PHYSICAL REVIEW VOLUME 111, NUMBER 6 SEPTEMBER 15, 1958

Ions in Nitrogen*

MYKOLA SAPOROSCHENKO
Department of Physics, Washington University, St. Louis, Missouri

(Received May 19, 1958)

N^+, N_2^+, N_3^+, and N_4^+ ions have been identified in nitrogen gas by use of a mass spectrometer operated with the ion source in the pressure range from 10^{-3} mm Hg to 0.6 mm Hg. Appearance potentials occur at 15.5 ± 0.2 ev for N_2^+, at 15.8 ± 0.3 ev for N_4^+, at 22.1 ± 0.5 ev for N_3^+, and at 24.2 ± 0.4 ev for N^+; N_3^+ ions thus are formed only at much higher electron energies than N_2^+ but still at 2 ev less energy than N^+. It is believed that the N_4^+ is formed by the process $N_2^+ + N_2 \rightarrow N_4^{+*}$ (excited vibrationally) and the N_3^+ is formed by the process $N_2^{+*} + N_2 \rightarrow N_3^+ + N$, where N_2^{+*} is an excited ion. N_4^+ and N_3^+ currents decrease with increasing E/p in the source, suggesting that they may be dissociated by molecular impacts. The N_4^+ ions are considerably more readily lost than the N_3^+ ions. Since the formation of N_3^+ must necessarily release a nitrogen atom, this process constitutes a form of dissociation of N_2 which may account for the value of the dissociation energy of 7.38 ev found by some methods.

INTRODUCTION

STUDIES by modern techniques since 1946 of mobilities of ions in gases disclosed the presence of molecular ions of types not previously known to exist.[1,2] Hornbeck and Molnar[3] confirmed the identity of the molecular ions in He, Ne, and A by mass spectrometric analysis, but no further work has been reported on other ions of interest except for one recent paper by Dreeskamp.[4] The object of the present work was to identify ions in nitrogen by use of a mass spectrometer.

It must be emphasized at the beginning that the entire purpose of the present work was to draw ions from a source in which they had many collisions, in marked contrast to the objective in normal, analytical mass spectrometry. Both the work of Hornbeck and Molnar[3] in the rare gases and the mobility work indicated that the ions of interest would be greatly increased in abundance with increased gas pressure. Source pressures as high as 0.5 mm Hg were aimed for and successfully used, but while the pressures were extremely high for a mass spectrometer, they were barely adequate to form the desired ions in measurable numbers.

Finally, the mobility work indicated that the unusual ions in nitrogen could not be strongly bound, a figure of 0.14 ev having been estimated by Kovar.[5] It was thus clear that the ions upon emergence from the ion source would have to be well removed from the effluent gas stream before being accelerated by the mass analysis accelerating system or they would surely be dissociated by even minor brushes at higher energies with gas molecules.

EXPERIMENTAL METHOD

The mass spectrometer used was a standard 90° sector-type single focusing instrument with the radius of curvature of the ion beam in the magnetic field 4.5 cm. It is presented schematically in Fig. 1(a). A permanent magnet and an electromagnet were employed at various times. The electromagnet produced fields up to 4600 gauss at 1 amp. The tube, made of Pyrex glass, was out-gassed by prolonged heating until the background mass spectrum was negligible. The tube and the analyzer were evacuated by two silicone DC-704 oil-diffusion pumps of rated speed 50 liters/sec each and rotary oil fore pumps. The ultimate pressure in the system was 1.5×10^{-6} mm Hg before the experimental

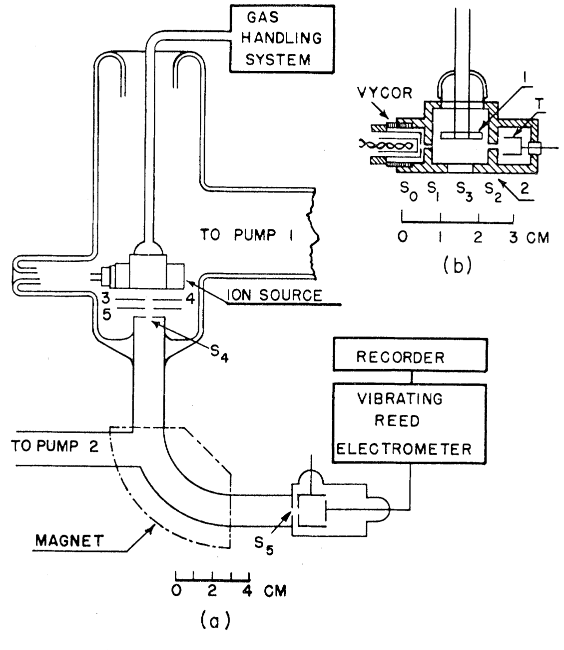

FIG. 1. (a) Schematic diagram of mass spectrometer (the electron gun has been turned 90°). (b) The ion source. Dimensions of the orifices are: S_0—1 mm, S_1—1 mm, S_2—2.5 mm diameter; S_3—0.35 mm×8 mm, S_4—0.6×8 mm, S_5—1×9 mm rectangular.

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* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, and by a generous grant from Research Corporation.

[1] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951).

[2] R. N. Varney, Phys. Rev. **88**, 362 (1952).

[3] J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951).

[4] H. Dreeskamp, Z. Naturforsch. **12a**, 876 (1957).

[5] Kovar, Beaty, and Varney, Phys. Rev. **107**, 1490 (1957).

gas was introduced. Low gas pressure was measured with a VG-1A ionization gauge, and the experimental gas pressure was measured with a thermocouple gauge. Since the ion source was operated at relatively high pressures (up to 0.5 mm Hg), differential pumping was employed between the ion source region and the analyzer, the pressure in the latter during operation being 10^{-4} mm Hg or less. The gas to be analyzed was admitted to the ion source by means of a Type C Ultra-High Vacuum Valve. Highly pure gases obtainable commercially (Linde) with an impurity of about 2 parts in 10^5 were used. The ion source, made of stainless steel, was so designed as to have considerable resistance to flow of gas into the tube. It was adopted after several changes had been made on it and is shown in Fig. 1(b). Electrons emitted by an indirectly heated oxide-coated filament were accelerated by voltage V_e into the ionization chamber through the orifices S_0 and S_1. Electron emission current was controlled by the space-charge control regulator.[6] The emission was slightly affected by a change in pressure in the ion source, but it remained constant during several runs at the same pressure. The electrons collimated by a small auxiliary magnet on passing through the ionization chamber were caught in an electron trap which was maintained at higher potential than the chamber. The ions formed in the ionization chamber were caused to drift downward by a small electric potential V_{12} (0.5–2 v) between the repeller and the exit slit of the ionization chamber. The ions passing through the slit S_3 were accelerated by the larger electric fields between the electrodes 2 and 3–4, and between 3–4 and 5. The electrodes 2, 3–4, and 5 formed a system of two aperture lenses by means of which the ion beam was focused upon the entrance slit of the analyzer. A variable potential between the electrodes 3 and 4 permitted deflection of the ion beam so that it passed through the slit in the electrode 5. After the deflection by the magnet field the resolved ion beam traveling through the exit slit of the analyzer was collected by the ion collector. This current was measured with a vibrating reed electrometer and recorded with a Speedomax recorder. The position of the mass peaks was determined by electrostatic scanning. It was observed that the ion intensity at the peak depended upon the ion accelerating voltage V_1. Therefore, in the measurements of relative abundances of ions at the mass peaks, the same accelerating voltage V_1 (500 v) was used for all types of ions and the appropriate corresponding magnetic fields of several thousand gauss were applied.

TEST OF MASS-SPECTROMETER PERFORMANCE

To test the mass spectrometer, argon gas was first used as the atomic and molecular ions of argon were already well understood.

In agreement with the results of Hornbeck and Molnar, ions of mass 40 and mass 80 were found and were interpreted to be A^+ and A_2^+. (Since the occurrence of A_3^+ or A_4^+ has been suggested recently by Dalgarno,[7] it is commented in passing that no trace amounting to 1% of the A^+ or A_2^+ was seen at masses 120 or 160.) Variation of the energy of the ionizing electrons disclosed onsets for A^+ at 15.7 ev and for A_2^+ at 15.0 ev in further agreement with the earlier work. At low gas pressures, the plot of A_2^+ ion current as a function of electron energy also corresponded. The only new finding was that at higher pressures than were used by Hornbeck and Molnar, the A_2^+ ion-current curve took a turn upward at higher electron energies, as shown in Fig. 2. It is suggested that this rise may indicate a new mechanism of ion formation even more sensitive to gas pressure and hence possibly involving three-body collisions according to the equation $A^+ + A + A \rightarrow A_2^+ + A$.

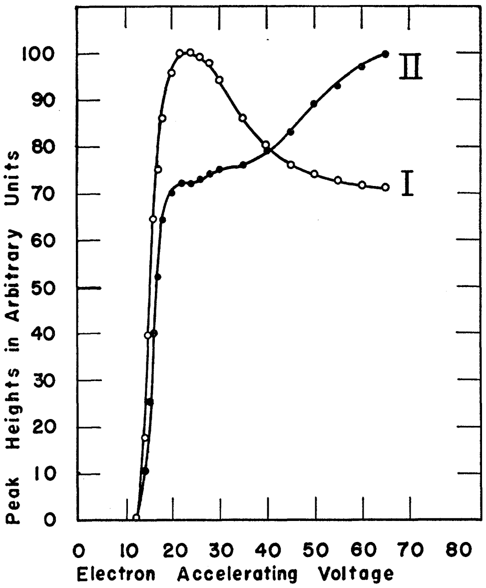

FIG. 2. A_2^+ ion current *versus* the electron accelerating potential (uncorrected for contact potential difference) at two different gas pressures: I—at 0.052 mm Hg, II—at 0.165 mm Hg.

The atomic and molecular ion currents increase with the pressure but ultimately decrease again at high enough pressures presumably because of excessive scattering of the ions at the higher pressures. The fall-off for A^+ ions sets in above 0.06 mm Hg and for A_2^+ ions above 0.175 mm Hg. The difference is due to the shorter mean free path of atomic ions in argon arising in turn from the readier charge exchange for A^+ ions than A_2^+ ions in argon. The ratio of the molecular ion current to the atomic ion current is a function of the pressure and of the electron energy. The range of this ratio is from 1% to 20%. Order of magnitude of the atomic ion current is 10^{-10} amp and of the molecular ion current is 10^{-12} amp.

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[6] E. B. Winn and A. O. Nier, Rev. Sci. Instr. **20**, 773 (1949).

[7] A. Dalgarno, Trans. Roy. Soc. (London) **250**, 426 (1958).

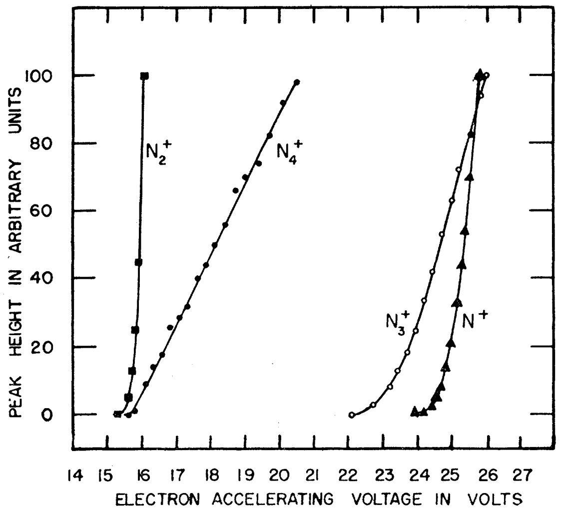

FIG. 3. Ionization in nitrogen *versus* the electron accelerating potential (uncorrected). The lowest points correspond to currents of 2×10^{-16} amp.

STUDIES OF NITROGEN GAS

Following the testing of the apparatus with argon, nitrogen was introduced into the mass spectrometer. With suitable adjustment of the numerous variables it was found that ions identifiable as N^+, N_2^+, N_3^+, and N_4^+ were all present.

Figure 3 shows the currents of the various ions as a function of the ionizing electron energy. The onsets of ionization occur at 15.5±0.2 ev for N_2^+, at 15.8±0.3 ev for N_4^+, at 22.1±0.5 ev for N_3^+, and at 24.2±0.4 ev for N^+. The onsets of N_2^+ and N^+ are in good agreement with standard values.[8] The curves for N^+ and N_3^+ have much more rounded feet than for N_2^+ and N_4^+, the latter two curves being actually sharper than indicated in the figure. No attempts were made to obtain high-precision onset potentials because the requirement of high gas pressure in the source was intrinsically unfavorable to such a goal. The formation efficiency curves for all four ions as a function of the electron accelerating potential were taken at fixed gas pressure, at constant V_{12}, and with constant electron emission current. The ion accelerating voltage was also held constant and the magnetic field was adjusted for each ion peak. The electron collector was held at the same potential as that of the ionization chamber. The relative abundances of the N_4^+ ions and of N_3^+ ions amount to 3.5% of the N_2^+ ions at optimum conditions. The ratio of the N^+ ions to the N_2^+ ions varies from 0.1 to 1.5. The relative abundance of the ions is indicated by the steepness of the ion-current curves, N_2^+ being most abundant and N_4^+ least. The abundance figures refer only to ions reaching the final collector and may be much altered from the source values by dissociation or scattering in flight.

The ion-current peak heights were measured for all four ions as a function of gas pressure and are shown in Fig. 4 on a log-log plot. The current scale is arbitrary. The electron accelerating potential (50 volts) and the electron emission current were kept constant. Since the N_4^+ ion current depends strongly, and the N_3^+ current somewhat less strongly, on the ratio E/p in the ion source (see Fig. 5), the precaution was taken to obtain the ion peak heights for these ions at a constant ratio of E/p. It was established that the N^+ and N_2^+ ion-current peak heights varied linearly with gas pressure p, whereas the N_3^+ and N_4^+ ion currents increased quadratically with p. As in the case of argon ions, a decline of the slopes at higher gas pressures occurs and probably represents a failure of ions to reach the collector because the high gas pressure exceeds the capacity of the pumps and permits scattering of the beam. Positions of the maxima of the ion-current peak heights *versus* gas pressure in Fig. 4 indicate that the mean free paths of the various ions are different. The N_2^+ ions have the shortest mean free path followed in turn by those of N^+, N_3^+, and N_4^+ ions. The N_4^+ ions have, by this observation, more than three times the mean free path of N_2^+. Such a conclusion is in good agreement with mobility data.[2]

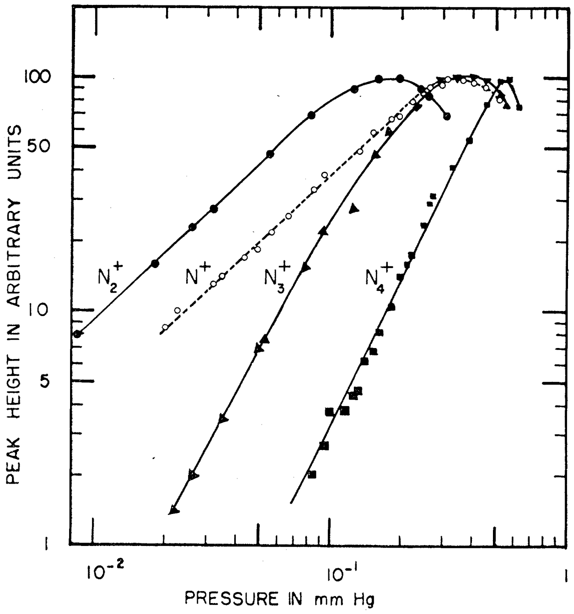

FIG. 4. Ion currents of all four ions in nitrogen *versus* gas pressure. The electron accelerating potential was 50 volts for all ions. The N^+ and N_2^+ lines have slopes of one, and the N_3^+ and N_4^+ lines have slopes of two.

It was noticed that the ion currents of the various ions depended upon V_{12}, the voltage between the ion repeller and the exit slit of the ionization chamber. The potential V_{12} serves to drive the ions out of the ionization chamber and into the mass-spectrometer accelerating system, so that the ion currents might be

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[8] F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press, Inc., New York, 1957).

expected to rise as V_{12} is increased. However, the ions have many gas collisions within the ionization chamber so that the ratio E/p, where E is V_{12}/d, may also be expected to influence the ion current. The variable, E/p, is familiar in ion mobility work as an indicator of the mean energy of impact of drifting ions. The curves showing N^+ and N_2^+ ion currents *versus* V_{12} or E/p increase in height up to 5 volts and then flatten. This observation suggests a simple saturation effect dependent on the value of V_{12}. But the N_3^+ and especially the N_4^+ ion currents are sensitive to the variation of V_{12} or E/p as may be seen from Fig. 5. Experimental variation of both V_{12} and p discloses that, for N_3^+ and N_4^+, E/p is the significant variable. The decline of these ion currents with increasing E/p is evidence of the weak binding energy of these ions and the readiness with which they are dissociated by more energetic impacts with gas molecules.

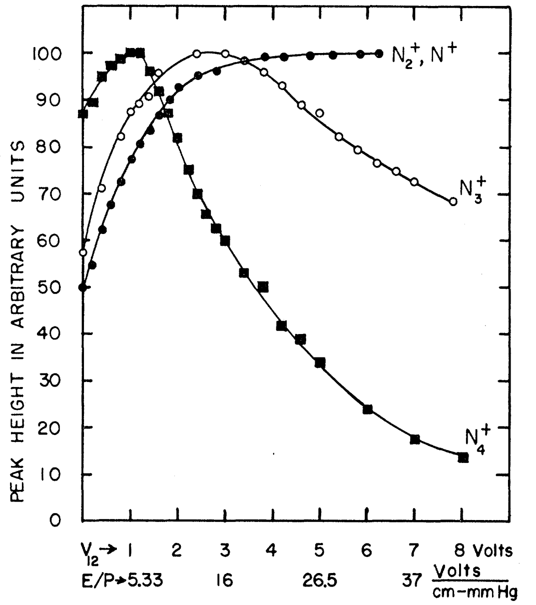

FIG. 5. Ion currents *versus* V_{12}, potential between the ion repeller and the exit slit of the ionization chamber, or E/p.

ANALYSIS

The ion-current peaks of all four ions depend linearly upon the electron-beam current in the ion source. This seemingly trifling observation is significant as it means that in the formation process of both N_3^+ and N_4^+ only one N^+ or N_2^+ ion is involved. The quadratic pressure dependence of the number of N_3^+ and N_4^+ ions, given in Fig. 4, is considered to be sufficient evidence that these ions are formed by secondary processes. The processes are accomplished in two steps; first, ionization (with additional excitation for N_3^+ formation) of an N_2 molecule, and then collision of this ionized molecule with a normal N_2 molecule.

The onset potential of the N_4^+ ion is so close to that of the N_2^+ ion that it may be said to coincide within the probable error of the measurements. This suggests that the N_4^+ may be formed by the following process: $N_2^+ + N_2 \rightarrow N_4^{+*}$ (vibrationally excited), a process that was suggested as a hypothesis by Varney[9] in connection with mobility measurements. The N_3^+ ion, however, has an appearance onset at 22.1±0.5 ev which is much higher than for N_2^+ ions and appreciably lower than for N^+ ions at 24.3 ev. One is obliged to conclude that N_3^+ is not formed directly from N_2^+ *nor from* N^+. The process of formation of the N_3^+ given by Dreeskamp[4] and by Luhr,[10] $N^+ + N_2 \rightarrow N_3^+$, is thus ruled out. The onset potential of 22.1±0.5 ev of the N_3^+ ion suggests that the N_3^+ ion is formed by the following reaction: $N_2^{+*} + N_2 \rightarrow N_3^+ + N$, where N_2^{+*} is an excited ion, possibly to the well-established negative band system[11] of N_2^+ with origin at 1847 A or 6.7 ev above the ground state of N_2^+, or 22.276 ev above the ground state of N_2.

Results of the mobility experiments[5,9] on nitrogen ions in nitrogen gas support the presence of N_4^+ at low E/p in agreement with the present work. The N_3^+ ions are absent with Hornbeck-Varney type of apparatus since higher energy electrons are required for their formation which are not available in the mobility experiments. However, N_3^+ ions may have occurred in the mobility work of Mitchell and Ridler[12] who use a discharge type of ion source.

The presence of N_3^+ ions with considerable stability is an interesting finding as the ions seem to be appreciably more stable than N_4^+. It is not surprising that N_3^+ and N_4^+ are rarely found together since much higher ionizing electron energies are needed to produce the N_3^+ ions, and these conditions serve to dissociate the N_4^+ ions.

The extensive debate in the literature[8,13] over the energy of dissociation of N_2^+ may be resolved by the present work. According to the analysis above, free atomic nitrogen is produced at 22.1 ev as a by-product of the N_3^+ ion formation and at 24.3 ev as a by-product of the N^+ ion formation. Which mode of production of free atomic nitrogen occurs is likely to depend on p, E/p, and available electron energies. The former reaction would lead to the 7.38-ev value of the molecular binding energy; the latter would give the 9.76-ev value.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor R. N. Varney under whose direction this work was done, for his assistance, advice, and helpful discussions during the course of the work. The generous assistance of Research Corporation is also gratefully acknowledged.

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[9] R. N. Varney, Phys. Rev. **89**, 708 (1953).

[10] O. Luhr, Phys. Rev. **44**, 459 (1933).

[11] W. W. Watson and P. G. Koontz, Phys. Rev. **46**, 32 (1934).

[12] J. M. Mitchell and K. E. W. Ridler, Proc. Roy. Soc. (London) **A146**, 911 (1934).

[13] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1939).