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Reexamining if long-lived N^- anions are produced in fast dissociative electron-capture collisions

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The existence of long-lived states of N^- has been a topic investigated with conflicting experimental results. Highly excited spin-aligned states, however, were predicted to have long lifetimes and even be stable against autodetachment. We repeated the measurements of N^- formation in 0.9 MeV N_2+Ar charge-exchange collisions and found that the ions reported previously as N^- [Heber *et al.*, Phys. Rev. A **38**, 4504 (1988)] are an O^- fragment from a 0.9 MeV H_2NO^+ impurity beam. This result adds to the comulating data indicating that N^- is not going to affect carbon dating measurements using accelerator mass spectrometry.

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I. INTRODUCTION

The existence and structure of negatively charged nitrogen ions N^- have been the subject of several theoretical [1–3] and experimental [4–9] studies. Schaefer *et al.* [1] predicted that the $N^-(2p^4;{}^3P)$ ground state is unstable against autodetachment and that the two excited states $N^-(2p^4;{}^1D)$ and $N^-(2p^4;{}^1S)$ are metastable against autodetachment because this transition is spin-flip forbidden. Other calculations [2,3] gave the same metastable states.

The interest in metastable states of N^- has increased in recent years, because of the improvement of carbon dating using accelerator mass spectrometry (AMS) techniques. In this method the sample is introduced into a negative ion source and the ratio of ${}^{14}C^-$ to ${}^{12}C^-$ is measured with high precision after acceleration through a tandem accelerator (see, for example, Ref. [10]). If N^- has long-lived states that survive the flight time through a typical AMS system (i.e., of the order of a few microsecond), it will increase the background, thus affecting the longest lifetime one can measure as well as the accuracy of the measurement. This is because it is not easy to distinguish ${}^{14}C^-$ from ${}^{14}N^-$ even with the high resolution of most AMS systems [10]. In contrast, metastable state of N^- with lifetimes much smaller than a microsecond will have no impact on AMS carbon dating and thus are referred to in this context as short lived.

New theoretical treatments of the structure and decay rate of N^- states belonging to the $2p^4$ configuration by Cowan *et al.* [11] suggest that the lowest-lying excited states have short lifetimes, 130 and 70 ps for the metastable ${}^1D$ and ${}^1S$ states, respectively. These values are much shorter than earlier calculations that suggested lifetimes of the order of 1 μs (see, for example, Boldt [12]). The lifetime Cowan *et al.* [11] calculated for the unstable ${}^3P$ ground state of N^-, 38 fs, is in excellent agreement with the measurements of Mazeau *et al.* [13,14]. In contrast to the short lifetimes of the low-lying excited states, low-lying maximum spin states, namely, the highly excited $(1s\ 2s\ 2p^3\ 3s\ 3p^2)$ ${}^9P^o$ and $(1s\ 2s\ 2p^3\ 3p^3)$ ${}^9S$ states of N^- embedded in the continuum, were predicted to be stable against autodetachment by Piangos and Nicolaides [15]. Their findings also suggests that highly excited states with high spin, though below the maximum value, might be long lived. The question is *how do such high spin states form*, and explicitly for carbon dating measurements, *can such long-lived states of* N^- *be formed in the reactions taking place in a negative ion source?*

Experimental evidence about the existence of long-lived states of N^- is conflicting. It seems that most measurements in which N^- was found were repeated by others with null results, although it is not always easy to find the latter reports, because null results are seldom reported in major publications. Due to the importance of this issue, we give here a summary of the experimental evidence thus far.

An early work by Fogel *et al.* [4] reported an extremely small cross section on 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 ns or the cross section is much less than 10^{-22} cm^2. An experiment in the mid 1980s by Bae *et al.* [6] found no N^- in two-step electron capture of N^+ on Cs vapor at an energy lower than 2 keV. This suggests that long-lived states of N^- are not formed in slow double-electron capture reactions.

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 $N^-({}^1D)$ upon dissociation. An attempt to confirm the electron-impact result by Klots and Compton [8] yielded null results. This suggests that long-lived states of N^- are not formed by electron attachment.

In contrast to the conflicting reports about N^- formation above there are a couple of measurements that have not been refuted so far to the best of our knowledge.

The more recent one by Muller *et al.* [16,17] reports the formation of the metastable ${}^1D$ state of N^- by electron capture in grazing incidence collisions on a surface partly covered with cesium. The energy of the detached electrons was

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found to be 1.4±0.1 eV in agreement with theory. An upper limit of 200 ns was determined for the lifetime of this state, for which theory predicts 130 ps [11]. They have seen no evidence for the other expected low-lying metastable state (the ^1S), which is predicted to have a lifetime of 70 ps [11]. The difference between the lifetimes of these two metastable states is too small to be the reason for not observing the ^1S state [18]. On a practical note, the experimental evidence of Muller *et al.* [16,17] suggests that the metastable ^1D state of N^- will not affect AMS carbon dating measurements, though a mean lifetime of about 100 ns, resulting in a reduction factor of the order of 10^{-3}, might still have a non-negligible contribution if large amounts of this state are produced initially.

Our older reported observation of long-lived N^- ions was in dissociative charge-exchange collisions of (0.5–1.0) MeV N_2, NO, and NO^- molecular projectiles with argon atoms [19]. The measured long-lived states were associated with the metastable ^1D and ^1S states whose lifetimes were estimated, at that time, to be of the order of microseconds [12]. It has been recently suggested that "*past publications concerning long-lived species of N^- in fact must have involved some other (most likely molecular) ion*" [11]. We revisited our earlier work motivated by the recent publications [11,16–18], and the renewed interest in long lived N^-, mainly driven by the impact of long lived N^- on carbon dating. Repeating our measurements was further motivated by the new theoretical prediction of stable maximum-spin states of N^-, thus suggesting that there are long lived high-spin states [15]. Therefore, high-spin states of N^- provide a new interpretation of our "old" measurements of long lived N^-. If this is the case, then, dissociative charge exchange will become the first possible mechanism for forming such exotic atomic states. In the measurements reported in this paper, we took advantage of the improved energy resolution of particle detectors and used a few recently reported experimental methods that can help one distinguish between an atomic and molecular ion [20–22].

II. EXPERIMENT

The experimental setup and method are the same as used in our early measurements (see Fig. 1 of Ref. [19]), and thus they are described only briefly. The improvements, in contrast, are explained in more detail.

To study the $N_2 + Ar \rightarrow N^-$ reactions, a beam of N_2^+ was accelerated to 900 keV, momentum analyzed, and directed to the target by a 15° analyzing magnet. Before reaching the target the N_2^+ beam was neutralized in a small gas cell immediately following the magnet and an electrostatic field was used to divert all ions, thus allowing only the neutral N and N_2 beams to go through the target cell, which has small entrance and exit collimators (0.5 and 1.0 mm, respectively). Note that the neutral fragment beam is greatly reduced because the entrance collimator is much smaller than the radius of the dissociation sphere, i.e., the sphere formed by the dissociation velocity of the fragments. Furthermore, the N beam plays no role as we have shown previously [19], because N^- production in N+Ar single electron capture collisions is negligible. The target pressure (Ar gas) in the differentially pumped 50 mm-long target cell was a few millitorr while the pressure in the rest of the system was better than 1×10^{-6} Torr.

The reaction products emerging from the target cell were separated according to their energy to charge ratio E/q by a horizontal electrostatic deflector. Proper vertical alignment of the beam was assured using a vertical electrostatic deflector. The negative ions were detected by a pin-diode detector placed at about 5° off the beam axis. The yield of negative ions was normalized to a constant number of neutral fragments detected by a similar detector placed on the beam axis. It is important to note that these detectors are 100% efficient, and more importantly, they provide a signal proportional to the energy of the detected ion. This additional information helps in identifying the ion species. The detectors used in the recent measurements have better energy resolution for the ions of interest (C, N, O at about 450 keV) than the surface barrier detectors used previously, mainly because of their thinner dead layer. The improved resolution played a crucial role in these measurements as discussed later.

To distinguish between atomic and molecular ions following the same trajectory (i.e., having the same E/q) we used the "foil-mesh" method described in detail elsewhere [20–22]. Briefly, a thin foil is placed on the trajectory of the ion of interest a few centimeters in front of the detector and the detector is covered with a low transmission mesh (about 30%). Both the foil and mesh could be placed in or out using a manipulator. The thin foil will lower slightly the energy of the atomic ions and spread them on a larger spot on the detector while the mesh will just reduce the count rate. In contrast, all the molecular ions will dissociate while traversing the foil and their fragments will either hit the detector or be stopped by the mesh. As a result there will be a few peaks in the energy spectrum. For a heteronuclear diatomic molecule, for example, there will be one peak for each fragment and one for a simultaneous hit of both fragments in which case the whole energy of the molecular ion is detected. The thin foil was placed on a 0.8 mm wide slit such that it could be placed on the trajectory of only one ion, such as N^-, while the C^- and O^- on both sides were stopped.

To summarize, the experiment was repeated as reported previously [19], but with improved energy resolution and using the foil-mesh combination to exclude molecular ions as presented in the following section.

III. RESULTS AND DISCUSSION

The main obstacle in the measurement of N^- production in $N_2 + Ar$ collisions was, as in our previous measurement, the CO^+ contaminant beam originating from dissociative ionization of CO_2 leaking into the ion source from the high-pressure CO_2 buffer gas in the tank surrounding the ion source [19]. Having the same molecular mass and charge, they follow similar trajectories to the target gas cell. Even though the CO^+ beam is very small in comparison with the primary beam (less than 10^{-4} of the N_2^+ beam), the stability of both C^- and O^- in their ground state makes their yield orders of magnitude higher than that reported for N^- [19].

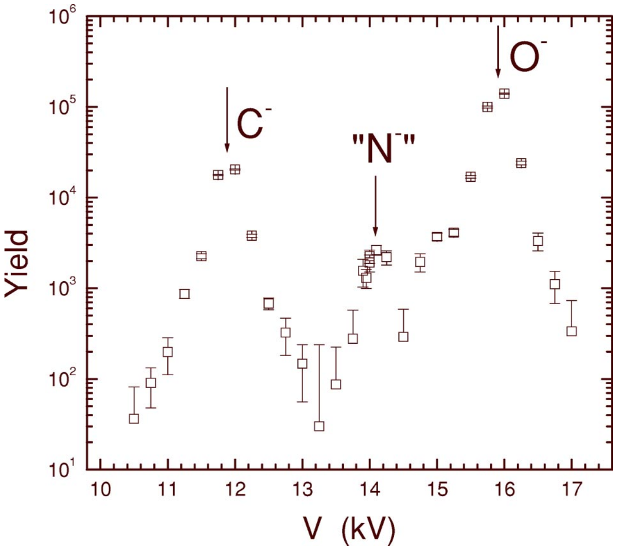

FIG. 1. The intensity of C$^-$, apparent N$^-$ (denoted as N$^-$ in the figure), and O$^-$ ions detected by the narrowly collimated detector as a function of the deflector voltage.

The contaminant C$^-$ and O$^-$ ions can be separated, however, from the N$^-$ ion of interest by their different trajectory, 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. In addition, they can also be distinguished by their different energy spectra, but that separation is not as clear as the one accomplished by a voltage scan on the deflector shown in Fig. 1. This figure is similar to the one presented in our earlier work (Fig. 3 in Ref. [19]), and it shows the yield of the new negative fragments data relative to the neutral fragments yield. A clear peak can be seen between the large peaks associated with the C$^-$ and O$^-$ contaminant ions, which falls at $E/2$ and was thus identified as "N$^-$." Furthermore, the energy spectrum measured at $V \simeq 14$ kV (where this negative-ion peaks in Fig. 1), shown in Fig. 2, is also about 450 keV as expected for a N fragment of a 900 keV N_2 molecule. It is important to note that the results reproduced nicely the same results as seen in the past though the experimental setup is not identical, however, one has to be careful before associating this $E/2$ peak with long-lived N$^-$ states in view of recent theoretical and experimental work [11,16].

It has been suggested recently that this negative-ion is most likely a molecular ion and not N$^-$ [11]. This possibility, in particular that the molecular ion, is CH_2^- from the dissociation of C_2H_4 or CD$^-$ from C_2D_2, was rejected by Heber *et al.* [19] because no light fragments of those molecules were seen in a complete voltage scan. One should note, however, that such a test does not directly verify that the negative ion is atomic. To directly verify that the negative ion claimed to be N$^-$ is atomic and not molecular, we placed a thin foil on the N$^-$ trajectory only, and measured the energy spectrum with the detector covered with a 30% transmission mesh (see Sec. II), as shown in Fig. 2. One can clearly see that the only impact of the foil and mesh combination (beside the reduction in yield) is an energy shift of about 100 keV, which is the energy loss expected for 450 keV nitrogen ions. If this ion was a molecular ion, like CH_2^-, there should have been more than one peak in the energy spectrum, which is clearly not the case (see Fig. 2). Thus, it was determined that *the negative ion at half the beam energy is atomic*.

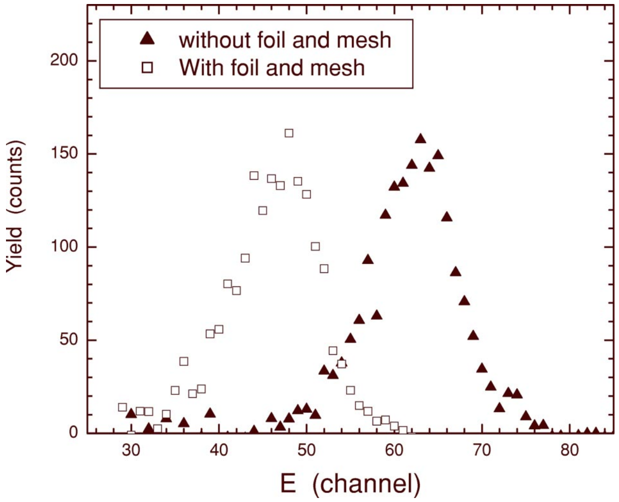

FIG. 2. The energy spectra of negative ions on the expected N$^-$ trajectory with (open squares) and without (triangles) foil and mesh. Note that only a shift to lower energy as expected for an atomic ion can be seen.

A comparison of the energy spectrum of the negative ion suspected to be N$^-$ with the energy spectrum of a N$^+$ fragment is shown in Fig. 3. It can be seen that the two peaks are similar, but that the negative-ion peak seems slightly shifted to lower energy. One would expect the two peaks to overlap if both ions were N fragments of N_2. We have checked for possible small pulse height deficit effects [23] due to local damage on the detector, but the difference between the en-

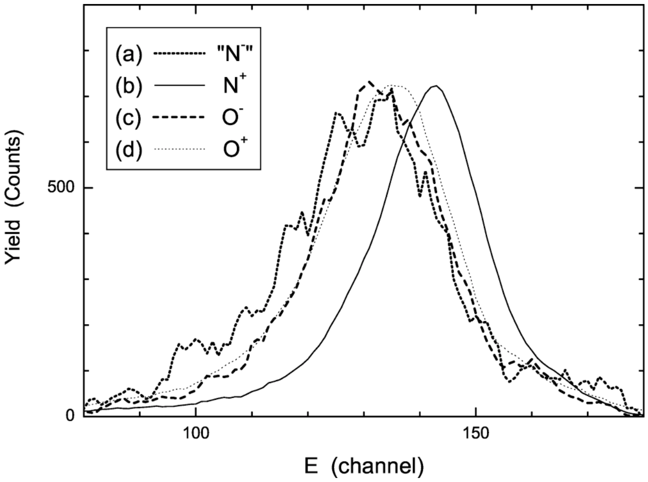

FIG. 3. The energy spectra of (a) negative ions on the expected N$^-$ trajectory, (b) N$^+$ ions, (c) 450 keV O$^-$ ions from a 844 keV NO$^+$ beam suspected to be the impurity generating the "N$^-$" signature (see text), and (d) 450 keV O$^+$ from the dissociation of a 900 keV O_2^+ beam. Note that the energy spectrum of the ions suspected as N$^-$ match the energy spectrum of the 450 keV O$^-$ and O$^+$, but it does not match the energy spectrum of the N$^+$ fragments (see text).

ergy spectra of the negative and positive ions persisted no matter where the ions were hitting the detector, thus excluding this possibility. It is important to note that the difference presented in Fig. 3 was not detectable with the detectors used by Heber *et al.* [19], and those detectors had pulse height deficit effects that were much larger than the difference shown in the figure. Furthermore, to increase the sensitivity to small energy shifts this measurement was done without the foil-mesh combination as it was already determined that the negative ion is atomic.

Given the small discrepancy between the energy spectra we carefully checked for other possibilities which are consistent with our data, that is: (i) a negative atomic fragment with half the beam energy (450 keV) hitting the detector, (ii) the mass of this ion being similar to that of C, N, or O as suggested by the typical energy loss through the thin foil, (iii) a positive parent ion with similar rigidity as a 900 keV N_2^+ being analyzed by the magnet, and (iv) a positive parent ion being accelerated by the 900 kV terminal voltage. Most possibilities are excluded by one or more of the conditions imposed on the negative fragment or its parent molecular ion, however, we have found one possible scenario which will also fulfill all the conditions.

If a H_2NO^+ molecular ion is accelerated to 900 keV then dissociates before the analyzing magnet, it produces among other fragments also 843.75 keV NO^+ ions that follow a similar trajectory through the analyzing magnet as the main 900 keV N_2^+ beam. Note that ions are separated by a magnetic field according to their momentum to charge ratio, i.e. $mv/q=(\sqrt{2mE}/q)$. The numerator is 224.5 for the main beam and 225.0 for the contaminant NO^+ (using amu for m and keV for E). This 0.5 difference is much smaller than the resolving power of our magnet-slit combination, which was about one mass unit for $m=28$ at 900 keV $[2(m+1)E-2mE=4]$. As a result of the insufficient resolution it is possible to have a small impurity of 843.75 keV NO^+ molecular ions in the beam. This impurity beam is also neutralized and directed through the target cell where the collision NO+Ar can result in some $N+O^-$ products. The energy of the O^- fragment of the NO impurity beam is exactly 450 keV, and thus it will be deflected by the electrostatic field on the same trajectory one would expect the N^- to follow. Furthermore, it will not dissociate in the foil and it will produce a similar energy spectrum as it has the expected energy of N^-. However, given the larger mass and nuclear charge of O than N one would expect a somewhat smaller signal due to larger nuclear energy loss and more energy loss in the dead layer. It is plausible that H_2NO^+ molecular ions are formed in recombination reactions between N_2 gas introduced into the ion source and water, which is a significant fraction of the residual gas. Such recombination reactions are common in the rf ion source of the accelerator used, which is known to produce a multitude of low current beams of different molecular ions, like H_3^+, He_2^+, HeH^+, and $HeNe^+$ [24–26]. The different experimental tests we impose are needed to rule out this long list of possible impurity beams.

To check this hypothesis, which assumes the production of H_2NO^+ molecular ions in the ion source without any prior evidence, we have accelerated NO^+ to 844 keV through the same geometry as used to detect the negative ions suspected of being N^-. The energy spectrum measured is shown in Fig. 3 and compared on the same figure to the energy spectrum of the ion suspected as N^-. We also show the energy spectrum of a 450 keV O^+ fragment from a 900 keV O_2^+ beam. It can be clearly seen that these three energy spectra are identical, thus suggesting that the negative ion measured with the main N_2^+ beam was a 450 keV O^- fragment produced in 843.75 keV NO+Ar collinsions and *not* N^- *as suggested previously* by Heber *et al.* [19]. Therefore, if N^- is formed in these collisions it has a much lower probability than the O^- impurity and it cannot be seen in this experiment. This test shows that H_2NO^+ molecular ions are most likely produced in the ion source, however, the identity of the parent molecule resulting in 450 keV O^- fragments is secondary.

The null results of the experimental search for long-lived states of N^- reported here as well as previous experimental [16,17] and theoretical [11] work brings one to the conclusion that metastable states of N^- would not interfere with high-precision AMS carbon dating measurements. However, the apparent N^- signal produced from the fragmentation of H_2NO^+ should be considered and excluded in AMS carbon dating studies, especially in setups were the resolution is limited, because of the similarity of the AMS technique and the experimental method used in the present experiment.

It is important to note that all the experimental methods used so far to produce N^- preferentially populate the ground state and a few low-lying states. The dissociative capture method studied in this work is expected to populate higher excited states, but appears to be inefficient in populating the predicted long-lived high-spin states. It is more likely that such exotic states, such as the maximum-spin state or other high-spin states of N^-, would be populated by multielectron capture reactions occurring in grazing incidence collisions between a slow bare nitrogen and a surface, especially if the spins of the target electrons can be aligned. Such experiments haven't been conducted yet to the best of our knowledge (see, for example, the review of Winter and Aumayr [27]).

IV. SUMMARY

We repeated the study of N^- formation in 900 keV N_2 +Ar dissociative-capture collisions and demonstrated that the ion previously identified as long lived N^- is a 450 keV O^- fragment produced in 843.75 keV NO+Ar collisions. The source of this 843.75 keV NO impurity beam is most likely fragmentation of a 900 keV H_2NO^+ impurity beam. The identification of the 450 keV O^- detection was made possible by the improved energy resolution of the particle detectors and the use of the foil-mesh technique that separates atomic and molecular ions. This new experimental evidence, refutes the last remaining experimental evidence of long-lived N^- states. This, together with the studies of Muller *et al.* [16,17], which set an upper limit of 200 ns on the mean lifetime, and the calculated short lifetimes of the $2p^4\ {}^1D$ and ${}^1S$ states (130 and 70 ps, respectively) of Cowan *et al.* [11], suggest that these metastable states of N$^-$ would not interfere with AMS carbon dating measurements. The production of the predicted [15] stable maximum spin states or long-lived high-spin states of N$^-$ most likely requires a different mechanism than dissociative electron capture studied in this work. One such mechanism is multielectron capture from a spin-aligned surface by bare nitrogen.

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