Search for long-lived doubly charged negative atomic ions

K. H. Chang, R. D. McKeown, R. G. Milner, and J. Labrenz
W. K. Kellogg Radiation Laboratory, California Institute of Technology, Pasadena, California 91125
(Received 27 October 1986)

We have searched for long-lived ($\geq 10^{-5}$ 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 VIb and VIIb 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 (DNAIs). There have been apparently conflicting claims about the existence of these ions in the literature. The more recent searches$^{6-10}$ failed to observe DNAIs under conditions similar to those of earlier experiments which claimed their observation. Nevertheless, the evidence for the existence of DNAIs 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 DNAIs 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 DNAIs depends critically upon not only the detection sensitivity of the apparatus, but also the ability of the ion source to produce DNAIs in long-lived ($\geq 1 \mu$s) 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 VIb and VIIb 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 $\sim 6$ keV energy to sputter a solid sample of a few milligrams) was used to produce copious currents (up to $\sim 100 \mu$A) 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 $V_{\text{inj}}$) 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
$E/Q = 2V_{inj} + 3V_T$. 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 back-
ground ions that underwent 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
or nearly equal to one-half that of the $X^2^-$ ions (be-
cause 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 tan-
dem. 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 be-
tween 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 se-
quence $Y^- \rightarrow Y^2^+ \rightarrow Y^+$ would have an electric rigidity
of $V_{inj} + 3V_T$, while the dimer-breakup ions of type (b)
with the charge-changing sequence $X_2^- \rightarrow X^- \rightarrow X^2^+\n\rightarrow X^+$ would have an electric rigidity of $V_{inj}/2 + 3V_T$. 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 separa-
tion of the background ions from the DNAI's depended upon
the ratio of the voltages $V_{inj}/V_T$ and the resolution of the
ESA. Because of the limited resolution of the ESA and
the relatively small $V_{inj}/V_T$ ratio, the tails of the back-
ground 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 dis-
tinguish the true signals of the DNAI's from these back-
ground counts caused by rare charge-changing sequences.

First, because of the well-known pulse-height defect 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 scan-
ing the ESA voltage, the background tails due to the di-
mer breakups or the half-mass ions could be identified
easily.

A typical experiment search for DNAI's began with the
formation 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 $X^2^- \rightarrow X^+ + 3V_T$ (with an electric rigid-
ity of $V_{inj} + 3V_T$) 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 ap-
propriate settings for the injection magnetic field, the
ESA, and the quadrupole lens could be accurately ob-
tained 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 $V_{inj}/2 + 3V_T$, and $V_{inj} + 3V_T$
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 rigid-
ity of $3V_T$ and this was attributed to the injection of inelas-
tically 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 $X^2^- \rightarrow X^+$ 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 termi-
nal voltage were partly motivated 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 conserva-
tive 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 elec-
tric 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 $H^- \rightarrow H^-$ 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, \( [X^2^-]/[X^-] \).

<table>
<thead>
<tr>
<th>Element (X)</th>
<th>Source sample</th>
<th>( [X^2^-]/[X^-] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Al₂O₃</td>
<td>( \leq 1.1 \times 10^{-16} )</td>
</tr>
<tr>
<td>S</td>
<td>PbS</td>
<td>( \leq 7.1 \times 10^{-14} )</td>
</tr>
<tr>
<td>Se</td>
<td>Se</td>
<td>( \leq 5.8 \times 10^{-14} )</td>
</tr>
<tr>
<td>Te</td>
<td>Te</td>
<td>( \leq 8.8 \times 10^{-13} )</td>
</tr>
<tr>
<td>F</td>
<td>CaF</td>
<td>( \leq 7.4 \times 10^{-16} )</td>
</tr>
<tr>
<td>Cl</td>
<td>BaCl</td>
<td>( \leq 8.0 \times 10^{-15} )</td>
</tr>
<tr>
<td>Br</td>
<td>NaBr</td>
<td>( \leq 2.0 \times 10^{-13} )</td>
</tr>
<tr>
<td>I</td>
<td>KI</td>
<td>( \leq 1.3 \times 10^{-12} )</td>
</tr>
<tr>
<td>H</td>
<td>TiH</td>
<td>( \leq 1.0 \times 10^{-16} )</td>
</tr>
</tbody>
</table>

\( \mathrm{H}^- \) 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. 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 \((350 \pm 150 \text{ ns})\) metastable \(3s^23p^44p^45s^3/2\) state of \( \mathrm{Ar}^- \) was recently observed\(^\text{15}\) in a two-step electron-capture process by \( \mathrm{Ar}^+ \) 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 \( \geq 10^{-8} \text{ s} \), 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.

We thank C. A. Barnes, W. Kutschera, A. E. Litherland, and G. Zweig for helpful discussions. This research was supported by the National Science Foundation under Grants No. PHY82-15500 and No. PHY85-05682.

---