Formation of metastable N^- ions by dissociative collisions of N_2, NO, and NO^- molecular projectiles in Ar gas targets

O. Heber,* I. Gertner, I. Ben-Itzhak,† and B. Rosner
Department of Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel
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The existence of metastable states of negatively charged nitrogen ions N^- has been confirmed following dissociation of (0.5–1.0)-MeV N_2, NO, and NO^- molecular projectiles in an argon gas target, by two different experimental procedures. The most intense reaction is the dissociation of NO^- after electron capture, $NO^- \rightarrow N^- + O^-$, which has a cross section of the order of 10^{-20} cm^2. This cross section is much larger than that of the reaction $N_2 \rightarrow N + N^-$ and comparable with that of $O_2^- \rightarrow O^- + O^-$. A lower limit of 1.6 μsec was obtained for the mean lifetime of the N^- ions.

I. INTRODUCTION

The existence and structure of negatively charged nitrogen ions N^- has been the subject of several theoretical[1–3] and experimental[4–9] studies. Schaefer *et al.*[1] predicted an unstable $N^-(^3P)$ ground state and two metastable states $N^-(^1D)$ and $N^-(^1S)$. Other calculations[2,3] gave the same metastable states.

An early work by Fogel *et al.*[4] reported an extremely small cross section in the order of 10^{-22} cm^2 for the $N^+ \rightarrow N^-$ double-electron-capture process for 34-keV N^+ ions on Kr. A later attempt to reproduce this result by Hird and Ali[5] found that either N^- has a lifetime of less than 50 nsec or the cross section is less than 10^{-22} cm^2. A recent experiment by Bae *et al.*[6] has found no N^- in two-step electron capture of N^+ on Cs vapor at an energy lower than 2 keV.

Using an electron-impact-excitation technique Hiraoka *et al.*[7] were able to measure N^- ions after impinging electrons of energy 5–40 eV on NO and N_2-O_2 mixture targets. The apparent potential measured was compatible with electron attachment by NO and N_2 to produce $N^-(^1D)$ on dissociation. An attempt to confirm the electron-impact result by Klots and Compton[8] yielded null results. Because of all these conflicting experimental results it is of great importance to measure the existence of N^- and its mean lifetime.

In this paper we report our observation of N^- ions after dissociative collisions of (0.5–1.0)-MeV N_2, NO, and NO^- molecular projectiles by single and multiple collision in an argon gas target. We also report our lower-limit mean-lifetime measurement for the N^- metastable state.

II. EXPERIMENTAL SYSTEM

A schematic diagram of the experimental setup used with our 1-MV Van de Graaff accelerator, which allows the selection of positive as well as neutral or negatively charged molecular and atomic projectiles, is shown in Fig. 1.

Positive ions accelerated to the terminal voltage were momentum-analyzed by an analyzing magnet and directed through a set of defining slits to the reaction volume of a gas cell. If negative ions were needed, such as NO^- molecular ions, the pressure in the differentially pumped charge-exchange region I was slightly increased to induce charge-exchanging processes in the NO^+ beam coming from the accelerator. The field of the analyzing magnet is reversed and adjusted to direct the negatively charged NO^- beam produced toward the gas cell.

Neutral beams could be obtained by increasing the pressure in the differentially pumped charge-exchange region II beyond the analyzing magnet, inducing charge exchange in the primary positive beam. With the aid of an electrostatic deflector D0 positioned near the gas target cell, all charged ions were diverted sideways allowing only the neutral fraction to reach the gas target volume.

The gas cell, which contains the target gas, has a cylindrical shape, 50 mm long and 25 mm in diameter, with variable entry and exit apertures. The entrance aperture, S2, typically had a diameter of 1.0 mm and the exit aperture, S3 of 3.5 mm. The cell was mounted over a differentially pumped region between S1 and S4 apertures. The working pressure in the gas cell was between 1 and 10×10^{-3} Torr. It could be raised to much higher values without significant change of pressure in the rest of the system.

The reaction products emerging from the gas target entered a 75-cm-diam vacuum chamber, where they were separated according to their charges by the horizontal deflector D2 and detected by a set of several solid-state detectors. This deflector was carefully positioned as shown in Fig. 1(b) so that no charged fragment would be scattered on it. A small vertical deflector D1 was also mounted at the entrance of the chamber to assure proper vertical geometry of the system.

The surface barrier (SB) detectors have the advantage that the signal is proportional to the particle energy with a typical resolution of the 30 keV at the energy range of our work and 100% detection efficiency.[10] The electrostatic analyzer combined with energy detection enables separation of fragments having different E/q in a well-defined geometry.

The fragments of the dissociated molecules have some kinetic energy in the rest frame of the molecule. As a

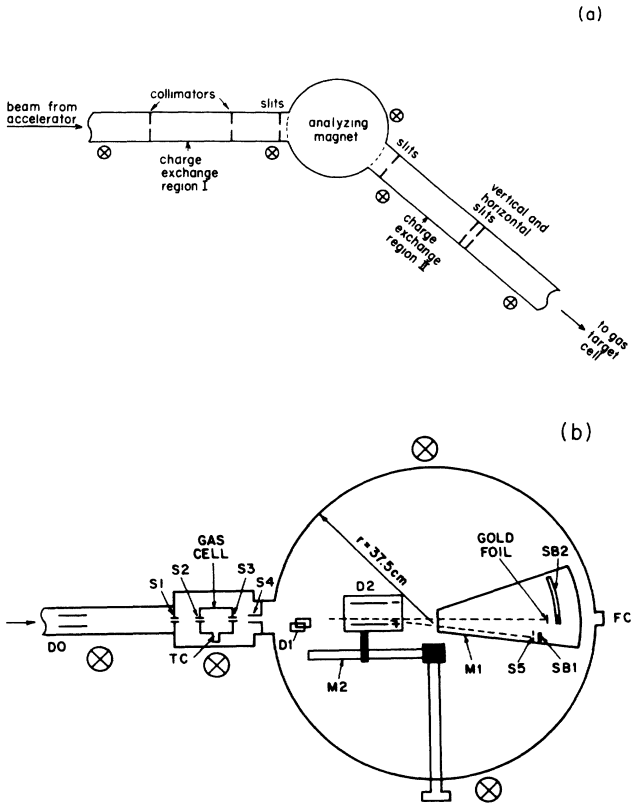

FIG. 1. Experimental setup. (a) Schematic diagram of the charge-exchanging regions used to form negative (region I), and neutral (region II) molecular beams. (b) Geometry of the differentially pumped gas cell, the deflector D2, and the detectors SB1, SB2 for the analysis of negatively charged outgoing particles. TC is a thermocouple vacuum gauge, M1 and M2 are movable arms, and FC is a Faraday cup.

consequence, the beam diverges slightly causing a bigger spot on the detector without a detectable broadening of the energy spectrum. A tight N_2 beam with a cross-sectional area of less than 1 mm^2 would form approximately a 25-mm^2 spot on the detector due to the internal kinetic energy of the order of 10 eV. Using a detector with a large active area, we can collect all fragments coming with the same E/q. Our other method uses a small detector, having a better energy resolution, and a narrow slit S5 on it, so that we can separate fragments in the order of 30 keV apart by scanning the deflector voltage. Both methods are used as described later.

III. $N_2 \rightarrow N^-$ EXPERIMENT

A 1-MeV beam from the accelerator had been partially neutralized by electron capture without dissociation in the poor-vacuum region II mentioned in the previous paragraph. By applying an electrostatic field between the plates D0, only the neutral beam containing N_2^0 and N^0 molecular and atomic projectiles could enter the argon gas target cell. Following the charge-exchange and dissociation reaction several different charge states emerged through S3 and were deflected by D2 to the proper detector for further analysis.[11] As only the negative-ion fraction was of interest in the present study, only two detectors have been used. Detector SB1 counted the number of ions that were negatively charged during their passage through D2, and detector SB2, which was mounted in the exact forward direction, monitored the neutral-beam intensity. When an intense beam was used, a thin gold foil was inserted in front of this detector to block the main beam so that only particles scattered at angles near 20° were measured, in order to reduce the counting rate.

Special care must be taken in the analysis of the negative fraction of the N^- ions due to the existence in the primary beam of small amounts (about 10^{-4} of the N_2^+ beam) of CO^+ molecular ions from the high-pressure gas tank surrounding the ion source. Having the same molecular mass and charge, they follow similar trajectories to the gas cell, and because of the much higher cross section for the production of the O^- and C^- ions, the number of these impurity ions is not small. However, with well-defined geometry, the electrostatic analyzer D2 can separate them, as the energies of the C^-, N^-, and O^- ions are $\frac{3}{7}E$, $\frac{1}{2}E$, and $\frac{4}{7}E$, respectively, where E is the energy of the incoming molecular beam. The energy signals as detected by the SB1 detector thus differ considerably.

In Fig. 2(b) we present the energy spectrum of detector

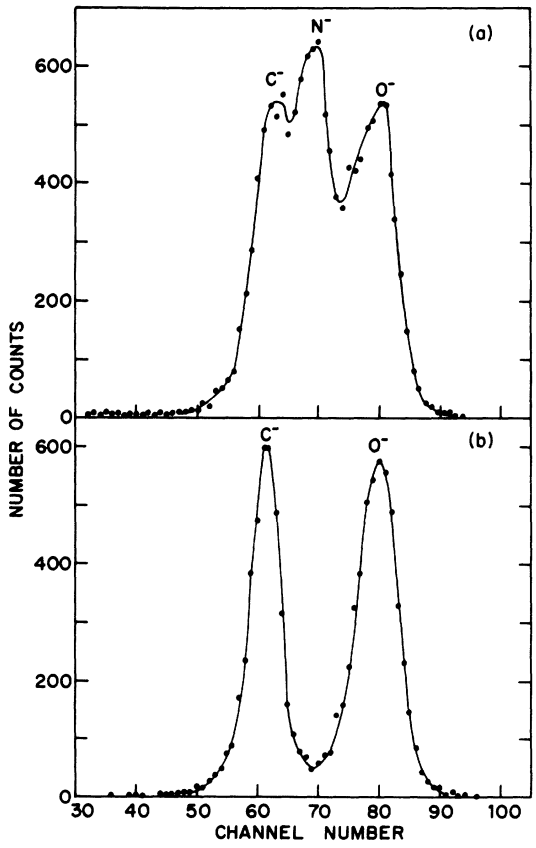

FIG. 2. The energy spectra of O^-, N^-, and C^- (a) with the slit S5 which reduces the amount of O^- and C^- that can reach the detector SB1 and (b) without the slit S5.

SB1 when the slit S5 enables all C^-, N^-, and O^- to hit the detector. In order to reduce the collision rate of C^- and O^- we used a narrower slit so that only a small fraction of C^- and O^- could go through. This energy spectrum is shown in Fig 2(a) and the N^- peak can be clearly seen. The relative yield of these negative ions can be seen in Fig. 3.

We measured the area underneath each peak in the energy spectrum as a function of the deflection voltage using another detector and a narrower slit S5 on the SB1 detector. The total number of counts for each of the three components (C^-, N^-, and O^-) normalized to the neutral-beam intensity is shown in Fig. 3 as a function of the deflection voltage on D2. The maximum count rate of C^- ions is obtained at 6-kV deflection voltage with the center of gravity (c.g.) in channel 147 in the energy spectrum. The corresponding values for the N^- and O^- ions were 7.1 and 8.1 kV, respectively, with c.g. values in the 173 and 191 channels, respectively. No more peaks of other negative ions were detected.

The possibility of the existence of other interfering negative molecular ions, such as CH_2^- from the dissociation of C_2H_4 or CD^- from C_2D_2, was rejected because of zero counts obtained for deflection voltages and energy signals for any other fragments of those molecules.

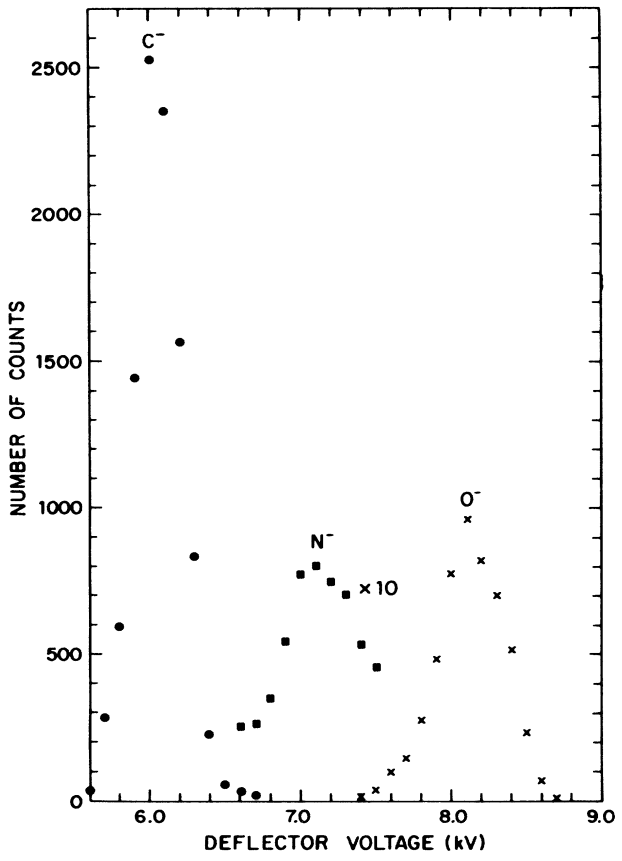

FIG. 3. The intensity C^-, N^-, and O^- ions detected by the narrowly collimated SB1 detector as a function of the D2 deflector voltage. Each set of points comes from a different region in the energy spectrum and only occurs when there exists a peak in this region. ●, c.g., channel 147; ■, c.g., channel 173; ×, c.g., channel 191.

IV. $NO \rightarrow N^-$ AND $NO^- \rightarrow N^-$ EXPERIMENT

In order to confirm the existence of the metastable N^- ion further experiments were performed, looking for N^- fragments formed by dissociation of other molecules. Use of NO and NO^- molecular beams avoids possible ambiguity due to CO^+ impurity molecules, which could not be separated from the main N_2 beam in the previous experiment. The energy spectrum of the negatively charged fraction obtained by the SB1 detector revealed not only an energy peak of the molecular fragments but also a full-energy peak. The partial-energy peak is mainly, due to the O^- ions, occurring in large numbers relative to the N^-. Without the slit S5 the two peaks could not be separated by the large-active-area detector used (300 mm^2), which has an energy resolution of only 50 keV. The reason for removing the slit S5 and using a larger detector was to increase the relative yield of full-energy events. A full-energy peak is a signature of all the fragments of the molecule hitting the detector simultaneously. These events indicate the dissociation of the molecules NO and NO^- into $N^- + O^-$ following a double- and a single-electron capture, respectively. With a big enough detector all N^- and O^- fragments were collected for the same voltage on D2.

The dissociation into the $(N^- + O^-)$ channel is expected to be much more probable if negatively charged NO^- molecular ions are used as projectiles because only a single-electron capture is needed during the dissociative collision. This turned out to be the case and a cross section as large as $\approx 10^{-20}$ cm^2 was determined for $NO^- \rightarrow N^- + O^-$.

Although doubly charged negative molecular ions, e.g., NO^{2-}, have never been reported, they will also appear as full-energy signals in the SB1 detector spectrum if they exist. To distinguish between the NO^{2-} molecules and the $(O^- + N^-)$ dissociation products, the mesh technique was employed.[12] In this method a fine mesh with transmission $t = 0.2$ was used. When placed in front of the detector, it reduces the number of counts in the full-energy peak by a factor of t, if the counts are due to the NO^{2-} molecular ions. However, if the full-energy peak is due to detection of the dissociated O^- and N^- ions arriving together, the number of counts in the full-energy peak will be reduced by a factor of t^2. The result of such analysis confirmed the nonexistence of NO^{2-} within statistical error, thus confirming the formation of N^- ions.

Another possibility, $C^{18}O^-$, was rejected because the probability of these two fragments to hit the detector at the same deflection voltage is low. Furthermore ^{18}O is only 0.2% of the oxygen gas and the full-energy peak at 20 mTorr is about 0.1% of the total fragment yield. Therefore no other molecular fragments can be in the full-energy peak.

This type of measurement was carried out over a wide range of gas target pressures, in the single-collision region and is shown in Fig. 4. It can be seen that the relative yield of $[N^- + O^-]/[NO^-]$ is linear in this Ar pressure

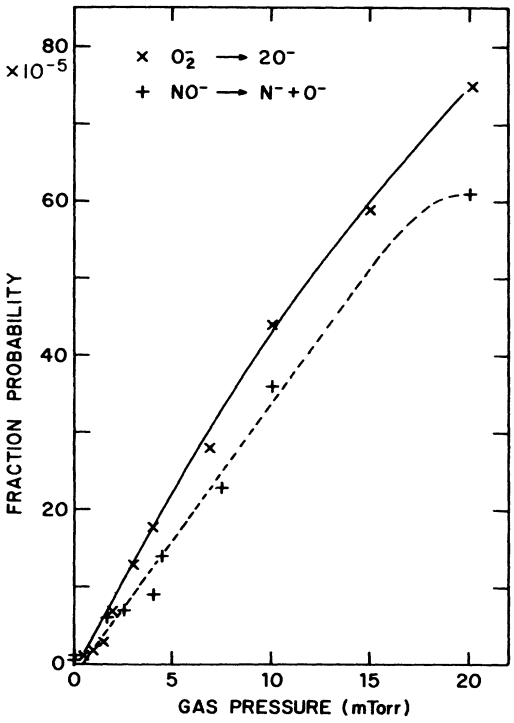

FIG. 4. The probability for formation of the ($N^- + O^-$) fraction from $NO^- + Ar$ at 600 keV and the probability for $2O^-$ fraction from $O_2^- + Ar$ at 600 keV in different gas target pressures.

range and is quite similar to the relative yield of $[O^- + O^-]/[O_2^-]$, both of them at 600 keV projectile energy.

V. $N^+ \rightarrow N^-$ AND $N^0 \rightarrow N^-$ EXPERIMENT

Single- and double-electron-capture reaction on N^0 and N^+ ions, respectively, to form negative N^- ions were attempted at several projectile energies between 0.5 and 1.0 MeV, but yielded null results. Fogel *et al.*,[4] working at projectile energy of 34 keV, reported a very small cross section of about $\sigma \approx 1.9 \times 10^{-22}$ cm^2 for the $N^+ \rightarrow N^-$ process in gaseous targets. Our null results indicate that the $\sigma_{1,-1}$ cross section decreases considerably at our higher energies.

VI. MEAN-LIFETIME MEASUREMENTS OF N^-

The mean lifetime of the N^- ions was measured by comparing integral intensities under the N^- peaks at different positions of the deflector D2, which was free to move along a 16.6-cm path along the direction of the beam [Fig. 1(b)]. The mean lifetime T of a short-lived ion produced in the gas cell could be determined by measuring the ratio between the number of counts reaching detectors SB1 and SB2, respectively, as a function of the displacement of the D2 deflector. The self-evident formula

$$T = \Delta l / v [\ln(K_1/K_2)]^{-1}$$

is used, where Δl is the displacement of the deflector between measurements 1 and 2, v the velocity of the ions, and K_1, K_2 the normalized integral intensities 1 and 2, respectively.

It should be noted that the N^- peak may include a contribution of N neutral species resulting from N^- autodetachment after passing through D2. Nevertheless, the integral intensity under the N^- peak is exactly the number of N^- ions that were negative in the deflector D2 and this number should be used for the mean lifetime derivation.

In the present experiment the numbers K_1 and K_2 were equal within the experimental error of 4% for the full displacement range of the deflector. This determines therefore only a 1.6-μsec lower limit for the mean lifetime of N^-. This long mean lifetime confirms that N^- can be formed in a metastable state.

VII. DISCUSSION

The observation of negatively charged N^- ions in the dissociation of the N_2, NO molecules, and especially the NO^- molecular ions, confirms N^- existence as reported by the capture of low-energy electrons.[4] The yield of N^- ions observed in the dissociation of NO or NO^- molecules is much smaller compared to the number of O^- ions observed in this process. This should not be surprising, because the ground state of O^- is stable, whereas calculations done by Bunge *et al.*[3] conclude that the ground state of $N^-(^3P)$ is unstable and can decay by a fast $E1$ transition to the ground state of the neutral nitrogen atom. This was also experimentally observed by Mazeau *et al.*[13] by measuring the width of the autodetachment energy from the shape resonance. However, according to theory[1,2] at least two metastable states of the negative nitrogen ion exist, the $N^-(^1D)$ and $N^-(^1S)$ states, for which an $E1$ transition is forbidden. These states may lose an electron to form the neutral atom with a much lower probability by spin-orbit or spin-spin coupling. In fact, Hiraoka *et al.*[7] claimed that a similar decay mechanism applies for the $He(^4P)$ metastable state, for which the shortest mean lifetime of 11 μsec was measured.[14] Our result of $T > 1.6$ μsec for both or at least one of the metastable states of N^- is in agreement with the above considerations.

There is a significant difference between the population of the low-lying metastable state of N^- by dissociative collisions of fast-moving molecules as compared to the low-energy electron-capture process. In the first case the negative ions may be formed in a great number of excited states. Some of these states will decay by photon emission to the metastable states and others will lose their extra electron faster by an electromagnetic transition. On the other hand, the second reaction is much more selective in the state population.

The negative nitrogen was detected as a single negative fragment coming from the dissociation of the diatomic molecule as well as together with the other negative fragment. The second case was an immediate dissociation of a doubly negative molecule formed by electron capture. For the N_2 projectiles we were not able to resolve this

channel ($N_2 \rightarrow N^- + N^-$) from the background but for NO projectiles it was detectable even though in both cases it is a two-electron-capture process. The higher background in the N_2 case is due to CO contamination in the beam. For NO^- projectiles only one electron capture is needed to dissociate the molecular ion into $N^- + O^-$. This process has the biggest cross section for forming N^- in the 0.5–1.0-MeV energy range of the processes we studied. The slope of $N^- + O^-$ formation by single-electron capture as a function of pressure is similar to that of the formation of $O^- + O^-$ in the same process as can be seen in Fig. 4. This similarity implies that the cross sections have the same order of magnitude.

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*Present address: Cyclotron Institute, Texas A&M University, College Station, TX 77843.

†Present address: Department of Physics, Kansas State University, Manhattan, KS 66506.

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