# *ON THE EXISTENCE OF THE NEGATIVE NITROGEN ION*

Ya. M. FOGEL', V. F. KOZLOV, and A. A. KALMYKOV

Physico-Technical Institute, Academy of Sciences, Ukrainian S.S.R.

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A beam formed by the passage of positive nitrogen ions through a gaseous target has been found to contain small amounts of negative nitrogen ions. The cross section for the $N^+ \rightarrow N^-$ process is estimated as $1.9 \times 10^{-22}$ cm$^2$. No negative molecular nitrogen ions are observed.

THE question of how the atoms in the periodic system form stable negative ions has been considered at great length in a number of papers by Dukel'skiĭ and his co-workers.[1-5] The experimental data seem to point to the following rule: atoms with unfilled electron shells form stable negative ions while atoms with filled shells do not form negative ions. Only one exception to this rule has been observed at the present time: the nitrogen atom, which has a $2p^3$ configuration in its outer electron shell. It has been shown by a number of authors[3,6,7] that $N^-$ ions are not produced in a gaseous discharge in nitrogen. Dukel'skiĭ and Zandberg,[3] in observing the spectrum of negative ions from a discharge in $NH_3$, observed a weak line at mass 14; however, as indicated by the authors, a line with an apparent mass of 14 may be produced by the $NH^-$ ions which result from the dissociation of $NH_2^-$ ions in the space between the ion source and the magnetic mass analyzer. It should be noted, however, that the absence of $N^-$ ions in the plasma of a gaseous discharge is still not proof of the nonexistence of this ion; because of the low electron affinity of the nitrogen atom the density of negative nitrogen ions in a plasma may be very small.

We have made an attempt to observe $N^-$ ions resulting from the $N^+ \rightarrow N^-$ process in the passage of a beam of $N^+$ ions through matter. As we have already indicated,[8-10] the effective cross section for the $I^+ \rightarrow I^-$ process in single collisions of a great many positive ions with heavy inert gas atoms reaches the gas-kinetic cross sections and, in those cases in which a comparison is possible, turns out to be considerably greater than the effective cross section for the formation of negative ions in collisions of electrons with gas molecules. Thus, the former would appear to be the most effective method of observing negative ions. The validity of this statement has been verified by the work of Dukel'skiĭ et al,[11] who used this method to observe metastable $He^-$ ions, which have a very small electron affinity (0.075 ev[12]).

In the search for $N^-$ use was made of the double mass spectrometer which has been described earlier.[13] A high-frequency ion source was used for obtaining $N^+$ ions. The beam of $N^+$ ions, with an energy of 34 kev, was analyzed by a magnetic mass monochromator and directed into the collision chamber, which was filled with krypton. In the mass spectrum of the beam, in addition to the line at mass 14, we observed a series of lines due to contamination of the nitrogen by gases evolved from the walls of the source chamber and by gaseous dissociation products of the diffusion pump oil. In particular, close to the line at mass 14 the following lines were observed: 12 ($C_{12}^+$), 13 ($C_{13}^+ + C_{12}H^+$), 15 ($N_{15}^+ + N_{14}H^+$), 16 ($O_{16}^+ + C_{12}H_4^+ + N_{14}H_2^+$), 17 ($O_{16}H^+ + N_{14}H_3^+$), and 18 ($O_{16}H_2^+$).

The resolving power of the mass monochromator was sufficient for complete separation of the line at mass 14 from the nearby lines at 13 and 15. The beam which passed through the collision chamber was analyzed by means of a magnetic analyzer. The negative ion current was measured with a vacuum-tube voltmeter (sensitivity $10^{-14}$ amp/div).

The first experiments, at a current strength of the order of $10^{-7}$ amp, indicated that the beam contained a small amount of negative ions of mass 14; the number of negative ions increased with increasing pressure of the krypton in the collision chamber. The mass-spectrometer method (cf. references 8 and 13) was used to measure the effective cross section for the conversion of a positive ion of mass 14 into a negative ion of the same mass. This cross section was found to be $3.2 \times 10^{-22}$ cm$^2$. However, this result, in itself, is not necessarily proof that the effect is due exclusively to the $N^+ \rightarrow N^-$ process. In an ion beam of mass 14, in addition to the $N^+$ ions there may be $CH_2^+$ ions or fragment ions with apparent mass 14 which arise as a result of the dissociation of heavier positive ions in the space between the ion source and the mass monochrometer. Using the formula $m^* = m_1^2/M$ (where $m^*$ is the apparent mass of the fragment ion, $m_1$ is the mass of the fragment ion and $M$ is the mass of the ion before dissociation) we find that the quantity $m^*$ can be near 14 for $O^+$ ions resulting from $H_2O^+ \rightarrow O^+ + H_2$ ($m^* = 14.2$) and for $NH^+$ ions resulting from $NH_2^+ \rightarrow NH^+ + H$ ($m^* = 14.1$). Thus the negative ions of mass 14 can result from two-electron charge exchange on $CH_2^+$ and the fragments $O^+$ and $NH^+$ in addition to the $N^+ \rightarrow N^-$ process.*

The effect of $O^+$ on the size of $\sigma_{1-1}^{14}$ was established by investigating the effect of the $H_2O^+$ ion current in the primary beam on the measured value of this cross section. The value $3.2 \times 10^{-22}$ $cm^2$ indicated above for this cross section was measured when the $H_2O^+$ ion current was $2.4 \times 10^{-10}$ amp. As a result of extended processing of the walls of the source chamber and careful purification of the nitrogen it was possible to reduce the $H_2O^+$ current to $4.7 \times 10^{-11}$ amp. At this value of the $H_2O^+$ current $\sigma_{1-1}^{14}$ was found to be $1.9 \times 10^{-22}$ $cm^2$. A simple calculation indicates that for this value of the $H_2O^+$ current the admixture of residual $O^+$ ions has no effect on $\sigma_{1-1}^{14}$. There still remains the possibility of contamination of the $N^+$ beam by $CH_2^+$ ions and residual $NH^+$ ions, the existence of which was verified by the presence of $N^+$ and $H_1^+$ in the beam; these arise as a result of the following dissociation processes: $CH_2^+ \rightarrow CH + H^+$ and $NH^+ \rightarrow N + H^+$. We have carried out additional experiments in order to determine the cross sections for $CH_2^+ \rightarrow CH_2^-$ and $NH^+ \rightarrow NH^-$ in krypton at positive ion energies of 34 kev; these cross sections were found to be $5.3 \times 10^{-19}$ $cm^2$ and $5.3 \times 10^{-18}$ $cm^2$ respectively. On this basis an experimental estimate was made of the contamination of the primary beam by $CH_2^+$ ions.

Calculations carried out on the basis of these measurements indicate that only part of the negative ions observed in the beam can result from the $CH_2^+ \rightarrow CH_2^-$ and $NH^+ \rightarrow NH^-$ processes; hence part of the effect is due to the $N^+ \rightarrow N^-$ process, the cross section of which is estimated as $1.1 \times 10^{-22}$ $cm^2$.

The extremely small value for the $\sigma_{1-1}$ cross section for the $N^+ \rightarrow N^-$ process indicates that the binding energy of the excess electron in the $N^-$ ion must be very small, in agreement with the estimates of this quantity made on the basis of empirical formulas for isoelectronic sequences and the nature of the electronic configuration of this ion.[17]

In addition to the measurements described above an attempt was made to observe negative molecular nitrogen ions; the $N_2^+ \rightarrow N_2^-$ process in krypton was used for this purpose. However, no $N_2^-$ ions were observed; it follows that the cross section for the $N_2^+ \rightarrow N_2^-$ process is smaller than $1.5 \times 10^{-22}$ $cm^2$.

*$CH_2^-$ ions have been observed by a number of authors[14-16] and the $NH^-$ has been observed by Dukel'skiĭ and Zandberg.[3]


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