Evidence for a Stable Negative Ion of Calcium

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We present experimental evidence for the existence of a stable Ca^- ion formed in the bound $4s^2 4p\ ^2P$ state. This result represents the first report of a stable negative ion for a group-IIA element. The structure of Ca^- was determined by means of photoelectron detachment spectroscopy. The electron affinity of Ca was measured to be 0.043 ± 0.007 eV, which is in good agreement with a recent calculation.

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In this paper we report on the first experimental determination of the structure of the Ca^- ion. We show, using photoelectron detachment spectroscopy, that this ion is stably bound, being formed in the $4s^2 4p\ ^2P$ state. This result is unexpected since in the past it has been generally believed that negative ions of all the group-IIA (alkaline earths) elements are unstable.[1,2] The $2s^2 2p\ ^2P$ state in Be^-, for example, has been shown to lie ≈ 0.5 eV above the ground state of Be.[3,4] Similarly, the $3s^2 3p\ ^2P$ state in Mg^- has been detected as a shape resonance in the electron-atom elastic-scattering cross section at ≈ 0.15 eV.[5]

The existence of the Ca^- ion has been known for some time. Heinicke *et al.*,[6] for example, extracted this ion from a cold-cathode Penning-discharge source and, on the basis of time-of-flight arguments, estimated a lower limit of ≈ 10 μs on its lifetime. The ion has also been produced in double electron-capture collisions between Ca^+ ions and alkali-metal vapors.[7,8] Calculations such as those of Kurtz and Jordan,[9] however, failed to predict a stable state for the Ca^- ion but a calculation by Bunge *et al.*[10] did predict a metastable state, the spin-aligned $4s4p^2\ ^4P$ state. Earlier, we made an unsuccessful search for the electrons that should have served as a signature of the autodetaching decay of this metastable state. We were successful, however, in identifying the $2s2p^2\ ^4P$ state at the lighter group-IIA element, Be^-, in similar experiments.[11] Subsequently, it was shown by Beck[12] that the lifetimes of the levels associated with this metastable state in Ca^- were reduced to the subnanosecond range by the strength of the magnetic interactions that drive the autodetachment process. In our case the time delay between the production of the ions and their detection was a few microseconds. It thus became clear that metastable states such as the $4s4p^2\ ^4P$ state could not be responsible for the existence of the long-lived Ca^- ions observed in this experiment and earlier by Heinicke *et al.*[6] As a result we were led to conclude that the Ca^- ion was probably stable despite the lack of theoretical evidence at that time. In a recent calculation involving extensive correlation effects, Froese Fischer and co-workers[13] predicted that the $4s^2 4p\ ^2P$ state in the Ca^- ion is bound by 0.045 eV with respect to the ground state of the Ca atom.

The present photodetachment spectroscopy measurements were made with the crossed-beam apparatus shown schematically in Fig. 1. The overall apparatus is similar to that used in our earlier autodetachment measurements[11,14,15] and a previous photodetachment cross-section measurement.[16] A beam of Ca^- ions was produced by our passing Ca^+ ions in the energy range from 60 to 80 keV through a Li-vapor charge-exchange cell. A study of the production of Ca^- ions as a function of beam energy and Li target density has been reported by Alton *et al.*[8] Following a delay of a few microseconds, the beam leaving the charge-exchange cell was charge-state analyzed and the negative component was deflected through 10° into a beam line containing a spherical-sector electron energy analyzer. Just prior to the entrance of this analyzer the negative-ion beam was crossed perpendicularly with a photon beam from a linear flashlamp-pumped pulsed dye laser (Candela Corporation model LFDL-8). The laser was operated at a repetition rate of 10 Hz and the pulse duration was 2.2 μs. The linear polarization vector of the laser beam was aligned along the ion beam axis. The bandwidth of the laser was 2 Å. A 10-cm focal-length lens was used to focus the laser beam onto the ion beam. The lens produced a focal diameter of about 0.2 mm. The maximum laser power used in the experiment was ≈ 0.5 MW which produced a power density of $\approx 10^8$ W/cm^2 in the interaction region. The optical or ac Stark effect on a bound-continuum transition is known to be generally small (except for possible resonances in the continuum) at photoionization thresholds. Similarly, at photodetachment thresholds the cross sections are small and any

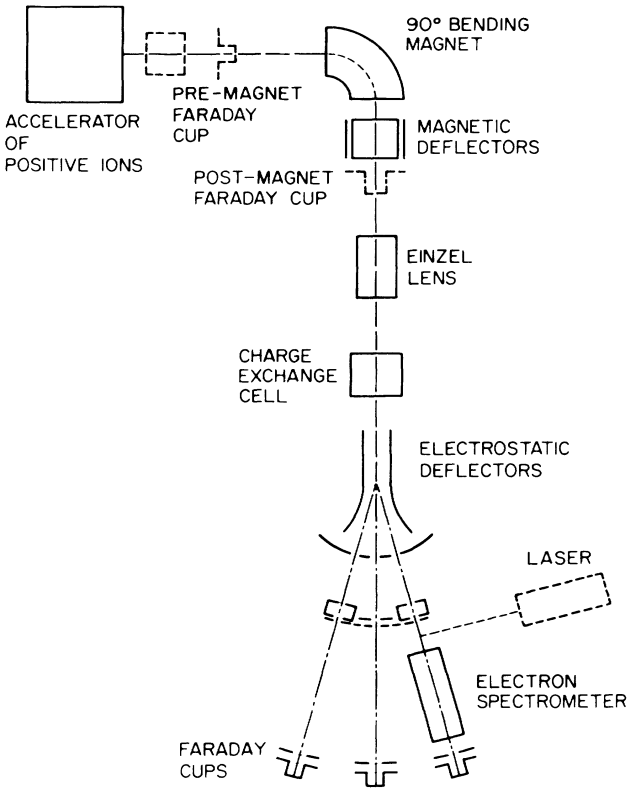

FIG. 1. Schematic of the crossed-beam photodetachment spectroscopy apparatus.

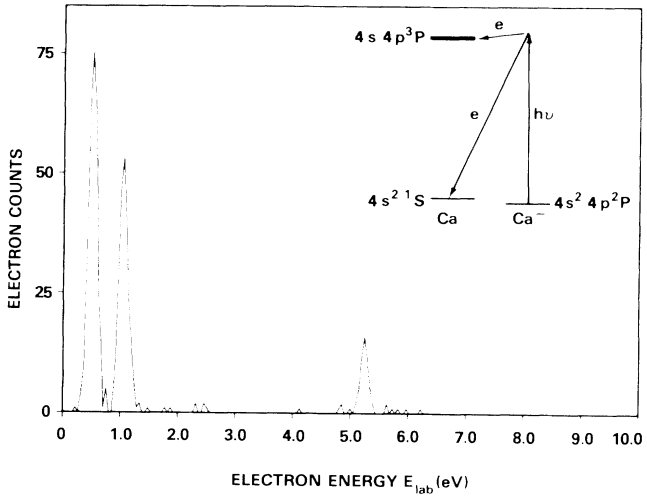

FIG. 2. Photoelectron spectrum produced by laser ($\lambda = 635.2$ nm) photodetachment from a 60-keV beam of Ca^- ions. The pair of low-energy peaks are the result of the photodetachment of the $4s^2 4p\,^2P_{1/2,3/2}$ levels of Ca^- into the $4s4p\,^3P_{0,1,2}$ levels of Ca while the higher-energy peak corresponds to the Ca atom being left in the $4s^2\,^1S_0$ ground state.

negative-ion resonances are usually broad as a result of their short lifetimes. For a pulsed laser, the ac Stark effect results in a shifting and broadening of a threshold or energy level. A typical shift or broadening is $\approx 10I$ in units of radians per second when the power density, I, is expressed in watts per square centimeter. In our case this yields a maximum shift or broadening of $\approx 10^9$ rad/s or 10^{-2} cm^{-1}. Such an effect is much smaller than the bandwidth of the laser and the electron energy resolution. Lowering the laser power by an order of magnitude resulted in no measurable change in energy or width of the photoelectron peaks.

Photoelectrons ejected from the field-free interaction region in the direction of the ion beam entered the energy analyzer and were detected. The data were stored in a CAMAC-based multichannel analyzer data acquisition system. Three multichannel scalars (MCS) were used to record the data. The first MCS was triggered by the laser pulse with use of a fast *p-i-n* detector and gated on for 4 μs to count the electron signal associated with the laser firing. The second MCS, which had the same gate width as the first, was triggered 2 μs after the first MCS was turned off. The purpose of this MCS was to sample, with the laser off, the continuously distributed background associated with electrons generated by ion impact with apertures and, to a lesser extent, electrons resulting from collisional detachment of the ions with the residual gas. By subtracting the contents of the two multichannel scalars, one could effectively discriminate against the background and obtain the true photoelectron signal. A third MCS was used to monitor the intensity of the ion beam so that the photodetachment signal could be normalized to ion-beam intensity fluctuations.

The photoelectron energy, E_c, as measured in the rest frame of the ion, is related to the photon energy E_γ by

$$E_c = E_\gamma - E_e - E_a, \tag{1}$$

where E_e is the excitation energy of the residual atom relative to the ground state and E_a is the electron affinity of the atom. In the reference frame of the laboratory the energy, E_L, of electrons photodetached in the forward direction from an ion beam of energy E_i is related to the electron energy in the rest frame of the ion, E_c, by the kinematic transformation equation

$$E_L = \epsilon + 2(\epsilon E_c)^{1/2}\cos\theta_c + E_c. \tag{2}$$

In this equation, $\epsilon = (m_e/M_i)E_i$ is the electron equivalent energy of the ion beam and θ_c is the angle of ejection of the photoelectrons with respect to the motion of the ion beam, as measured in the rest frame of the ion. Electrons photodetached into the forward ($\theta_c = 0$) and backward ($\theta_c = \pi$) directions are separated in the laboratory frame by an energy ΔE given by

$$\Delta E = 4(\epsilon E_c)^{1/2}. \tag{3}$$

Figure 2 shows an electron energy spectrum obtained by

photodetachment from Ca^- ions with laser light of wavelength $\lambda = 635.2 \pm 0.2$ nm ($E_\gamma = 1.9518 \pm 0.0008$ eV). The low-energy backward- and forward-directed peaks appearing at 0.62 eV and 1.06 eV, respectively, are the result of the photodetachment process in which the residual Ca atom is left in the $4s4p\ ^3P$ excited state. The higher energy peak in the spectrum at 5.24 eV is the result of the photodetachment process in which the residual Ca atom is left in the $4s^2\ ^1S$ ground state. The presence of the strong signal associated with the process that leaves the atom in the $4s4p\ ^3P$ state strongly suggests that Ca^- is formed in the $4s^24p$ configuration as opposed, for example, to the $4s^23d$ configuration. Tuning of the energy of the laser beam closer to the threshold of the excited ^3P state resulted in the expected reduction in the separation of the forward- and backward-directed photoelectron peaks. Eventually, only a single peak was observed corresponding to the case where the photoelectrons are moving with approximately zero energy in the ion rest frame.

The electron affinity of the Ca atom was determined by an analysis of the separation of the forward- and backward-directed photoelectron peaks with use of Eqs. (1) and (3). By measuring the difference in energies of two closely lying peaks, one can greatly minimize errors associated with contact and surface potentials in the electron analyzer and eliminate the need for precise knowledge of the analyzer constant. Measurements were made at different ion- and photon-beam energies. The final result is $E_a(\mathrm{Ca}) = 0.043 \pm 0.007$ eV. The error bar reflects uncertainties associated with the determinations of the ion and laser beam energies, the excitation energy E_e used in Eq. (1), and the separation of the two peaks. The latter measurement involved the largest source of uncertainty. Statistical fluctuations in the data points and the finiteness of the step size used in the electron energy scale set a limit on how well the energy difference between the forward- and backward-directed peaks could be measured. The electron energy resolution was insufficient to resolve the fine-structure components of the peaks. The peaks appeared symmetric and were only slightly broadened by the presence of the unresolved fine-structure lines. These observations were supported by calculations of the expected relative intensities and spacings of the component lines. Application of the selection rules to the photodetachment process, $Ca^-(^2P_J) + h\nu \rightarrow Ca(^3P_{J'}) + e^-(kp)$ shows that only the $J = \frac{1}{2}$ to $J' = 0,1$ and $J = \frac{3}{2}$ to $J' = 1,2$ transitions are allowed. The formalism developed by Engelking and Lineberger[17] was used to calculate the branching ratios for these four transitions and they are listed in Table I. The relative intensities of the fine-structure lines were then calculated on the assumption that the $J = \frac{1}{2}, \frac{3}{2}$ levels of the $4s^24p\ ^2P$ state of Ca^- are statistically populated in the production process. The assumption seems justified since the fine-structure splitting in this case is expected to be small. The relative spacings of the lines are determined primarily by the fine-structure splittings between the $J' = 0,1,2$ levels of the $4s4p\ ^3P$ state of Ca which are expected to be much larger than the splitting between the $J = \frac{1}{2}, \frac{3}{2}$ levels of the $4s^24p\ ^2P$ state of Ca^-. The results of these calculations were also used to determine the relative populations of the $J' = 0,1,2$ levels of the $4s4p\ ^3P$ state of Ca after the photodetachment process. The center of gravity of the fine structure of this state was calculated with the relative populations of the levels and their known spacings. With use of the calculated position of the center of gravity, the excitation energy appearing in Eq. (1) was determined to be $E_e = 1.894$ eV.

TABLE I. Calculated branching ratios for photodetachment of $Ca^-(^2P_{3/2,1/2})$ into various fine-structure levels of $Ca(^3P_{0,1,2})$.

	Branching ratios
$^2P_{1/2} + h\nu \rightarrow\ ^3P_0 + e^-(kp)$	0.33
$^2P_{1/2} + h\nu \rightarrow\ ^3P_1 + e^-(kp)$	0.66
$^2P_{3/2} + h\nu \rightarrow\ ^3P_1 + e^-(kp)$	0.33
$^2P_{3/2} + h\nu \rightarrow\ ^3P_2 + e^-(kp)$	1.67

Other methods of analysis of the spectral data were used to cross check the result obtained by the method just described. One method involved measurement of the separation of the forward- and backward-directed photoelectron peaks for two different photon wavelengths, with the ion-beam energy fixed. This method eliminates the need to know the ion-beam energy. Another method of analysis involved the determination of the position of the higher-energy peak in the spectrum (the peak associated with leaving the residual atom in its ground state) relative to a photoelectron peak produced by photodetachment from the ions of a reference beam of the same energy. For convenience we chose a B^- beam, although improvements could be made by use of an O^- beam instead, since in this case the electron affinity is much better known. The major source of uncertainty in this method was the uncertainty associated with the electron affinity of B which has been measured by Feigerle, Corderman, and Lineberger[18] to be 0.278 ± 0.010 eV. Both of these alternative methods of analysis, although somewhat less accurate, produced values for the electron affinity of Ca in good agreement with that determined by the measurement of the separation of the forward- and backward-directed peaks with a single photon energy.

In conclusion, we have determined, using the photoelectron detachment spectroscopy, that the Ca^- ion is formed in the stable $4s^24p\ ^2P$ state. The electron affinity of $Ca(^1S)$ has been measured to be 0.043 ± 0.007 eV which is in good agreement with the calculation of Froese Fischer and co-workers.[13] Future studies of Ca^-

will involve photoelectron detachment measurements for the $^1S_0$ channel, photodetachment threshold measurements for the $^3P_{0,1,2}$ channels, and the determination of the photoelectron angular distributions.

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