# Mobility of Mass-Analyzed $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$ Ions in Nitrogen Gas*

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Drift-velocity measurements as a function of $E/p_0$, the ratio of field intensity to normalized gas pressure, have been obtained for positive ions $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$ in nitrogen gas using the "four-gauze" electrical shutter method of Tyndall *et al.* Extrapolation of the low-field measurements to zero field yields the values of the mobility $\mu_0$, corrected to 0°C: 2.54±0.05, 1.70±0.05, 1.90±0.05, and 2.34±0.05 cm²/V sec for $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$, respectively. The actual data were obtained at gas temperatures 28–32°C. The ions have been identified mass-spectrometrically during the process of measurement of the drift velocities. Gas pressure in the drift tube was in the 0.55–1.5 mm Hg range. Relative intensities of the four nitrogen ions were measured as functions of $E/p_0$. Approximate cross sections for formation of the secondary ions were also determined. The reversible reaction processes $N_2^++N_2 \rightarrow N_4^+$ and $N_4^++N_2 \rightarrow N_2^++2N_2$ were observed experimentally.

## I. INTRODUCTION

COMPARISON of positive nitrogen-ion mobility values reported by several authors is complicated by the fact that the ions under study had not been mass-spectrometrically identified. The drift velocity of nitrogen ions in nitrogen gas has been measured by a number of investigators[1–9] and recently, with the identification of the ions, by McAfee and Edelson[10] and by Keller *et al.*[11] The reduced mobility $\mu_0$, which is the mobility adjusted to the standard conditions of 273°K and 760 mm Hg, has been quoted by several authors.[1,2,3,8,11] In the present experiment, the drift velocities for various nitrogen ions in nitrogen gas have been measured over the following ranges of $E/p_0$: $25<E/p_0<160$ for $N^+$ and $N_3^+$, $35<E/p_0<160$ for $N_2^+$, and $21<E/p_0<180$ for $N_4^+$ where $p_0$ is the pressure reduced to the corresponding value for 0°C. Measurements of the drift velocities were taken at different values of gas pressure over the range $0.55 \leqslant p \leqslant 1.5$ mm Hg. Ion-molecule reactions of formation of the secondary ions have been discussed and their cross sections have been determined.

## II. RESULTS AND DISCUSSION

Brief descriptions of the experimental procedures have been given in the preceding paper on mobility of hydrogen ions.

Nitrogen gas was admitted after passing the gas through a liquid nitrogen trap into the drift tube by means of a bakeable Alpert-type valve from a Pyrex flask of highly pure gas obtainable commercially (Linde). The mass spectrum obtained after baking the drift tube at 200°C shows the only ions observed to be $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$. The drift velocities of the $N^+$ and $N_2^+$ ions are shown in Fig. 1 and those of the $N_3^+$ and $N_4^+$ ions in Fig. 2 plotted as functions of $E/p_0$. These drift velocities were calculated from the measured drift times in the 1-cm distance between shutters using the "four-gauze" electrical shutter method of Tyndall *et al.*[12,13] The data of the present experiment were obtained at temperatures 28–32°C measured directly in the drift tube with a calibrated thermocouple.

Lines of logarithmic slopes having values of one and one-half are shown in Figs. 1 and 2 in order to compare

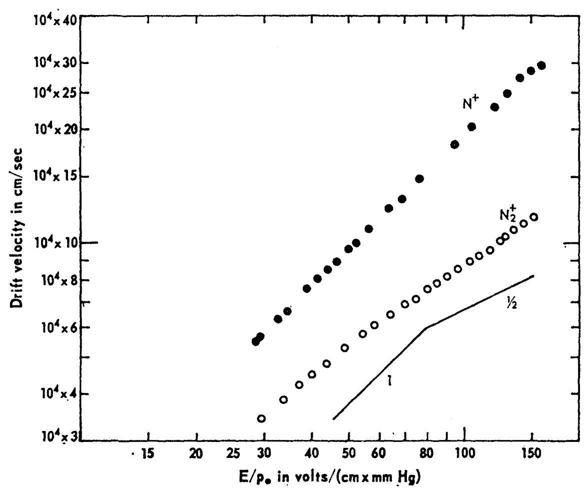


FIG. 1. Log-log plot of drift velocity of the $N^+$ and $N_2^+$ ions in nitrogen gas at 303°K versus $E/p_0$. Lines of logarithmic slope 1 and ½ are shown for reference.

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13 A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, England, 1938).

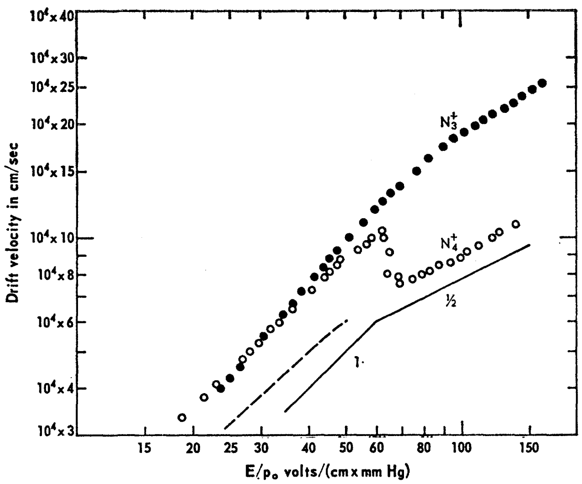


FIG. 2. Log-log plot of drift velocity of the $N_3{}^+$ and $N_4{}^+$ ions in nitrogen gas at 303°K $E/p_0$. Keller, Martin, and McDaniel results for the $N_4{}^+$ ions are shown (---). Lines of logarithmic slope 1 and $\frac{1}{2}$ are shown for reference.

present experimental results with Wannier's[14] theory for drift velocity as a function of $E/p_0$. At low field, Wannier's calculations show that the drift velocity varies directly with $E/p_0$ regardless of the interaction assumed. Lines through the typical data points of the drift velocity versus $E/p_0$ curves for $N^+$ and $N_4{}^+$ have a slope of unity and are approaching unity for $N_2{}^+$ and $N_3{}^+$. At high $E/p_0$ when the ion has an energy in excess of that of the surrounding molecules, Wannier's theory predicts that the drift velocity is proportional to $(E/p_0)^{1/2}$. With the exception of the $N^+$ ions, the drift velocities at high $E/p_0$ approach a slope of one-half on the log-log plot. For the $N^+$ ions, calculated energies greater than the thermal energies ($\frac{3}{2}kT$) of the nitrogen molecules are at $E/p_0 > 145$. Therefore, the drift velocity of the $N^+$ ions reported in this work is not in excess of thermal speeds and is proportional to $E/p_0$ for all values of $E/p$ measured.

The drift velocity of the $N_2{}^+$ ions obtained in the present experiment is in good agreement with Varney's[4] for $E/p_0 \geqslant 80$ and with Dahlquist's[9] for practically all values measured. Dahlquist's drift velocity of the faster ions is higher by about 10% than for either $N^+$ or $N_3{}^+$ for $E/p_0 < 90$ in this work. Considerable disagreement exists between the present results and Keller's[11] mass-analyzed measurements of the drift velocity at low $E/p_0$ for the $N_4{}^+$ ions shown in Fig. 2. This is believed to be due to the fact that Keller's measurements were made at lower pressures (0.2 mm Hg) and the $N_4{}^+$ ions were formed within the space where drift measurements were made. Comparison of the other three ions shows that the $N_2{}^+$ ion drift velocity is about ten percent higher than Keller's and the $N^+$ and $N_3{}^+$ drift velocities agree at lower $E/p_0$ but disagree by a few percent at higher $E/p_0$ yielding different slopes which lead to different values of mobility.

The conventional zero-field mobilities of all four ions are shown in Fig. 3. The results of the zero-field mobilities of Bradbury, Mitchell and Ridler, Davies *et al.*, and Huber[15] are indicated by arrows at the left in Fig. 3. It is presumed that data were taken by Mitchell and Ridler at 20°C and their data were correspondingly reduced to 0°C by the writer. Since they used a glow-discharge ion source as in this work, higher temperature of the gas may be expected. Therefore their zero-field mobility may be lower. Bradbury's values were reduced from 22°C and Huber's from 20°C. The results of Vogel and of Frommhold are drawn. The results obtained by Keller *et al.* for the $N^+$, $N_2{}^+$, and $N_4{}^+$ were 2.47, 1.44, and 1.84, respectively, and are not shown in Fig. 3. Zero-field mobility of 1.85 for $N_2{}^+$ was obtained by Wobschall *et al.*[16] from measurements of the thermal energy elastic collision cross section for $N_2{}^+$ ions in $N_2$ gas by ion cyclotron resonance techniques. This value of mobility also is not shown in Fig. 3. The resulting values of the reduced mobility obtained in this work by extrapolation to zero value of $E/p_0$ are $N^+$:2.54; $N_2{}^+$:1.7; $N_3{}^+$:1.9; and $N_4{}^+$:2.34 in $cm^2/V$ sec. Decline of mobility of $N_3{}^+$ for $E/p_0$ below 65 may be explained by the hypothesis that, at low values of $E/p_0$, $N_3{}^+$ ions in an encounter with $N_2$ molecules have a good chance

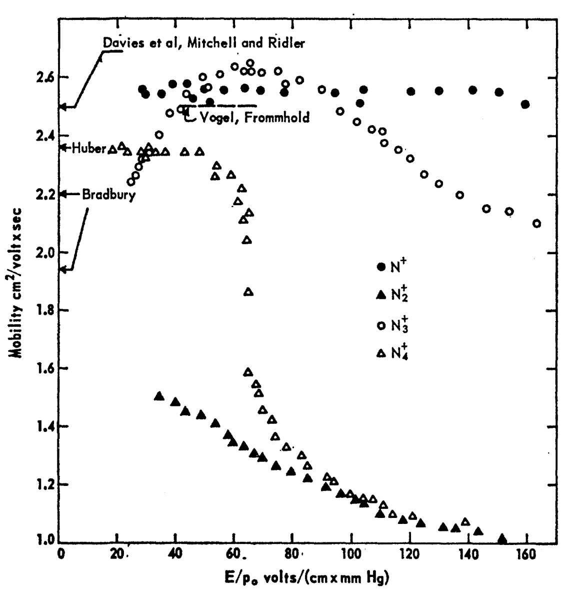


FIG. 3. Reduced mobility ($\mu_0$) of the $N^+$, $N_2{}^+$, $N_3{}^+$, and $N_4{}^+$ ions in nitrogen gas at 303°K as a function of $E/p_0$. Low-field mobilities of Davies *et al.*, Mitchell and Ridler, Huber and Bradbury and $\mu_0$ versus $E/p_0$ by Vogel and by Frommhold are also shown.

[14] G. H. Wannier, Phys. Rev. **83**, 281 (1951).

[15] E. L. Huber, Phys. Rev. **97**, 267 (1955).

[16] D. Wobschall, J. R. Grahm, and D. P. Malone, Phys. Rev. **131**, 1565 (1963).

of either clustering together to form $N_5^+$ ions of very low binding energy or exchanging $N^+$ and thereby decreasing the effective drift velocity of the $N_3^+$.

Figure 4 shows the composition of the ion current emerging from the drift tube. Indicated normalized ion intensities, expressed in percent, were obtained for any given ion by dividing the ionic current of that ion by the total ionic current at that $E/p_0$. Data were taken at 1 mm Hg gas pressure in the drift tube. The field strength was uniform from the ion source through a two-cm-long thermalizing space and the drift space including the spaces within both sets of shutters. The intensity of the secondary ions, $N_3^+$ and $N_4^+$, depends

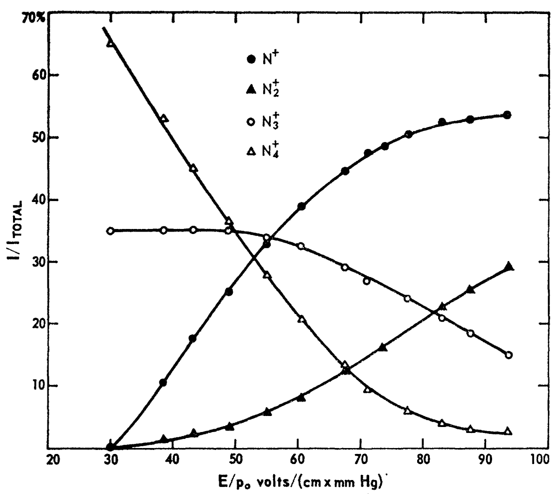


FIG. 4. Variation of normalized intensities of the $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$ ions with $E/p_0$ in the drift tube at the pressure of 1 mm Hg.

on the pressure and the energy of the primary ions. Few secondary ions are formed in the ion source, since the field strength in the cathode fall-through, which the ions have to pass before entering the thermalizing region, is higher than 200 V/cm. The constant value of the normalized intensity of the $N_3^+$ ions for lower $E/p_0$ for a given pressure is believed to be due to the process of formation of these ions by collision of $N_2^+$ in the excited state with nitrogen molecules. Curran[17] found the appearance potential of $N_3^+$ to be 21.04±0.05 V with breaks observed at 21.8±0.1 V and at 22.2±0.2 V. Kaul and Fuchs'[18] value is 21.7±0.5 V and the author's[19] is 22.1±0.5 V. At higher values of $E/p_0$, not all excited $N_2^+$ ions react to form $N_3^+$ ions. This conclusion is supported by results shown in Figs. 5 and 6. Here the normalized intensities of ionic currents are shown as functions of $E/p_0$ in the drift space at two different constant values of electric field strength of 20 V/cm in

[17] R. K. Curran, J. Chem. Phys. 38, 2974 (1963).
[18] W. Kaul and R. Fuchs, Z. Naturforsch. 15a, 326 (1960).
[19] M. Saporoschenko, Phys. Rev. 111, 1550 (1958).

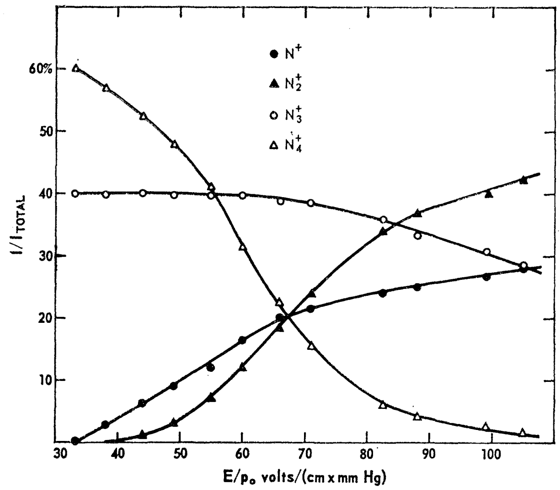


FIG. 5. Variation of normalized intensities of the $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$ ions with $E/p_0$ in the drift space between the shutters and at constant electric field strength of 20 V/cm in 2-cm thermalizing region.

Fig. 5 and 80 V/cm in Fig. 6 in the 2-cm thermalizing region.

The normalized intensity of the $N_4^+$ ions decreases rapidly with increasing $E/p_0$. Formation and dissociation of the $N_4^+$ ions strongly depend on the energy of the reacting ions, much more so than in the case of the $N_3^+$ ions. This can be seen from Figs. 4, 5, and 6. Varney[20] evaluated the binding energy of the $N_4^+$ ion against dissociation into $N_2^+$ and $N_2$ obtaining a value of 0.5 eV. Figure 7 shows the energies for dissociating $N_3^+$ into $N_2^+ + N$ as 3.7±0.5 and into $N^+ + N_2$ as 2.6±0.5 eV, using 21.7 eV as the appearance potential

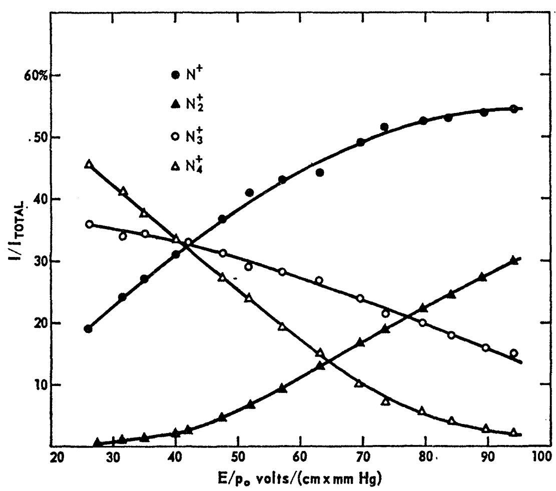


FIG. 6. Variation of normalized intensities of the $N^+$, $N_2^+$, $N_3^+$, and $N_4^+$ ions with $E/p_0$ in the drift space between the shutters and at constant electric field strength of 80 V/cm in 2-cm thermalizing region.

[20] R. N. Varney, J. Chem. Phys. 31, 1314 (1959).

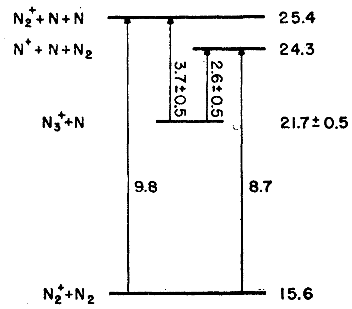


FIG. 7. Energy-level diagram of the nitrogen-ion system. Energies are in electron volts. 21.7 ±0.5-V value of the appearance potential of $N_3^+$ of Kaul and Fuchs is used.

of $N_3^+$. Franklin *et al.*[21] find the corresponding dissociation energies 3.6 and 2.56 eV.

Both secondary ions, $N_3^+$ and $N_4^+$, are formed mainly by two-body collisional processes. This can be seen from Fig. 8 where the normalized intensities of ionic currents are shown at different pressures but for a constant $E/p_0=55$ V/(cm×mm Hg). Ratio of normalized intensities of the secondary ions to the pressures are constant for all pressures. Deviations from this constant are observed for the $N_3^+$ ions for pressures below 0.8 mm Hg. This is due to the fact that the constant value of the normalized intensity of the $N_3^+$ ions at lower pressures is reached at higher value of $E/p_0$ than 55. Calculated values of the three-body collisions of the primary $N_2^+$ ions in the drift space is at least one order of magnitude lower than the number of the secondary ions at the highest pressure measured. The cross sections of formation of $N_3^+$ and $N_4^+$ ions were determined from the relation

$$e^{-n\sigma l}=1-i_s/i_p,$$

where $l$ is the drift distance of the primary ions, $n$ is the number of molecules per cm$^3$, $\sigma$ is the cross section, $i_s$ is ionic current of the secondary ions, and $i_p$ is the total ionic current measured which is assumed to be proportional to the primary $N_2^+$ ion current emerging

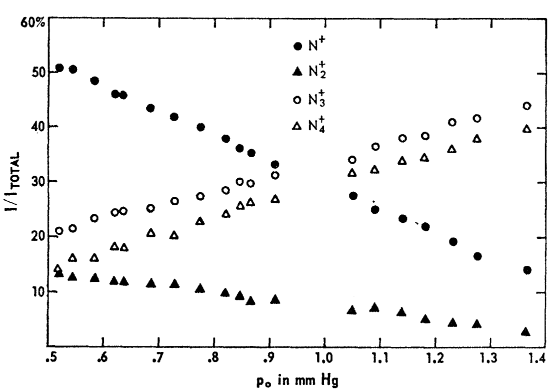


FIG. 8. Variation of normalized intensities of primary and secondary ions on reduced pressure $p_0$ of nitrogen gas in the drift tube. $E/p_0=55$.

[21] J. L. Franklin, V. H. Dibeler, R. M. Reese, and M. Krauss, J. Am. Chem. Soc. **80**, 298 (1958).

from the ion source. This total current contains the $N^+$ ion current. It is assumed that the main contribution to the $N^+$ ion current takes place within the drift region due to the dissociation of some excited $N_2^+$ ions. This assumption is supported by the data in Figs. 5 and 6 where strong dependence of the $N^+$ ion current on the electric field intensity in the thermalizing region is shown. The cross sections were found within experimental error to be independent of the pressure at constant $E/p_0$. At $E/p_0=55$, the cross section $\sigma$ for formation of the $N_4^+$ is $(3.00\pm0.03)\times10^{-18}$ cm$^2$ and for the $N_3^+$ $\sigma=(3.75\pm0.03)\times10^{-18}$ cm$^2$. The cross sections for formation of the secondary ions are strongly dependent functions of $E/p_0$, especially for the $N_4^+$ ions. Table I shows the cross sections for the $N_4^+$ and $N_3^+$ ions for various $E/p_0$, taken at a pressure of 1 mm Hg. The fourth column shows the calculated cross sections

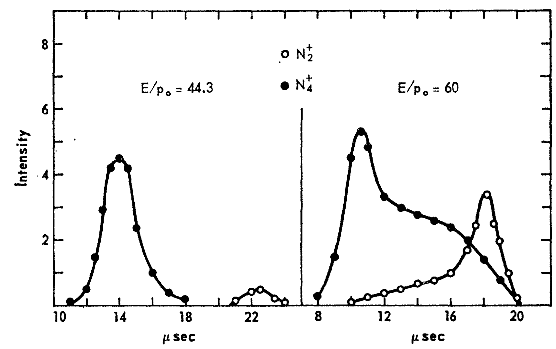


FIG. 9. Simultaneous measurement of ion transients of the $N_2^+$ and $N_4^+$ ions at $E/p_0$ of 44.3 and 60 V/(cm×mm Hg).

for the $N_4^+$ ions using the rate constant $k=5\times10^{-13}$ cm$^3$/sec for the formation of these ions obtained by Fite *et al.*[22] The relative velocity of approach $v_{12}$ of

TABLE I. Measured reaction cross sections for formation of the secondary ions $N_3^+$ and $N_4^+$ at various values of $E/po$ in V/(cm×mm Hg).

| $E/p_0$ | $(\sigma_{N_3^+})\times10^{18}$ | $(\sigma_{N_4^+})\times10^{18}$ | $(\sigma_{N_4^+})=k/v_{12}$ |
|---|---|---|---|
| 30 | 4.17 | 10.3 | 7.0 |
| 40 | 4.17 | 6.6 | 6.1 |
| 50 | 4.17 | 4.1 | 5.75 |
| 60 | 3.75 | 2.43 | 4.93 |
| 70 | 3.32 | 1.03 | 4.54 |
| 80 | 2.54 | 0.49 | 4.27 |
| 90 | 1.81 | 0.24 | 3.94 |

the primary ion and molecule was calculated from Wannier's[14] equation for the impact energy of the collision applicable at low $E/p_0$:

$$\tfrac{1}{2}m_{N_2^+}v_{12}^2=\tfrac{1}{2}(m_{N_2^+}+m_{N_2})v^2_{\text{drift}}+\tfrac{3}{2}kT.$$

Giese and Maier[23] studied the formation of the $N_3^+$ ions

[22] W. L. Fite, J. A. Rutherford, W. R. Snow, and V. A. J. van Lint, Discussions Faraday Soc. **33**, 264 (1962).

[23] C. F. Giese and W. B. Maier, J. Chem. Phys. **35**, 1913 (1961).

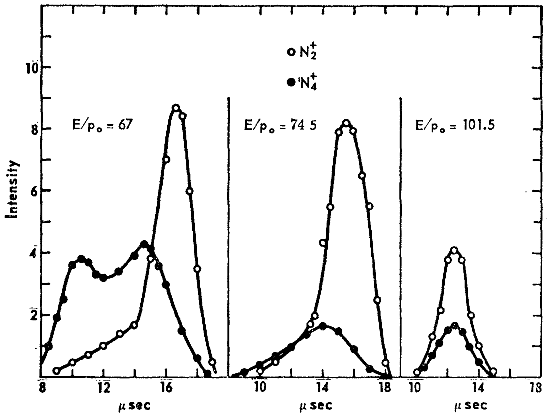


FIG. 10. Simultaneous measurement of ion transients of the $N_2^+$ and $N_4^+$ ions at $E/p_0$ of 67, 74.5, and 101.5 V/(cm×mm Hg). Shown intensity of the $N_2^+$ current is reduced ten times for $E/p_0$ of 101.5.

in collision of the $N_2^+$ in ground state with kinetic energy of 4±0.6 eV. They found the cross section for this ion equal to $20\times10^{-18}$ cm$^2$.

Figures 9 and 10 show the superposed ion transients for $N_2^+$ and $N_4^+$ ions at several different values of $E/p_0$. The abscissa is the time during which the electrical shutters are open for the passage of the ions in the drift space and the ordinate is the ion intensities measured in the collector of the mass spectrometer focused for one type of ion at a time. In all of the measurements shown in Figs. 9 and 10, the pulse width was 2 μsec which is much longer than that used in measurements of the drift velocities. This was done in order to have higher intensities of the $N_2^+$ and $N_4^+$ ions at low and high $E/p_0$, respectively, for better comparison. These ion transients illustrate the reversible reaction process proposed by Varney in 1953:

$$N_2^+ + N_2 \rightarrow N_4^+, \quad (1)$$

$$N_4^+ + N_2 \rightarrow N_2^+ + 2\,N_2. \quad (2)$$

At $E/p_0=44.3$, the reaction (1) predominates. There is no dissociation of the $N_4^+$ ions. Most of the $N_4^+$ ions have formed by attachment in the thermalizing region. At $E/p_0=60$, a considerable number of the $N_4^+$ ions are formed in the drift space or, in terms of time, they spend a certain time drifting as $N_2^+$ ions. On the other hand, the $N_2^+$ ions drift through part of the space as $N_4^+$ ions which dissociate and are shown as a tail toward the shorter drift time. With the increasing $E/p_0$ the reaction (2) predominates and the $N_4^+$ ions spend a longer time and hence go a greater distance in the drift space as $N_2^+$ ions. Results shown in Figs. 9 and 10 explain the sharp drop in drift velocity of the $N_4^+$ ions at $E/p_0=65$, shown in Fig. 2. Similar ion transients have been recorded for the other two nitrogen ions, $N^+$ and $N_3^+$, in wide ranges of $E/p_0$ and pressures. The transients were found to be symmetrical, therefore no reversible reactions were observed. Most of these two ions were formed in the 2-cm thermalizing region.

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