Resonant Ionization Spectroscopy of Ba^-: Metastable and Stable Ions

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A new technique based on the combination of laser photodetachment and resonance ionization spectroscopy has been used to characterize the state composition of a fast, negative-ion beam of barium and to determine the binding energies of its long-lived components, the metastable $5d6s6p\,^4F_{9/2}$ state and the $6s^26p\,^2P_{3/2,1/2}$ ground state, with an accuracy previously inaccessible for the weakly bound, negative alkaline-earth ions. Additional information about the Ba^- states was obtained from lifetime studies in the ASTRID storage ring.

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Studies of the structure and dynamics of negative ions are of fundamental interest for atomic physics (for recent reviews, see Ref. [1]). Negative ions can also have important practical implications, playing a significant role in a variety of atomic and plasma phenomena and providing the basis for ultrasensitive accelerator mass spectroscopy (AMS) [2], which is now routinely applied but only to a few species. An extension to many other potentially interesting candidates, however, depends in part on the knowledge of the associated negative ions, which is often lacking. The present Letter provides a greatly improved understanding of the atomic negative ions of Ba, both stable and metastable. It further demonstrates, as described below, the application of resonance ionization spectroscopy in negative-ion studies and the further utilization of storage-ring techniques in the elucidation of negative-ion structure. The negative ions of Ba are of considerable current interest, both as an extension of the recent studies of Ca^- (Refs. [3–5] and in the context of prospective AMS applications involving the negative ion of Cs.

Laser-photodetachment threshold studies of atomic negative ions have so far yielded the most accurate information about their structural properties such as the electron affinities (EA's) [6]. The determination of EA's is accomplished by measuring the threshold photon energy of the transition from the negative-ion state to the parent state of the neutral atom, or to an excited state in the neutral atom, for which the excitation energy is known very accurately. For weakly bound negative ions, the lack of tunable laser light in the far infrared region limits the experimental studies to the latter method, which often leads to lower accuracy of the EA values obtained. The reason is that changes in the photodetachment cross section from the opening of a new detachment channel will be superimposed on large photodetachment cross sections for the lower-lying atomic states. Since the energy dependence of the photodetachment cross section near threshold follows the Wigner threshold law [7] ($\sigma \propto E^{l+1/2}$, E being the center-of-mass electron energy), the opening of a new and weak channel with $l > 0$ can be difficult to identify with the traditional technique for detection of the total number of neutral atoms. To reduce greatly this problem, we have adopted the state-selective and very sensitive resonant laser photoionization method [8] to study the structure of the Ba^- ion. This method facilitates the distinction between close-lying photodetachment channels as well as between different negative-ion states. The feasibility of channel separation has been demonstrated before, using photoelectron spectrometry [9], but the photoelectron-detection technique strongly limits the selectivity and sensitivity.

The Ba^- ion belongs to the heavier alkaline earths, together with Ca^- and Sr^-. Since the discovery of the stable Ca^- ion in 1987 [10], the exploration of its structural properties has received a lot of attention, from both theorists [4,11] and experimentalists [3,5,12,13]. In spite of this effort, neither the EA values of the two Ca^- $4s^24p\,^2P$ fine-structure components nor the fine-structure splitting have so far been measured—only the average EA value has been obtained. Much less experimental attention has been devoted to Sr^- and Ba^-. The experimental proof for the existence of a long-lived or stable Ba^- ion has been available for years [14], but only theoretical predictions [4,15–17] are available about its structural properties. The average electron affinity of the $6s^26p\,^2P$ ground state is predicted to be in the range 110–220 meV, with the fine-structure splitting being ~55 meV. Information about the Ba^- ion is also required for developing the very long-lived ^{135}Cs isotope as a potential tracer for oceanographic studies [18]. It is essential for AMS measurements of this isotope at low-level concentrations that contamination from the ^{135}Ba isobar can be eliminated.

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The experiments were carried out using a fast beam of Ba^- produced from a 70 keV Ba^+ beam by two-step electron capture in a Na vapor. The Ba^+ ions were extracted from a plasma ion source, and mass and charge state analyzed before entering the Na cell, with the Ba^+ beam present in the $6s$ or the $5d$ state. Typical beam currents were 0.2 μA for Ba^+, with a conversion factor of 10^{-3} for producing Ba^-. Following the separation of the different charge-state components of barium ~60 cm after the Na cell, the negative ions entered a 1 m field-free drift region, terminated by 12 mm^2 defining apertures, in which the ion beam is overlapped collinearly with the output from a pulsed laser system consisting of two 10 ns dye lasers pumped by the second harmonic of a Nd:YAG laser. The first dye laser was used to detach the negative ions, the second to probe the produced neutral atoms, with pulses delayed 27 ns with respect to the detaching pulses, utilizing resonant laser ionization of the Ba state under investigation. After the exit aperture of the interaction region, the beam was charge analyzed again, using a second electrostatic deflector. This deflector could also be applied at higher voltage as a state-selective transverse electric-field ionizer [8] optimized for detection of specific Rydberg states. To eliminate direct photodetachment of the negative ions, leading to population of excited Ba states by the probe pulse, a powerful 10 mJ pulse of the fundamental ir light of the Nd:YAG laser (1064 nm) was applied 10 ns after the original detachment pulse to detach remaining negative ions before the probe pulse was applied. Figure 1 illustrates schematically the experiments performed, with dotted lines representing the photodetachment channels, while the full lines represent the ionization processes, either via resonant two-photon absorption or via high-lying Rydberg states which can be field ionized.

Since the flight time of the Ba^- ions from the charge-exchange cell to the interaction region was 2 μs, the possible existence of a metastable, excited Ba^- state could be studied by performing saturated photodetachment of the negative ions by the fundamental ir radiation from the Nd:YAG laser, followed by analysis of the population of excited Ba levels. We observed that approximately 13% and 1% of the Ba atoms were produced in the $5d6s\,^3D_3$ and $6s6p\,^3P_2$ states, respectively, whereas the populations of the other ^3D and ^3P levels were less than 0.1%. The populations of the $^3D_3$ and $^3P_2$ levels were independent of the energy of the laser pulse when this exceeded 1 mJ. Since the ir irradiation of the $6s^26p\,^2P$ ground state of Ba^- only leads to the population of the Ba ground state, the population of the excited $^3D_3$ and $^3P_2$ states can be accounted for only by the existence of an excited Ba^- state with a lifetime longer than a few μs. Taking into consideration that a strong population of the Ba($5d6p\,^3F_4$) state was obtained using detaching laser light with an energy above 15 324 cm^{-1}, the long-lived, excited Ba^- state can be identified as the $5d6s6p\,^4F_{9/2}$

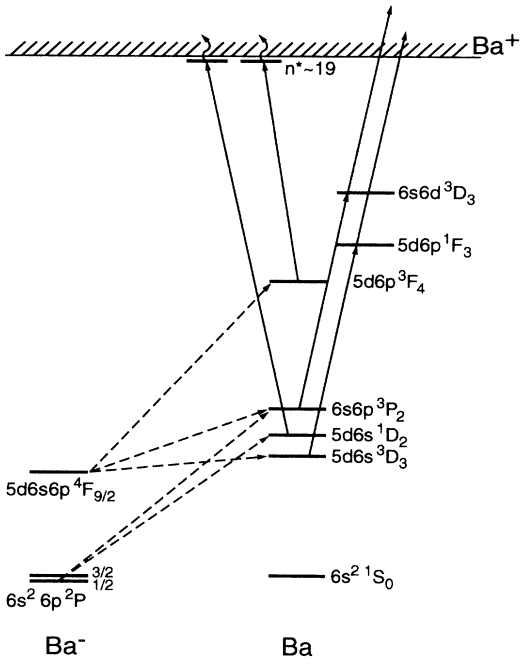

FIG. 1. Schematic energy diagram of Ba and Ba^- states with the studied detachment and detection channels indicated; see text.

state located below the first excited state in neutral Ba. Of the four possible ^4F_J components, only $J = 9/2$ can exhibit as long a lifetime as observed since the spin-orbit-induced Coulomb autodetachment to the Ba ground state will be possible for other J components.

The binding energy of the $5d6s6p\,^4F_{9/2}$ state relative to its $5d6s\,^3D_3$ parent state was determined by measuring the position of the p-electron threshold for detachment to the $5d6p\,^3F_4$ neutral state, from which photoionization was performed via a Rydberg level with the effective quantum number $n^* \simeq 19$, followed by field ionization. This detection technique significantly increases the selectivity and reduces the collisionally induced background signal [8]. Figure 2 shows the p threshold at 15 324.1 cm^{-1}, which yields a 144.2 $\pm$ 0.5 meV electron affinity with respect to the $5d6s\,^3D_3$ state. The small photoionization rate (less than 0.05 counts/laser pulse) before the onset of the p-electron threshold is mainly due to the probe-laser photodetachment of the negative ions, not being detached by the ir laser pulse.

The lower limit for the lifetime of the $^4F_{9/2}$ Ba^- state was estimated to exceed ~5 μs since it was not possible to detect a reduction in the beam content of the $^4F_{9/2}$ component during its passage of the equipment. We have also utilized the ASTRID heavy-ion storage ring to gain more information about the $^4F_{9/2}$ lifetime. The storage-ring technique has proved useful to measure lifetimes of light negative ions [19], which undergo autodetachment in the 10 μs–100 ms region. For a 100 keV Ba^- beam, the short time limit set by the round trip of the ions in the ring

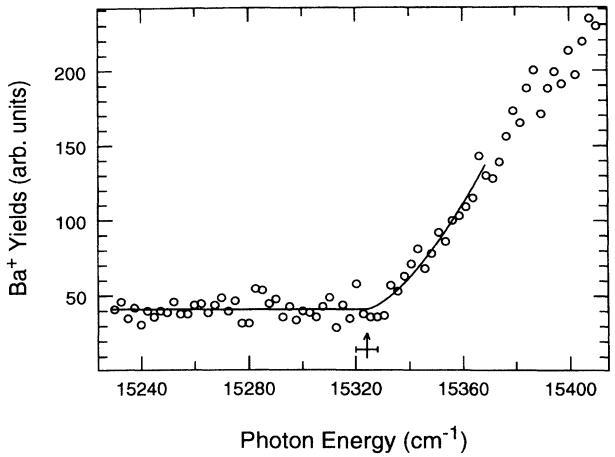

FIG. 2. Ba^+ yield following the photodetachment of the $Ba^-(^4F_{9/2})$ component to the $Ba(^3F_4)$ state. The arrow indicates the εp threshold. The fit is limited to 40 cm^{-1} above threshold due to saturation effects.

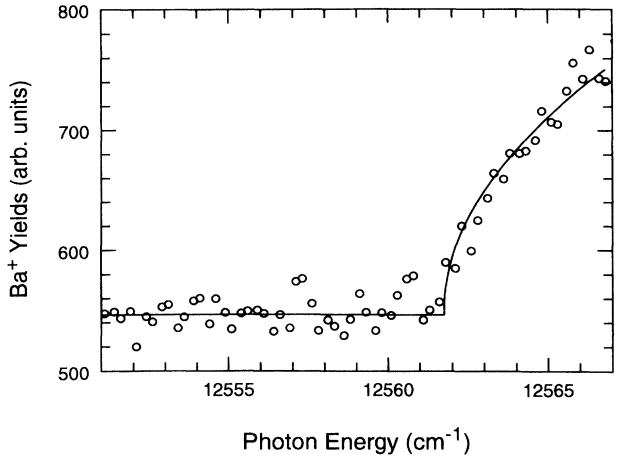

FIG. 3. Ba^+ yield following the photodetachment of the $Ba^-(^2P_{1/2})$ component to the $Ba(^1D_2)$ state.

is 100 μs, but a few round trips are needed to properly store the beam. Taking into consideration that ~15% of the injected Ba^- beam was present initially in the $^4F_{9/2}$ state, it would be possible to observe the decay of this component provided its lifetime exceeded ~100 μs, with the stable ground-state component being destroyed by collisional detachment. No Ba^- component with a lifetime in the ~100–~400 μs range could be observed, the upper limit being due to the blackbody-induced photodetachment [12] of the weakest-bound fine-structure component in the Ba^- ground state; see below. Since the $^4F_{9/2}$ state can undergo spin-spin-induced Coulomb autodetachment to the Ba ground state, its lifetime is most likely shorter than can be observed with the present storage ring [19].

The binding energies for the two fine-structure components of the $6s^26p\,^2P$ Ba^- state were measured by utilizing the s-electron threshold signal, which can be obtained by using the $5d6s\,^1D_2$ channel. It would not be possible to use a traditional detection technique, based on the measurement of the total production of neutral atoms as a function of laser frequency, for this weak s-electron threshold channel, which constitutes only 0.5% of the atoms, but probing via the sensitive resonant ionization method makes the measurements possible. Figure 3 shows the recorded s-electron thresholds for the strongest bound fine-structure component ($^2P_{1/2}$). On the basis of more than twenty s-electron-threshold measurements, the EA values for the two fine-structure components were determined to be $E(^2P_{3/2}) = 89.60 \pm 0.06$ meV, $E(^2P_{1/2}) = 144.62 \pm 0.06$ meV, with the uncertainty representing 1 standard deviation. The fine-structure splitting can thus be given as 55.02 ± 0.09 meV.

The storage-ring experiments revealed the presence of two components in the Ba^- beam; see Fig. 4. The lifetimes of these could be determined at room temperature by a two-exponential fit to yield 1.75 ± 0.10 ms and 10.5 ± 0.2 ms, respectively. By increasing the rest-gas pressure by a factor of ~100, the lifetimes decreased less than 10%, indicating that blackbody-induced photodetachment is the limiting factor [12] since intrabeam scattering and electric-field stripping can be eliminated as possible destruction mechanisms under the present experimental conditions. The storage-ring data show that the population ratio between the two components is 2:1, consistent with the statistical population of a ^2P component as the Ba^- ground state. By increasing the temperature of half the storage ring to 130 °C, the decay times were reduced to 570 ± 20 μs and 2.65 ± 0.10 ms, respectively. The temperature rise degrades the vacuum by a factor of ~20, which can increase the decay rate by only ~2%. On the basis of the fractional changes in the decay rates of the two components and the spectral distribution and temperature dependence of blackbody radiation, it is possible to obtain an estimate of the fine-structure splitting, assuming that the lifetimes can be related to the total number of photons available above thresholds. The estimated ~50 meV splitting is consistent with the precise laser value. EA values for the two fine-structure components could also be estimated, consistent with the laser data, from the lifetime values and the theoretical Ba^- photodetachment cross sections available [16].

The EA values for the ^2P fine-structure components yield an average EA value of 108 meV, which may be compared with the theoretical predictions. Only the recent value (110 meV) of van der Hart, Laughlin, and Hansen [4] is in agreement with the experimental result, whereas the other calculations predict larger values. Taking the influence of core-valence interaction into account, van der Hart, Laughlin, and Hansen [4] were able to reproduce the ~18 meV experimental EA value [3] for Ca^-. The

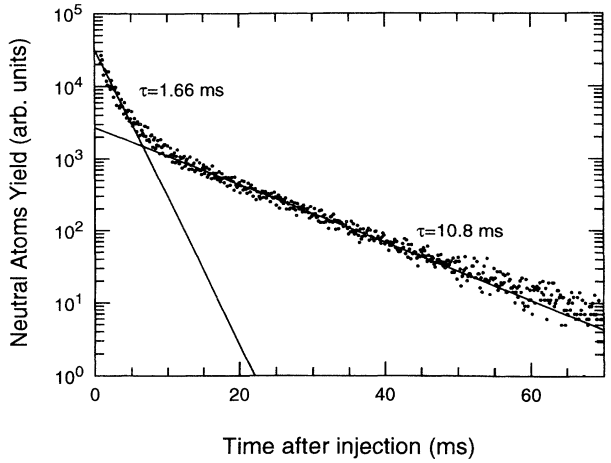

FIG. 4. Semilogarithmic plot of the detachment yield vs time following injection of a nA 100 keV Ba^- beam. The straight lines represent a two-exponential fit.

110 meV EA value for Ba^- was obtained from the Ca^- calculation by extrapolation. However, Sundholm and Olsen [11] have pointed out that the close agreement between experiment [3] and theory [4] for Ca^- may be considered fortuitous since neither core-core correlation nor relativistic effects, which for Ca^- are of the same magnitude as the EA value, were taken into account. The theoretical Ba^- fine-structure prediction [17] is in excellent agreement with the experimental value.

In summary, resonance ionization spectroscopy allows detailed spectroscopic studies of weakly bound negative ions such as Ba^-, yielding information about structural parameters such as detachment channels and EA values, but it also makes it possible to identify unpredicted metastable states such as the long-lived $5d6s6p\,^4F_{9/2}$ Ba^- state. This spectroscopic technique may prove well suited for yielding unambiguous EA values for the controversial Ca^- ground state [3–5,11], supply structural information (fine-structure splittings, term values) for weakly populated, stable components in ions such as Ge^-, Sn^-, and Pt^- (Ref. [6]), or open up for studies of the rare-earth ions so far inaccessible due to the lack of selectivity and sensitive detection techniques. Combined with a smaller storage ring (table-top), this method could also be applied for dynamic studies of weakly populated metastable states in negative ions.

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