Ca negative-ion binding energy

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We report our recent results of the measurement of the binding energy of the ground state of the calcium negative ion using electric field dissociation and accelerator mass spectrometry. The electron affinity of Ca was measured to be 17.5^{+4}_{-2} meV for a p-wave electron emission, which is in good agreement with recent photodetachment experiments performed by Walter and Peterson [Phys. Rev. Lett. **68**, 2281 (1992)].

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We report in this Rapid Communication our recent results of the measurement of the binding energy of the ground state of the calcium negative ion using electric field dissociation and accelerator mass spectrometry (AMS). The value of the electron affinity of Ca^- has recently become controversial, having been measured using laser photodetachment methods by two different groups leading to two irreconcilable results. Pegg et al. [1] have observed $E_b = 43 \pm 7$ meV while Walter and Peterson [2] obtained $E_b = 18.4 \pm 2.5$ meV. Also a measurement of the black-body-radiation-induced decay of Ca^- adds information concerning the possible metastable states of the calcium negative ion [3] and suggests that the lower value of the electron affinity might be more likely.

While these measurements were in progress [2,3], we were studying the negative ion of calcium. Combining the fact that weakly bound negative ions are destroyed in high electric fields with the sensitivity of AMS, we were able to track the destruction of Ca^- over 4 orders of magnitudes of intensity. Much to our surprise, Ca^- proved to be destroyed at a much lower electric field than expected from the earlier photodetachment measurement (i.e., 43 ± 7 meV) and actually below the designed operating voltage range of the apparatus [4]. The value of the electron affinity of calcium deduced from our measurements is 17.5^{+4}_{-2} meV which is consistent with the later photodetachment measurement [2].

Even though the existence of stable or metastable calcium negative ions has been established for more than 20 years [5], the actual stability of the negative ions of atoms with closed subshells such as Ca, Sr, Ba, and Ra have been questioned for a long time. Theoretical calculations using multiconfiguration Hartree-Fock theory have shown that the extra electron of the ground state should fill an np orbital instead of the expected $(n-1)d$ orbital [6]. The calcium electron affinity has also been used to calibrate the theoretical predictions regarding the binding energy of negative ions of this series which has been extended to other atoms with closed subshells like Yb ($[Xe]4f^{14}6s^2$) [7]. This makes the accurate determination of the calcium binding energy even more important.

According to the calculations mentioned above, the ground state of Ca^- is dominated by the $4s^24p\,^2P$ configuration. The spin-orbit splitting between the lower state $^2P_{1/2}$ and the excited state $^2P_{3/2}$ has been calculated

by Vosko, Chevary, and Mayer [7] and by Dzuba et al. [8]. Their calculations indicated a fine-structure splitting of 5.4 and 6.9 meV, respectively.

The theory of electric dissociation was developed by Smirnov and Chibisov [9] and others [10,11]. Its application to the present problem can be found in Nadeau and Litherland [2].

The experiment was conducted at the IsoTrace Laboratory at the University of Toronto. The accelerator mass spectrometry facility has been described elsewhere [12] and the detection capability for Ca^- of this equipment has already been demonstrated [13]. The spectrometer consists of a Cs^+ sputter ion source producing 20-keV negative ions which are subjected to electrostatic and magnetic analysis before entering a tandem accelerator. The ions are then stripped of some of their electrons by interactions with argon gas in the central electrode of the accelerator and made positive. This process has the advantage of destroying interfering molecules, if any, and provides the additional energy necessary for the high-resolution analysis. The positive-ion beam passes through a sequence of electric-magnetic-electric analyzers before reaching the final detector. The analyzers have resolutions of $E/\Delta E = 200$, $M/\Delta M = 2600$, and $E/\Delta E = 900$, respectively. The detector used is an ionization chamber especially designed for 5–20-MeV heavy ions, its energy resolution is ~4% in the present application [14]. The tandem accelerator was operated at 1 MV in order to use $+3$ ions and to increase the separation between atomic and hydride ion fragments in the last magnetic analyzer. (The accelerator is normally operated at 2 MV.) Several types of targets were prepared from metallic calcium or from calcium compounds such as CaF_2 and CaO mixed with different metallic powders to increase the electrical conductivity. The calcium negative ion yields differed, but variations in target material had no effect on the electric dissociation.

Riviere and Sweetman [15], among others, report the electric dissociation of H_2^+ and He^-. The dissociation was, however, the central part of their experiment and the electric gradient was provided by a single gap. Here, we had to integrate the electric dissociator between the ion source and injection magnet of an existing system and the ion optical properties of the dissociator had to match the rest of the system.

This device, which we call a dissociator, consists of a set of six electrodes (axially symmetric cylinders) forming two mirror-imaged lenses. The assembly, called a zoom lens, conserves its optical properties for a set of voltage solutions allowing gradient variations in order to probe the electronic structure of the ions over a range of electric gradients, in the present case from 3 to 10 MV/m [4]. Unfortunately, it was designed to dissociate ions with a binding energy of 43 meV and is too strong for the present application which required gradients from 1 to 5 MV/m. As a result, we had to use it in a nontelescopic mode for the Ca$^-$ ions. The magnitude of the field required demanded short electrode separation, the whole assembly is 13 cm long with a focal length of 1.5 cm when used in telescopic mode. The alignment of the device relative to the aperture preceding it and defining its object is critical. A misalignment will cause the ions to go through the stronger fields farther away from the axis and the calcium ions will be destroyed at lower electrode voltage.

The aperture defining the object of the dissociator was not attached to the electrodes and its size was not constant throughout the experiment. It was also too large in the light of experience. The variations of the aperture in size and position relatively to the electrodes caused the beam to experience different over all trajectories in the nonuniform field and shifted the dissociation curves toward lower voltages since the field is stronger farther away from the axis. The size of the aperture forced us to integrate the beam over a larger section of phase space consequently losing resolution on the dissociation curve but gaining beam intensity, which was an asset during the first stage of the experiment. A smaller aperture attached to the electrodes has already been constructed and will be used during the next set of experiments.

Because of the very intense electric fields involved, any misalignment between the electrodes or construction defects distorting the electrodes will steer the beam in a particular direction and destroy its symmetry. Those effects are voltage dependent and can be minimized but not eliminated. This will cause the transmission through the system to vary with dissociator voltage, creating the need for a transmission calibration. The calibration beam must be made of a negative ion without dissociatable states. We have compared several negative ions for this purpose and have shown that the atomic species and the mass have no effect upon the transmission for atoms of comparable masses. In the present case, ^{37}Cl$^-$, ^{41}K$^-$, and ^{48}Ti$^-$ were used depending upon which positive charge state or isotope of calcium was used. Fortunately, the transmission did not vary much in the region where calcium was dissociated which minimized the error that could arise from this correction.

Figure 1 shows the survival probability of Ca$^-$ versus voltage from five different trials. The survival probability consists of the ratio of ^{44}Ca to ^{37}Cl. The stability of the target was monitored and the calcium signal corrected when necessary. The injection system was reoptimized before each trial to reduce systematic errors. The data represented on the figure are from a larger group of dissociation experiments where the voltage distribution to the electrodes was varied. In the present case, the dissociator
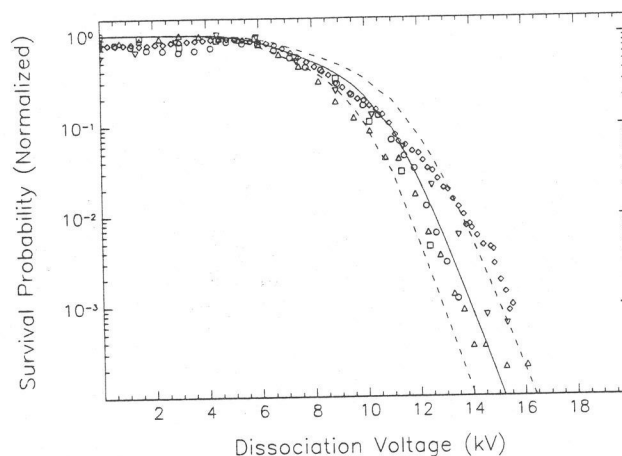

FIG. 1. Survival probability of ^{44}Ca vs dissociation voltage. The calcium signal is normalized to ^{37}Cl. Different symbols represent different trials. The solid curve represents the theoretical calculation for 17.5 meV and the dashed curves for 16.5 and 18.5 meV.

was operated as a single accelerating Einzel lens, the destructive gradient was distributed over two gaps. Experiments where the dissociator was set as a retarding lens or where the field was applied to four gaps gave similar results. Those will be the subject of a later publication and still need further investigation.

Because of the nonuniformity of the field, it was not possible to obtain an analytical function for the electric field in the dissociator. We had to rely upon numerical Laplace techniques to create a map of the electrical potential in the device and determine the trajectory of the ions into it. The grid size was reduced until changes had no effect upon the trajectory and the calculations were carefully tested against known cases.

The shape of each curve is approximately consistent with the theory. The differences between the curves are due presumably to changes in the size and alignment of the initial aperture. The data is consistent with a binding energy of 17.5 ± 1 meV, assuming that the extra electron is in the $4p$ orbital as calculated by Froese Fisher, Lagowski, and Vosko [6]. Since the shape and position of the theoretical curve depends significantly upon the estimate of the beam phase space, we had to comply with a larger error than what would be anticipated from the figure, $17.5^{+4.0}_{-2.0}$ meV.

We should have observed a structure in our dissociation curves indicating the spin-orbit splitting. The fact that we did not suggests only two possibilities: Either it is small or our apparatus does not have the resolution required to separate the two components or it is large and the higher state of the two, $^2P_{3/2}$, does not survive the electric field of the ion source.

In the first possibility, the limit from the data in the figure would be ~ 1.5 meV. In the second possibility, we have calculated that a negative ion with an affinity less than ~ 10 meV would not survive our ion source gradient. The spin-orbit splitting has been calculated to be around 6 meV (5.4 meV [7] and 6.8 meV [8]). It is important to note that our results at this point do not contradict these

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predictions, a small binding energy such as 11 meV would make the contribution from the $^2P_{3/2}$ difficult to detect. However, we can state from our results that the spin-orbit splitting between the Ca$^-$ $^2P_{1/2}$ and $^2P_{3/2}$ states is either larger than 6 meV or smaller than 2 meV.

We believe that the results of this experiment, even though preliminary, give strong independent support for the recent revision [2] of the electron affinity of Ca$^-$. We hope that further experiments using different voltage distributions and a more controlled beam phase space will al-low us to set a smaller error on the binding energy of Ca$^-$ and possibly see the structure in the dissociation curve due to fine-structure splitting.

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