Search for long-lived doubly charged negative atomic ions

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We have searched for long-lived ($\gtrsim 10^{-5}$ s) doubly charged negative atomic ions produced in a high-current cesium sputter source with a tandem-accelerator-based charge spectrometer. The results of these ultrasensitive searches for doubly charged negative atomic ions of group VI B and VIII B elements, and hydrogen that can survive the acceleration to the tandem terminal, are reported. No evidence of doubly charged negative atomic ions was observed, and upper limits for the ratio of production (and survival) of doubly charged to singly charged negative atomic ions were obtained for the cesium sputter source.

The possibility of a nucleus binding $Z+2$ electrons for a sufficient time for experimental observation has motivated numerous searches[1–10] for doubly charged negative atomic ions (DNAI's). There have been apparently conflicting claims about the existence of these ions in the literature. The more recent searches[6–10] failed to observe DNAI's under conditions similar to those of earlier experiments which claimed their observation. Nevertheless, the evidence for the existence of DNAI's cannot be completely dismissed. On the theoretical side, the situation is also uncertain. Despite recent advances,[11] a first-principles proof of the maximum number of electrons a nucleus can bind has not yet been obtained, although there are some *ab initio* calculations on DNAI's of few-electron atoms, and other, less accurate, semiempirical or variational calculations of electron affinities. More importantly, reliable predictions of electron affinity and lifetime for the multitudes of excited states of doubly charged negative atomic ions are generally not available. It should be pointed out that the probability of observing DNAI's depends critically upon not only the detection sensitivity of the apparatus, but also the ability of the ion source to produce DNAI's in long-lived ($\gtrsim 1$ μs) singly or multiply excited states.

In view of the need for better experimental data, we conducted a comprehensive, highly sensitive search for doubly charged negative atomic ions of group VI B and VII B elements and hydrogen using a novel experimental technique. The experimental method used for the DNAI search is a variant of that employed earlier in our fractional-charge (quark) search experiment.[12] The schematic diagram for the experimental setup is shown in Fig. 1.

The basic idea of the experiment is as follows. A high-current cesium sputter source[13] (which employs a Cs primary beam of ~ 6 keV energy to sputter a solid sample of a few milligrams) was used to produce copious currents (up to ~ 100 μA) of singly charged negative atomic ions (X^-) and possibly also doubly charged negative atomic ions (X^{2-}). The negative ions from the source were accelerated by a 78-kV potential (the injection voltage $V_{\rm inj}$) and then analyzed by a 30° magnet before they were injected into a tandem electrostatic accelerator with the terminal voltage (V_T) at $+1.195$ MV. The 30° injection magnet [with a full width at half maximum (FWHM) $\Delta M/M$ resolution of 1.4%] was tuned to select X^{2-} ions of magnetic rigidity $\sqrt{ME}/Q$ where M is the mass, E the energy, and Q charge state. The negative ions transmitted by the magnet were then accelerated by the tandem accelerator, and stripped of several electrons, to become positive ions of various charge states, by collisions with hydrogen gas inside the tandem high-voltage-terminal stripper. [These multiple atomic collisions at MeV energies also ensured the destruction (fragmentation) of molecular ions, and the possible complication arising

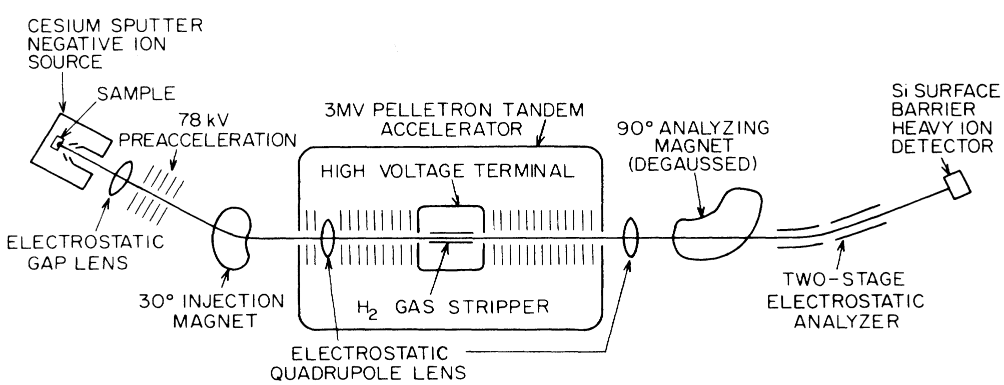

FIG. 1. Schematic diagram of the experimental setup for the doubly charged negative atomic-ion searches.

from doubly charged negative molecular ions was thus eliminated by the subsequent electrostatic analysis.] The positive ions leaving the tandem-terminal stripper were further accelerated to ground potential and, downstream from the exit of the tandem, they were analyzed by a two-stage electrostatic analyzer (ESA) whose FWHM $\Delta E/E$ resolution was about 0.4%. The ESA dispersed the positive ions according to their electric rigidity (E/Q) and, for the DNAI searches we chose to analyze charge state +1 (i.e., $X^{2-}\rightarrow X^{+}$) which has an electric rigidity $E/Q=2V_{\rm inj}+3V_T$. This choice was the most favorable for DNAI searches because the final electric rigidity for $X^{2-}\rightarrow X^{+}$ is very high and almost unique; only background ions that undergo an improbable charge-changing sequence could have nearly the same electric rigidity as the DNAI's, as explained below. Finally, the energies of the ions transmitted by the ESA were measured with a Si surface-barrier detector.

There were two significant contaminant beams that had the same magnetic rigidity as the X^{2-} beam and hence were injected into the tandem during the searches; a minute fraction of these contaminant ions eventually formed most of the background in the experiment. These contaminant beams were (a) ions (Y^-) with mass equal to, or nearly equal to one-half that of the X^{2-} ions (because of the limited resolution of the 30° magnet, negative ions of nearly the same magnetic rigidity as the X^{2-} ions could be injected into the tandem), and (b) ions (X^-) from the breakup of $X_2{}^-$ dimers upstream of the injection magnet but after the full preacceleration. (These ions would have the same mass as X^{2-} but only one-quarter of the injection energy of the X^{2-} ions, namely 39 keV.) In addition, inelastically scattered negative ions which lost some or nearly all of their kinetic energy could also be scattered through the magnet and injected into the tandem. The contaminant ions of both type (a) and (b) were injected into the tandem with charge state -1. They could reach electric rigidities close to (but smaller than) that of $X^{2-}\rightarrow X^{+}$ if they were stripped to charge state +2 at the terminal, accelerated to ground potential, and then picked up an electron to change the charge state to +1 by atomic collisions with residual gas molecules between the exit of the accelerator and the ESA (without any significant loss of kinetic energy). Thus, half-mass ions of type (a) which underwent the charge-changing sequence $Y^-\rightarrow Y^{2+}\rightarrow Y^+$ would have an electric rigidity of $V_{\rm inj}+3V_T$, while the dimer-breakup ions of type (b) with the charge-changing sequence $X_2{}^-\rightarrow X^-\rightarrow X^{2+}\rightarrow X^+$ would have an electric rigidity of $V_{\rm inj}/2+3V_T$. The differences between the electric rigidities of these background beams and the DNAI's arise entirely from the difference in their injection energies; thus, the separation of the background ions from the DNAI's depended upon the ratio of the voltages $V_{\rm inj}/V_T$ and the resolution of the ESA. Because of the limited resolution of the ESA and the relatively small $V_{\rm inj}/V_T$ ratio, the tails of the background ion peaks were seen by the Si detector when the ESA was tuned for the $X^{2-}\rightarrow X^{+}$ searches. However, there were two additional techniques that helped us to distinguish the true signals of the DNAI's from these background counts caused by rare charge-changing sequences. First, because of the well-known pulse-height defect[14] of the Si heavy-ion detectors, the pulse height of a lighter ion was larger than that of a heavier one at the same incident energy. Hence, the background counts caused by the half-mass ions [type (a)] were usually well separated from the possible DNAI's in the energy spectra. Second, the count rate at the appropriate energy window of the true DNAI's should peak at the correct ESA setting. By scanning the ESA voltage, the background tails due to the dimer breakups or the half-mass ions could be identified easily.

A typical experiment search for DNAI's began with the generation of negative ion beams from a suitable sample material for the Cs sputter source. Known beams of X^- ions were tuned through the injection magnet (magnetic field measured by a Hall probe), the accelerator, and the ESA to calibrate the settings for beam-transport elements. A weak beam of $X^-\rightarrow X^{2+}\rightarrow X^+$ (with an electric rigidity of $V_{\rm inj}+3V_T$) was then tuned in to calibrate the Si energy detector as well as the ESA and the electrostatic quadrupole lens. Based on these calibrations, the appropriate settings for the injection magnetic field, the ESA, and the quadrupole lens could be accurately obtained for the $X^{2-}\rightarrow X^{+}$ (DNAI) search. The X^- beam intensity was monitored before and after each run. Runs were also taken with ESA settings both above and below the setting for DNAI's. As expected, the count rate peaked at electric rigidities $V_{\rm inj}/2+3V_T$, and $V_{\rm inj}+3V_T$ in the appropriate energy windows, corresponding to the dimer breakup and half-mass backgrounds discussed above. Sometimes an increase in the count rate of the half-mass energy peak was observed at an electric rigidity of $3V_T$ and this was attributed to the injection of inelastically scattered negative ions with nearly zero injection energy. The charge state +1 yields from the tandem stripper for the $X^{2-}\rightarrow X^{+}$ searches at $V_T=+1.195$ MV were estimated by measuring $X^-\rightarrow X^+$ yields at $V_T=+2.39$ MV; the latter yields ranged from 10% to 20% in our experiment. A conservation figure of 10% was adopted for the $X^{2-}\rightarrow X^{+}$ yields for all ions. The choice of hydrogen as the stripper gas and the low terminal voltage were partly motived by the desire to have good $X^{2-}\rightarrow X^{+}$ yields.

Within the limit imposed by the fluctuations of the ion-source output, statistical uncertainties, and the slope of the background tail as a function of ESA voltage, no excess of counts in the appropriate energy window for the $X^{2-}\rightarrow X^{+}$ searches was observed. Thus, a conservative upper limit for the true DNAI total count was taken to be the background-subtracted number of counts in the full-mass energy peak at the ESA setting for $X^{2-}\rightarrow X^{+}$. This, together with the X^- current, the run time, and the $X^{2-}\rightarrow X^{+}$ yield, allowed us to set an upper limit for the ratio of abundances $[X^{2-}]/[X^-]$. The results of the search for long-lived DNAI's which can survive the electric field of the tandem accelerator are tabulated in Table I. The sensitivity for DNAI searches was highest for H^{2-} because of the absence of the half-mass background ions and the complete elimination of $H_2{}^-\rightarrow H^-$ background (since H^- cannot be stripped to charge state +2). No counts were observed for the H^{2-} search in 1897 s with a

TABLE I. Summary of the results for the search of long-lived doubly charged negative atomic ions. No positive evidence for these negative ions was seen in our experiment and the detection sensitivity for the doubly charged negative atomic ions is expressed as the upper limit of the ratio of doubly charged to singly charged negative ion abundances, $[X^{2-}]/[X^-]$.

Element (X)	Source sample	$[X^{2-}]/[X^-]$
O	Al_2O_3	$\leq 1.1\times10^{-16}$
S	PbS	$\leq 7.1\times10^{-14}$
Se	Se	$\leq 5.8\times10^{-14}$
Te	Te	$\leq 8.8\times10^{-13}$
F	CaF	$\leq 7.4\times10^{-16}$
Cl	BaCl	$\leq 8.0\times10^{-15}$
Br	NaBr	$\leq 2.0\times10^{-13}$
I	KI	$\leq 1.3\times10^{-12}$
H	TiH	$\leq 1.0\times10^{-16}$

H^- current of 7.3 μA.

We have demonstrated a detection sensitivity for a comprehensive number of long-lived doubly charged negative atomic ions that ranges from 2 to 8 orders of magnitude more sensitive than the best previous limits.[7,8] Although no evidence for the DNAI's was found in our experiment, the quest should be continued because the question of the most favorable type of ion source for the production of DNAI's has not been addressed in our work. It is possible that the chances of finding DNAI's could be dramatically increased by the production of multiply excited long-lived metastable states in a suitable ion source or in charge-changing collisions. For example, a long-lived (350$\pm$150 ns) metastable $3s^23p^54s4p\ ^4S^e_{3/2}$ state of Ar^- was recently observed[15] in a two-step electron-capture process by Ar^+ in Cs vapor. Similar isoelectronic and other kinds of long-lived states could also exist for DNAI's. Finally, we should note that the electric field intensity is about 3 kV/cm in the tandem accelerator and this field would tend to destroy DNAI's with an electron affinity of less than about 1 meV by field ionization, making them unobservable in our experiment. Furthermore, the flight time of DNAI's from the ion source to the tandem terminal restricts our searches to DNAI's lifetimes $\gtrsim 10^{-5}$ s, for the full sensitivity quoted in Table I. The sensitivity for DNAI's with a low electron affinity or a short lifetime will be reduced by the extent of field ionization or decay in flight.

The sensitivity of our DNAI search can also be greatly improved by (1) employing a high-resolution injection magnet so that one can choose to study odd-mass isotopes of X^{2-} to achieve a better suppression of the half-mass background ions, (2) the addition of an ESA between the injection magnet and the tandem accelerator to eliminate the dimer-breakup background, and (3) the use of a higher injection voltage and a higher-resolution ESA for a better separation of background ions from DNAI's.

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