480 Td (1 Td = 10⁻¹⁷ V cm²) and at pressures 0.2<p<0.5 Torr. The drift distance were held at 1 cm. The major ion peaks observed had mass numbers corresponding to the solvation of NH₄⁺. The ions identified were:

\[ \text{NH}_4^+ \cdot (\text{NH}_3)_n : \text{mass number} \ 18, 35, 52, 69, 86 \]  
(1)

Two other series of ion clusters were also observed. They are

\[ \text{NH}^+ \cdot (\text{NH}_3)_n : \text{mass number} \ 15, 32, 49, 66, 83 \]  
(2)

\[ \text{N}_2\text{H}^+ \cdot (\text{NH}_3)_n : \text{mass number} \ 63, 80, 87 \]  
(3)

The cluster series in (2) and (3) appeared as a small percent of the total ion intensity except for the NH⁺ ion which had an ion intensity about the same size as that of NH₄⁺ ion.

Comparison of the present work was made to that of Long and Franklin (1973) and Dawson and Tickner (1965). Their results are in good agreement with those obtained in this experiment. Dawson and Tickner obtained NH₄⁺ \cdot (\text{NH}_3)_n ions up to n=4. Small ions current at mass number 46 and 63 were suggested to be due to N₂H⁺ \cdot \text{NH}_3 and N₂H⁺ \cdot (\text{NH}_3)_2 or to impurities. Better agreement was obtained when the present data were compared with those of Long and Franklin. Cluster reactions up to n=8 were observed for the NH₄⁺ \cdot (\text{NH}_3)_n. The two smaller series, NH⁺ \cdot (\text{NH}_3)_n and N₂H⁺ \cdot (\text{NH}_3)_n were observed in smaller intensities.

Figure 2 shows the typical results of the variations of the relative intensity of the NH₄⁺ \cdot (\text{NH}_3)_n ions up to n=4 with E/N at constant pressure and distance. As can be seen, the higher order clusters formed at lower E/N and as E/N is increased, detachment of ammonia molecules was observed which led to the NH₄⁺ \cdot (\text{NH}_3)_n ions. At high E/N, only the NH₄⁺ ions were observed.

Pressure dependence of relative abundance of ammonia clusters up to n=4 is shown in Figure 3. From this plot one may consider a general clustering reaction sequence leading to the solvation of ammonium ions by

\[ \text{NH}_4^+ \cdot (\text{NH}_3)_n + \text{NH}_3 \leftrightarrow \text{NH}_4^+ \cdot (\text{NH}_3)_{n+1} \]  
(4)
Sulphur Hexafluoride

Mass-spectra were obtained by scanning the molecular masses in the range 1-300 amu using a quadrupole analyzer. Nine positive ion mass species in all were obtained in the spectrum of sulphur hexafluoride at 40<E/N<282 Td and pressure range 0.1<p<0.8 Torr. Temperatures measured ranged from 299 Kelvin to 344 Kelvin. The predominant ions were found to be SF$_3^+$, SF$_5^+$, and S$_2$F$_7^+$, accounting for more than 80% of the spectra formed under all experimental conditions. Other ions observed in less abundance were SF$_4^+$, SF$_7^+$, and S$_2$F$_6^+$ ions while S$^+$, SF$^+$, and S$_2$F$_5^+$ ions contributed less than 1% of the mass-spectra.

The plots of the relative ion intensities versus pressure as shown in Figure 4 for constant E/N and distance L travelled by the ions demonstrated the pressure dependence of the ions. Measurements of the relative ion intensities as a function of distance travelled by the ions is shown in Figure 5.

As can be seen from these figures, the increase and decrease in the intensity of the SF$_3^+$ affected the intensities of both SF$_5^+$ and S$_2$F$_7^+$ ions. Increase in the intensity of the SF$_3^+$ ions resulted in the decrease of the SF$_5^+$ ions' intensity while the decrease in the intensity of SF$_3^+$ ions led to an increase of the S$_2$F$_7^+$ ions. From the above observation, it is then possible to match the reduction in the 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 Figures 4 and 5 after the primary ionization, SF$_6^+$ + e → SF$_5^+$ + F + 2e, is

$$\text{SF}_3^+ + \text{SF}_6 \rightarrow \text{SF}_3^+ + \text{F}_2 + \text{SF}_6 \quad (5)$$

and as the pressure is increased

$$\text{SF}_3^+ + \text{SF}_6 \rightarrow \text{S}_2\text{F}_7^+ + \text{F}_2 \quad (6)$$

Typical plots of the variation of the relative abundance of the ions with E/N at constant pressure are shown in Figure 6. As can be seen, the only ion present at all the energy ranges studied was SF$_3^+$ ions. At lower E/N, the predominant ions were found to be S$_2$F$_7^+$ while at very high E/N, SF$_5^+$ ions dominate the mass-spectra.

Examining the variation of relative intensities of the ions with respect to the distance used, shown in Figure 5, we observed that increasing the distance at low E/N will favour the formation of S$_2$F$_7^+$...
Fig. 4: Variations of the relative ion intensities of $SF_n^+$ ions as a function of pressure at $E/N=85$ Td and $E/N=198$ Td with distance $= 2.75$ cm.

Fig. 5: Variations of the relative ion intensities of $SF_n^+$ ions as a function of distance at $E/N=74$ Td and $E/N=243$ Td with $p = 0.5$ Torr.
ions while at high E/N, it favours the formation of SF$_5^+$ ions.

Thus, from Figures 4 to 6, we can conclude that at a higher pressure, lower E/N, and longer distance between the repeller and the ion exit aperture will favour the reaction (6).

CONCLUSION

Thirteen positive ion mass species in all were observed in the spectrum of ammonia in the drift-tube mass spectrometer. All of the ions identified can be classified into three groups: NH$_4^+$, (NH$_3$)$_n^+$, NH$_3^+$, (NH$_3$)$_n^+$ with NH$_4^+$, (NH$_3$)$_n^+$ forming the major and most abundant group of ions and this was found to occur through NH$_4^+$, (NH$_3$)$_{n-1}^+ + \text{NH}_3 \leftrightarrow \text{NH}_4^+ \cdot (\text{NH}_3)_n^+$. For SF$_6$, nine positive ion mass species in all were observed and the most abundant ions were found to be SF$_5^+$, SF$_6^+$, and SF$_7^+$. The major reactions that took place were found to be reactions (5) and (6).

REFERENCES


Enthalpies and Entropies for the Reactions

\[ \text{NH}_4^+ (\text{NH}_3)_{n+1} \rightarrow \text{NH}_4^+ (\text{NH}_3)_n \]


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