

Mass Spectrometric Studies of Positive Ion/Molecule Reactions in NH_3 and SF_6 Gases

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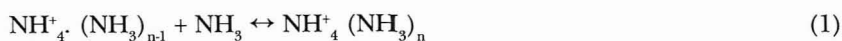
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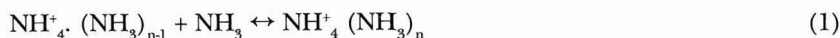
ABSTRAK

Satu kajian telah dibuat mengenai tindak balas ion-molekul positif ke atas gas NH_3 dan SF_6 . E/N (nisbah medan elektrik ke ketumpatan bilangan gas) telah diubah dalam julat 20-400 Td manakala tekanannya dalam julat 0.1 to 0.8 Torr. Di antara proses-proses yang penting yang didapati berlaku ialah



ABSTRACT

Positive ion-molecule reactions in NH_3 and SF_6 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



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 10eV 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-

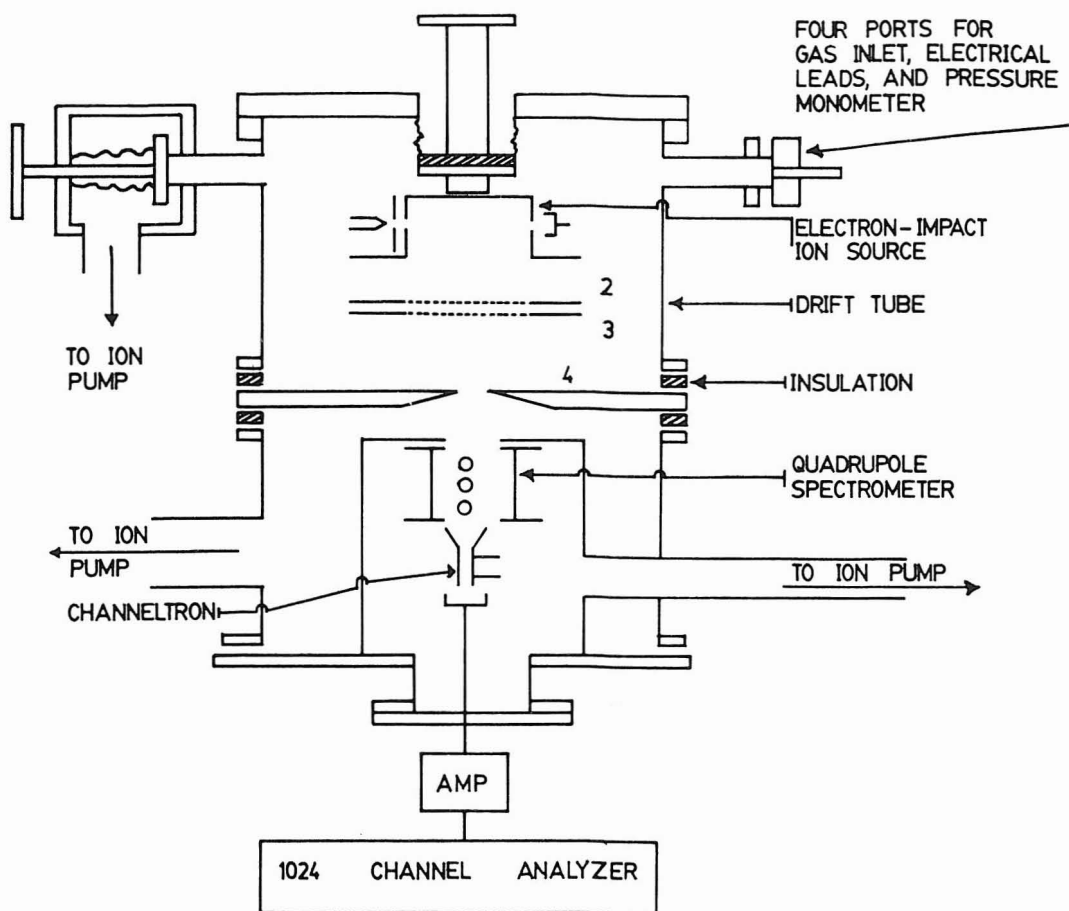


Fig. 1: Schematic diagram of drift-tube mass spectrometer

tral 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} (McGeehan *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 1/s, 200 1/s and 100 1/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%.

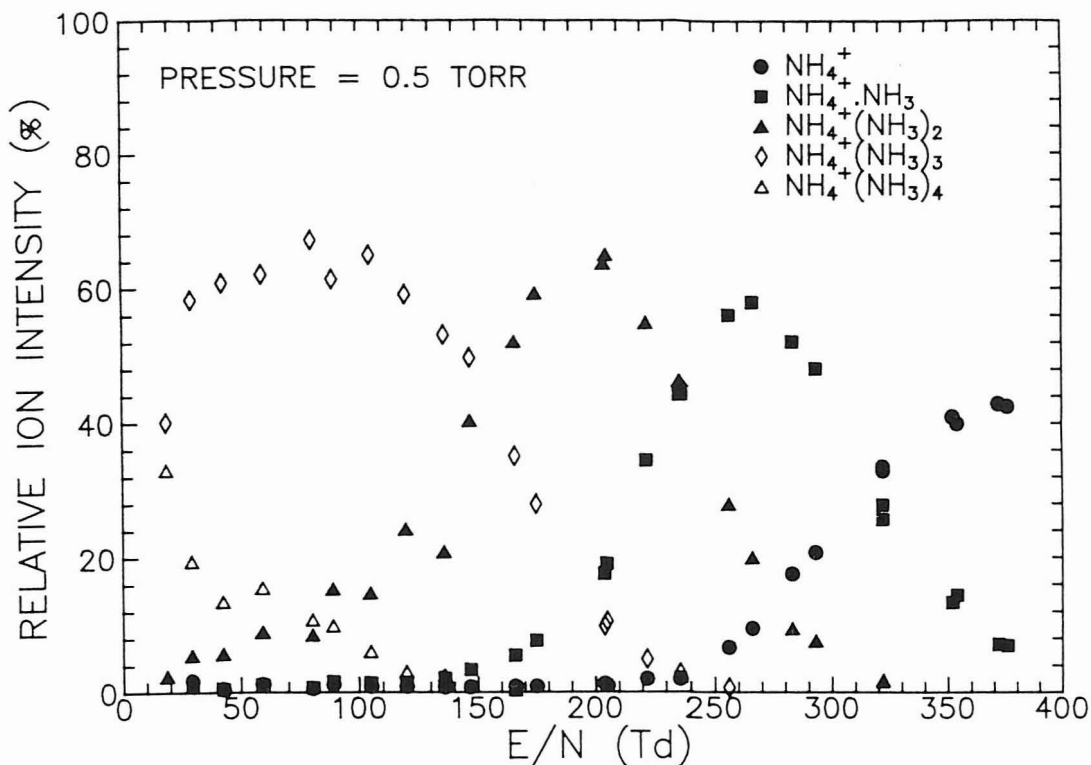
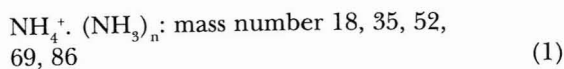


Fig. 2: Variations of the relative ion intensities of ammonia ion clusters as a function of E/N at $p = 0.5$ Torr

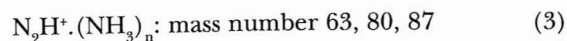
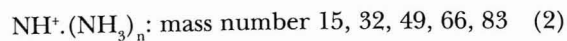
RESULTS AND DISCUSSION

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 ($1 \text{ Td} = 10^{17} \text{ V cm}^{-2}$) 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 NH_4^+ . The ions identified were:



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



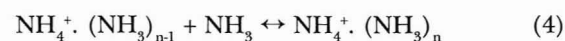
The cluster series in (2) and (3) appeared as a small percent of the total ion intensity except for the NH^+ ion which had an ion intensity about the same size as that of NH_4^+ ion.

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 $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ ions up to $n=4$. Small ions current at mass number 46 and 63 were suggested to be due to $\text{N}_2\text{H}^+ \cdot \text{NH}_3$ and $\text{N}_2\text{H}^+ \cdot (\text{NH}_3)_2$ 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 $\text{NH}_4^+ \cdot (\text{NH}_3)_n$. The two smaller series, $\text{NH}^+ \cdot (\text{NH}_3)_n$ and $\text{N}_2\text{H}^+ \cdot (\text{NH}_3)_n$ were observed in smaller intensities.

Figure 2 shows the typical results of the variations of the relative intensity of the $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ 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 $\text{NH}_4^+ \cdot (\text{NH}_3)_{n-1}$ ions. At high E/N , only the NH_4^+ 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



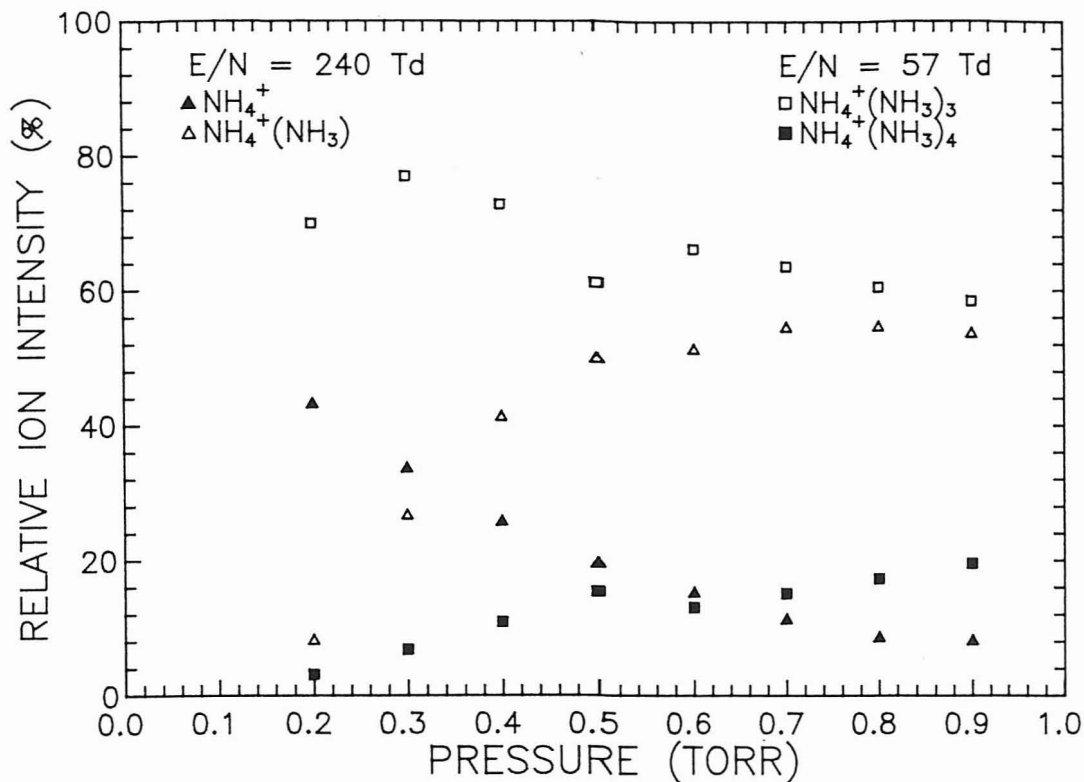


Fig. 3: Variations of the relative ion intensities of ammonia ion clusters as a function of pressure at $E/N=240$ Td and $E/N=57$ Td

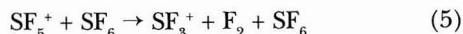
Sulphur Hexafluoride

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_2F_7^+ , accounting for more than 80% of the spectra formed under all experimental conditions. Other ions observed in less abundance were SF_2^+ , SF_4^+ , and S_2F_6^+ ions while S^+ , SF^+ , and S_2F_5^+ ions contributed less than 1% of the mass-spectra.

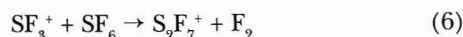
The plots of the relative ion intensities versus pressure as shown in Figure 4 for constant E/N and distance L travelled by the ions demonstrated the pressure dependence of the ions. Measurements of the relative ion intensities as a function of distance travelled by the ions is shown in Figure 5.

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_2F_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_2F_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, $\text{SF}_6 + e \rightarrow \text{SF}_5^+ + \text{F} + 2e$, is



and as the pressure is increased



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_2F_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_2F_7^+

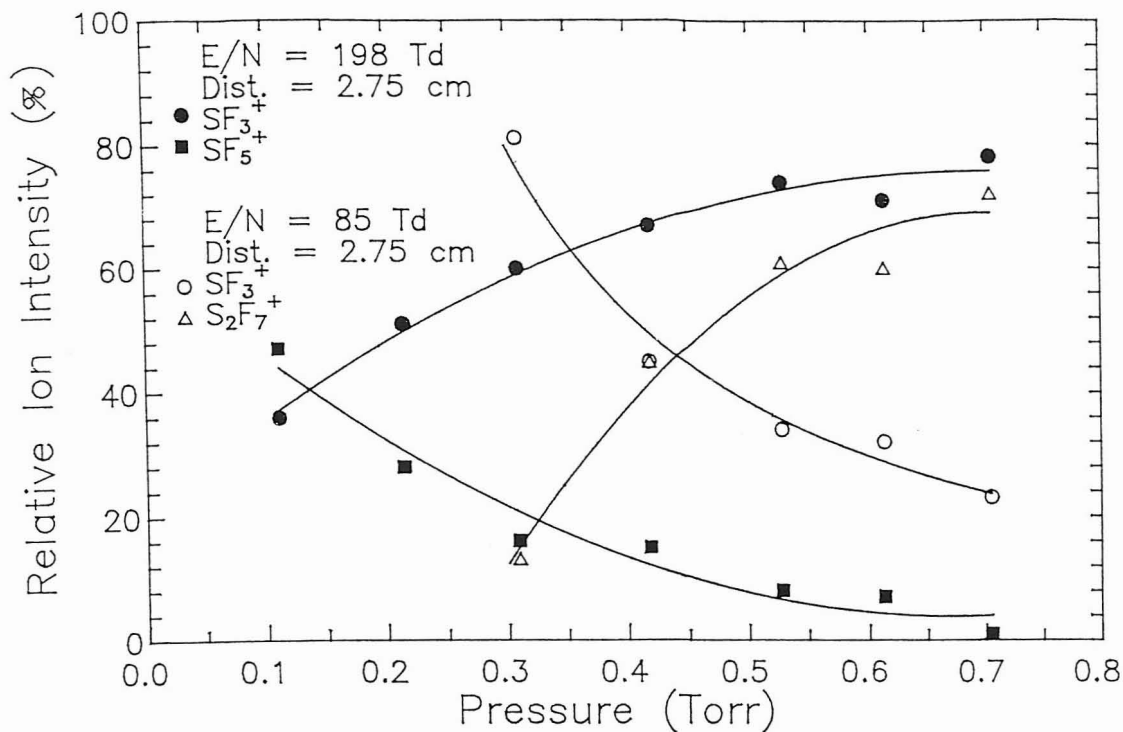


Fig. 4: Variations of the relative ion intensities of SF_6 ions as a function of pressure at $E/N=85 \text{ Td}$ and $E/N=198 \text{ Td}$ with distance = 2.75 cm

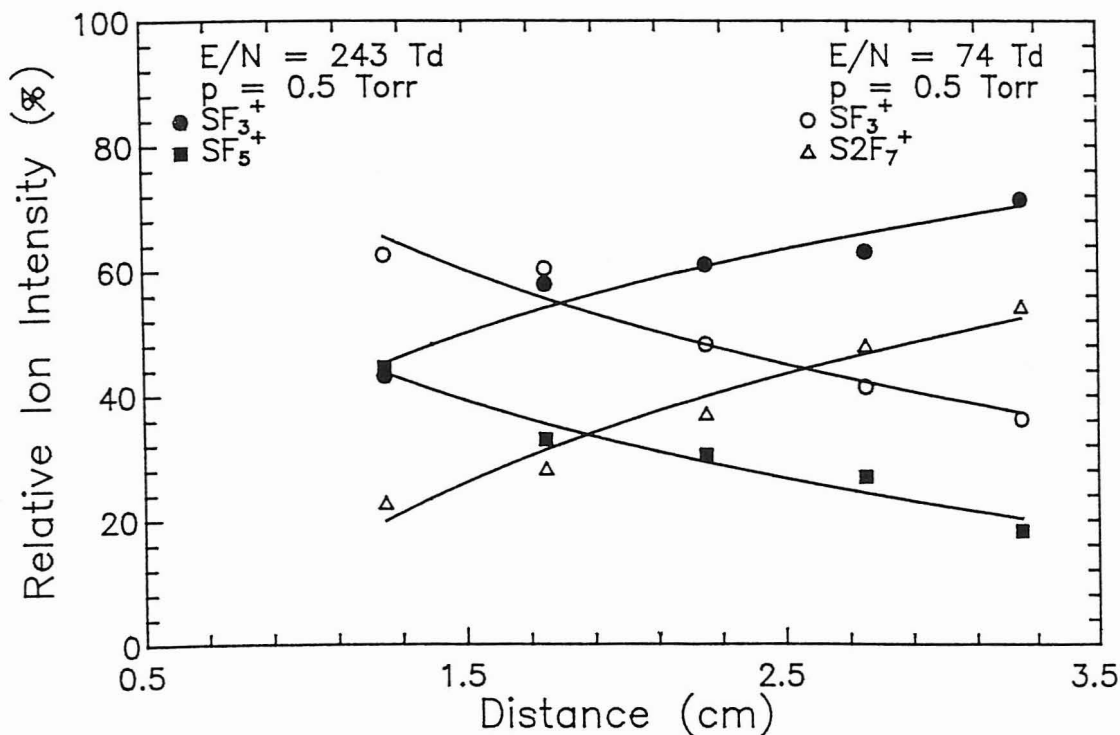


Fig. 5: Variations of the relative ion intensities of SF_6 ions as a function of distance at $E/N=74 \text{ Td}$ and $E/N=243 \text{ Td}$ with $p = 0.5 \text{ Torr}$

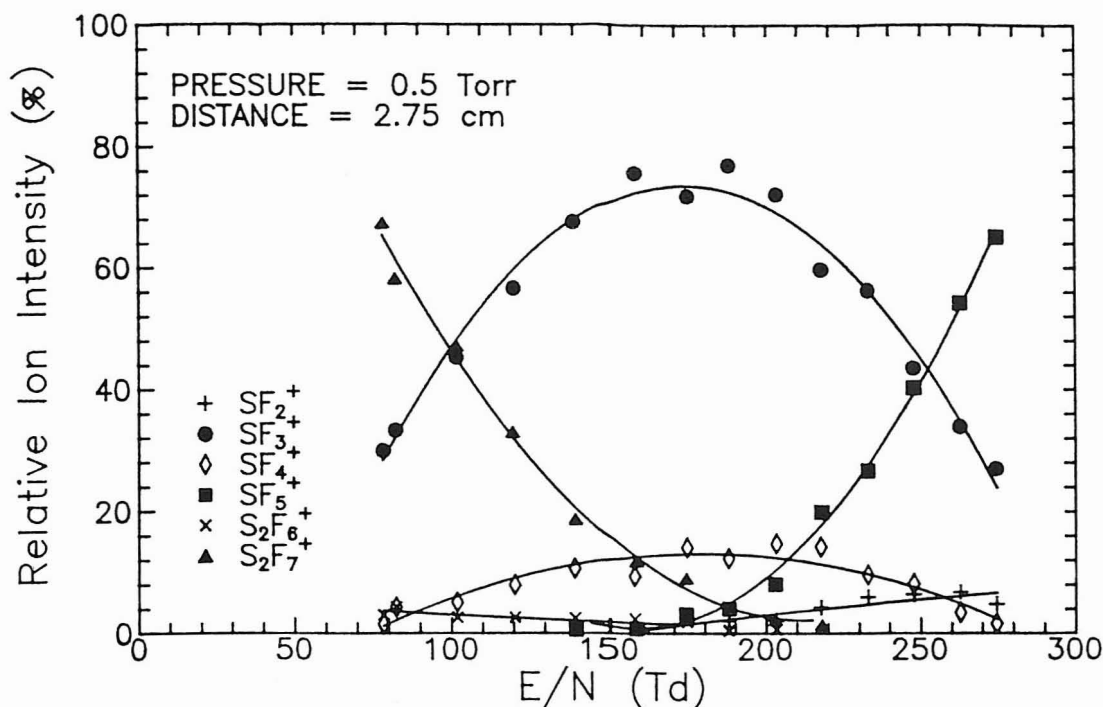


Fig. 6: Variations of the relative ion intensities of SF₆ ions as a function of E/N at $p = 0.5$ Torr and $dist. = 2.75$ cm

ions while at high E/N, it favours the formation of SF₃⁺ 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: NH₄⁺, (NH₃)_n⁺, NH₂⁺, (NH₃)_n and N₂H⁺, (NH₃)_n with NH₄⁺, (NH₃)_n forming the major and most abundant group of ions and this was found to occur through NH₄⁺, (NH₃)_{n-1} + NH₃ ↔ NH₄⁺, (NH₃)_n. For SF₆, nine positive ion mass species in all were observed and the most abundant ions were found to be SF₃⁺, SF₅⁺, and S₂F₇⁺. The major reactions that took place were found to be reactions (5) and (6).

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