Observation of Metastable Autodetaching Ca^-

D. Hanstorp,[a] P. Devynck, W. G. Graham,[b] and J. R. Peterson
Molecular Physics Laboratory, SRI International, Menlo Park, California 94025
(Received 10 April 1989)

The predicted $4s4p^2\,{}^4P$ metastable state of the negative calcium ion has been observed. Measured autodetachment rates yield a lifetime of $(2.9\pm1.0)\times10^{-4}$ s, which is concluded to pertain to the $J=\frac{5}{2}$ state. By means of laser photodetachment near the Ca ${}^3S_1$ threshold, the electron affinity of the Ca $4s4p\,{}^3P$ parent state is found to be 0.562 ± 0.005 eV.

PACS numbers: 32.80.Fb, 31.20.−d, 35.10.Hn

We report here the first confirmed observation of the predicted metastable autodetaching state of Ca^-. Until recently it was believed that the alkaline-earth atoms, with closed ns^2 valence subshells, like the closed-shell rare gases, were incapable of attaching bound electrons to their ${}^1S$ ground states, but that metastable $nsnp^2\,{}^4P$ negative-ion states might be bound with respect to the first excited triplet states.[1,2] The $1s2p^2\,{}^4P$ state of Be^- was indeed found to be metastable, with $J=\frac{1}{2}-\frac{5}{2}$ lifetimes in the range 1–100 μs,[3] and bound by 0.2 eV.[4] Bunge *et al.*[2] also predicted a metastable $4s4p^2\,{}^4P$ state of Ca^-, 0.550 eV below Ca $4s4p\,{}^3P$. The first evidence of a long-lived Ca^- ion came more than 15 years ago,[5] but its properties were undetermined, except that its lifetime exceeded 10^{-5} s. Surprisingly, recent experiments by Pegg *et al.*[6] showed that Ca^- exists in a *stable* state, as confirmed by Froese Fischer, Lagowski, and Vosko[7] who calculated that Ca^- $4s^24p\,{}^2P$ is bound to the Ca ground state by 45 meV, in agreement with the 45 ± 7 meV found by Pegg *et al.*[6] However, the metastability of the $4s4p^2\,{}^4P$ state and the energy predicted by Bunge *et al.*[2] were still experimentally untested. Earlier experiments in this laboratory had shown metastable autodetachment from Ca^-, with rates $<10^4$/s, but its energy was unexamined.[8] We report here on new experiments that confirm the existence of the predicted ${}^4P$ state, and determine both its autodetaching decay rate and its energy.

Figure 1 shows the energies (in 10^3 cm^{-1}) of the lower states of Ca[9] and two states of Ca^-. The lowest Ca^- state, ${}^2P^0$, has the energy reported by Pegg *et al.*,[6] and the ${}^4P_{5/2}$ energy is from the results that we report here. We have measured relative photodetachment cross sections to determine the threshold for photodetachment to the Ca $4s5s\,{}^3S+\epsilon p$ channel in order to determine the electronic energy of the Ca^- state. To examine the autodetachment lifetime(s) we have measured the rate of Ca^- decay to Ca by autodetachment.

The experiments were carried out using a fast beam of Ca^- produced from a 3.0-keV Ca^+ beam by two-step electron capture in Cs vapor.[3] The first step creates the parent Ca $4s4p\,{}^3P$ atom in the reaction

$$Ca^+ + Cs \rightarrow Ca\ {}^3P + Cs^+ ,$$

which is nearly resonant, being exothermic by only 0.32 eV. Similar capture to the $3d\,{}^3D$ state is endothermic by 0.30 eV, and it decays to $4p\,{}^3P$ by allowed radiation. Thus, most electron-capture reactions yield ${}^3P$. In a subsequent collision within the Cs oven Ca^- is formed by

$$Ca\ {}^3P + Cs \rightarrow Ca^-\ {}^4P + Cs^+ .$$

Figure 2 shows the experimental setup. Ca metal was placed in a Colutron ion source. A discharge in He gas heated the ion source and after a few minutes a stable beam of Ca^+ ions was obtained with a typical current of 10^{-7} A. The ion source had to be refilled with Ca after about 5 h of running. The ions were accelerated to 3.0 keV, focused, mass analyzed in a sector magnet, and directed into a Cs oven where Ca and Ca^- were formed by charge exchange. The conversion factor from positive to negative ions was about 10^{-4}, giving 10^{-11} A of negative ions. An electrostatic quadrupole deflector (Q1) was used to separate the three different charge com-

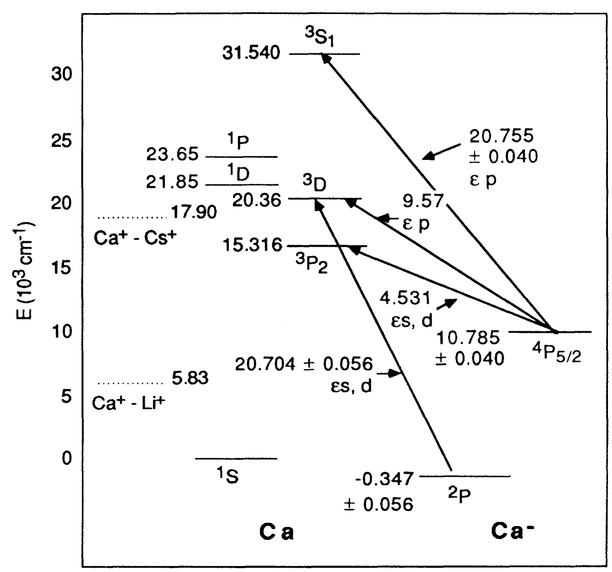

FIG. 1. Energy levels of the lower states in Ca and two states of Ca^-. Energies of resonant electron capture are also shown.

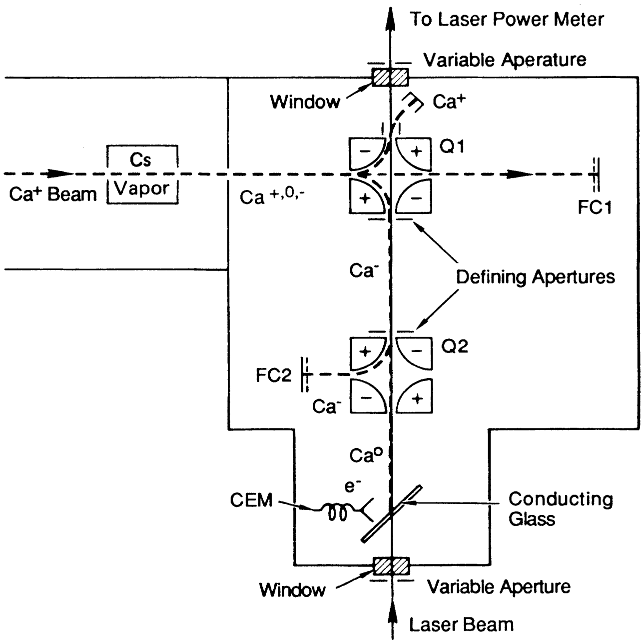

FIG. 2. Schematic diagram of the experimental setup.

ponents of calcium. After a 90° deflection, the negative ions entered a field-free drift region terminated by two (1×2)-mm^2 defining apertures. After traversing this region the Ca^- ions were deflected 90° in a second quadrupole (Q2) and then collected by a Faraday cup (FC). Fast Ca atoms produced in the drift region either by photodetachment, autodetachment, or collisional detachment were undeflected by Q2 and traveled to a glass plate where they created secondary electrons. A positively biased channel electron multiplier (CEM) collected the electrons and its output was connected to a computerized photon counting system. The measurement of these fast neutral products of either autodetachment or photodetachment from Ca^- formed the basis of this work.

We first tested our earlier findings that metastable autodetachment occurs.[8] As previously,[3,8] the production of fast neutral Ca between Q1 and Q2 (the CEM count rate), normalized to the Ca^- beam current deflected at Q2, was measured as a function of the ambient pressure in the chamber, by admitting air into the chamber. The extrapolated value for zero pressure results from autodetachment only. The zero of the pressure-gauge scale was determined by repeating the measurements using H^-, which is stable, extrapolating the data to zero neutral yield. This procedure also checked the linearity of the pressure scale. We obtain an effective decay rate from the first-order relation $\Gamma_{\rm eff}=I_0^0 v/I^- L$, where v is the ion speed, L is the Q1-Q2 separation, and I_0^0 and I^- are the autodetached neutral (zero pressure) and negative-ion particle arrival rates at their detectors.[10] By moving the second quadrupole, the drift distance was varied to look for any systematic change. The rates obtained at 1.9, 4.0, 6.3, and 8.2 cm were 5.0 ± 2.5, 1.9 ± 1.5, 3.8 ± 1.0, and 3.8 ± 0.8 (units of 10^3/s), respectively, showing no systematic effects. We evaluate the weighted average $\Gamma_{\rm eff}=(3.5\pm 1.2)\times 10^3$/s to obtain an effective lifetime $\tau_{\rm eff}=(2.9\pm 1.0)\times 10^{-4}$ s.

If there is a mixture of the $J=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ states in the beam, which is expected to be initially formed with a statistical distribution, the measured autodetachment rate is an upper limit to the slowest of them. After some consideration, however, we attribute it entirely to the $J=\frac{5}{2}$ state, which populates $\frac{1}{2}$ of the initial Ca ^4P beam. The $\frac{1}{2}$ and $\frac{3}{2}$ substates of quartets can autodetach to the doublet continuum by spin-orbit coupling to doublet resonances, while $\frac{5}{2}$ states require spin-spin interactions which are 30 to 50 times weaker in He^-. Since our ions are created about 3.8 μs before reaching Q1, shorter-lived species have already decayed out of the beam. If the beam contained states with $\tau=3$–30 μs, our measured rates would be much higher. We present evidence below that the beam contains negligible amounts of ground-state Ca (considering the estimated uncertainty in the decay rate), so we conclude that we observe only the $J=\frac{5}{2}$ state, which thus has a lifetime of 290 ± 100 μs. We are unaware of any published theoretical values. Some preliminary calculations by Beck indicated considerably shorter lifetimes, but more rigorous calculations are required before reliable predictions are available.[11]

For the photodetachment experiments, a dye laser pumped by a Kr^+ laser was narrowed in width by a telescope, and directed through the conducting glass plate, through the apertures defining the Q1-Q2 drift space, where its photons traveled coaxially (at 180°) with the Ca^- beam, and finally, through a window in the vacuum chamber wall and into a power meter. The wavelength was measured with a monochromator calibrated against the lines of an argon-ion laser.

To determine the electron affinity of the metastable state, we measured the relative photodetachment cross section in the wavelength region 464 to 513 nm, i.e., photon energies of 19490–21550 cm^{-1}. This range includes the calculated[2] threshold for the Ca^- $4s4p^2\,{}^4P \rightarrow$ Ca $4s5s\,{}^3S+\epsilon p$ transition shown in Fig. 1, and is accessible by our continuous-wave (cw) dye laser (ϵp represents the ejected p-wave electron at energy ϵ). This threshold is in the photodetachment continua of the $4s4p\,{}^3P+\epsilon s,d$ and $4s3d\,{}^3D+\epsilon p$ outgoing channels from ^4P. However, it is over 11000 cm^{-1} above the closest of their thresholds, so we expected a relatively flat background from them over our small photon energy range, which should not interfere with the onset of the opening channel.

The results are shown in Fig. 3. The laser beam was chopped and the data shown are the differences between the on and off cycles. Each datum is normalized against the laser power and the negative-ion current, and thus is

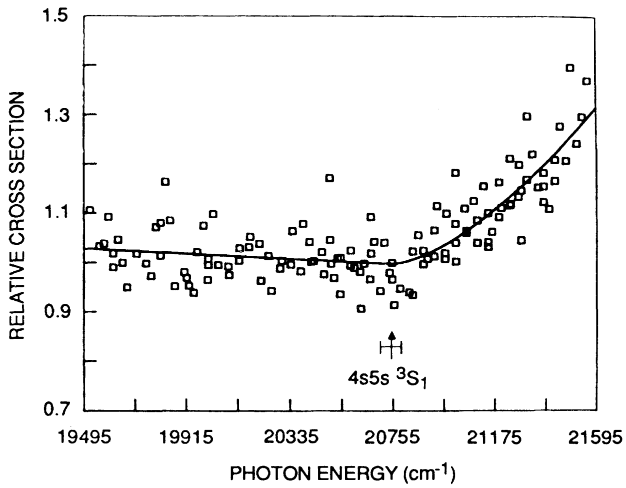

FIG. 3. Ca^- photodetachment cross section (squares), and least-squares fit to the experimental data (solid line). Arrow, with uncertainties, indicates the $^3S+\epsilon p$ threshold.

proportional to the photodetachment cross section. The dispersion in the data results mostly from an inconsistent overlap of the beams; the counting statistics alone would give less scatter. The effective overlap depends on the alignment and mode structure of the dye-laser beam, and on the density distribution in the ion beam. The data shown in Fig. 3 are the sum of five complete runs taken over a total acquisition time of 20 h. The photon energies include the Doppler shift. It shows the cross section to be quite flat up to around 20 800 cm^{-1} where the onset of a new channel occurs. We found that this behavior characterized all runs, but there were variations in the average cross section of the "flat" region from one run to another, again associated with an inconsistent average overlap of the two beams between different runs. To overcome this effect, the data at energies below the onset at 20 800 cm^{-1} were averaged from each and normalized to unity. This normalization factor was then used for all data from a given run. The combined normalized data from all runs are given in Fig. 3.

By studying the energy-level diagram it will be clear that only two photodetachment thresholds could correspond to the observed onset. There are only two spin-allowed photodetachment transitions between states in the negative ion and the atom that have thresholds near 20 800 cm^{-1}:

$$4s^2 4p\,^2P+h\nu\rightarrow 4s3d\,^3D+\epsilon s,\epsilon d\,, \tag{1}$$

which would come from any ground-state ^2P components in the beam, and

$$4s4p^2\,^4P+h\nu\rightarrow 4s5s\,^3S+\epsilon p\,. \tag{2}$$

These two channels can be distinguished since the s- and p-wave thresholds have different energy dependences. In the absence of interferences from other channels or nearby resonances,[12] the Wigner-threshold law[13] describes the energy dependence of the photodetachment cross section just above a threshold E_0 as

$$s(E)=\text{const}\times(E-E_0)^{l+1/2}\,,$$

where E is the photon energy and l is the angular momentum of the outgoing electron. The s-wave ($l=0$) cross section varies as $(E-E_0)^{1/2}$ with a sudden (infinite-slope) onset at E_0, while the p wave varies as $(E-E_0)^{3/2}$, rising gradually from a zero slope at E_0. The d-wave products from reaction (1) would be strongly suppressed at threshold by their $(E-E_0)^{5/2}$ behavior.

Our experimental data clearly show the slow onset corresponding to a p wave, reaction (2), indicating photodetachment from the metastable state. Even though the new threshold is near the $^2P\rightarrow{}^3D$ threshold of 20704 ± 56 cm^{-1} obtained from the results of Pegg *et al.*,[6] it clearly does not have a vertical s-wave threshold behavior. The cross section was therefore fitted by the function

$$s(E)=a_0-a_1E+a_2(E-E_0)^{3/2}\,,$$

where the continuous background has a very small slope $-a_1$, and a_2 corresponds to the strength of the onset at the threshold E_0. The fit gives $E_0=20755\pm40$ cm^{-1}. Subtracting E_0 from the known energy, 31 540 cm^{-1}, of Ca $4s5s\,^3P$ gives the energy of Ca^- ^4P to be 10785 ± 40 cm^{-1} above the Ca ^1S ground state. From our autodetachment results, we associate this energy with the $J=\frac{5}{2}$ level of Ca^- ^4P. To obtain an electron affinity for the parent Ca ^3P state, we use the energy difference between the $J=2$ level of ^3P, 15316 cm^{-1}, and our value of 10875 ± 40 cm^{-1} for the $J=\frac{5}{2}$ level of Ca^- ^4P. Bunge *et al.*[2] calculated a value of 550 meV for the electron affinity of $3s4p\,^3P$. However, they did not include fine-structure effects, so their calculations are for some average of fine-structure levels for ^3P and ^4P states. The agreement is surprisingly good, considering that the calculations were considered to be preliminary to more accurate work.[2]

Since no abrupt s-wave onset at the $^2P\rightarrow{}^3P$ threshold is observable within the statistical distribution of our data, it is evident that no substantial amount of Ca^- (^2P) is in our beam. We estimate the upper limit of its population to be about 5%, which is the "noise level" in the photodetachment background. Its only effect would be to increase the apparent lifetime of the $\frac{5}{2}$ state by $<5\%$, which is well within our estimated uncertainties. An obvious question raised by these results is why we find the metastable ^4P while Pegg *et al.*[6] observed only the stable ion. The difference probably results primarily from the different charge-exchange vapors and beam energies used. We used Cs vapor and a low-energy Ca^+ beam, which favors near-resonant capture. As mentioned above, the first electron capture is only 0.32 eV exothermic for capture into the ^3P parent of metastable Ca^-. The "resonant" energy for this reaction is shown by the dotted line labeled Ca^+-Cs^+ in Fig. 1. Capture to the ^3D state (0.32 eV endothermic) will also occur, but it radiates to ^3P in an estimated[14] 0.7 μs, the transit time in the oven, so all near-resonant final Ca products end in ^3P. Small yields of $3d\,^1D_2$ will occur, but it is metastable; $4p\,^1P$ can radiate to produce ^1S products, but it is 0.7 eV above the resonant level. On the other hand, Pegg *et al.*[6] used Li as the charge-transfer vapor, whose resonant capture energy is 0.72 eV above the ^1S ground state, but is 1.18 eV below the ^3P state. The resonant level is shown by the dotted line in Fig. 1 labeled Ca^+-Li^+. Even if their beam Ca^- contained some ^4P states, it is possible that the $\frac{1}{2}$ and $\frac{3}{2}$ components decayed before observation, and that the slow autodetachment rate of the $\frac{5}{2}$ state prevented its detection.

We have also examined the Ca^- photodetachment spectrum of Heinicke *et al.*[5] and found it consistent with detachment entirely from the stable ^2P ions. Their ions were extracted directly from a Penning ion source, which should not yield ^4P ions as efficiently.

In conclusion, we have shown the existence of the metastable state in Ca^- predicted by Bunge *et al.*[2] The $4s4p^2\,^4P_{5/2}$ state is found to have an energy of 10785 ± 40 cm^{-1} above Ca ^1S and its autodetachment lifetime is 290 ± 100 μs. The electron affinity of the $4s4p\,^3P$ state is 562 ± 5 meV, compared to the 550 meV calculated by Bunge *et al.*[2]

We are grateful to Dr. Y. K. Bae and Dr. M. J. Coggiola, and Dr. P. C. Cosby for help with experimental details, and for helpful theoretical discussions with Dr. D. L. Huestis, and with Professor D. L. Beck regarding ^4P autodetachment. This research was supported by Air Force Office of Scientific Research Contracts No. F49620-85-K-0017 and No. F49620-89-K-0002, National Science Foundation Grant No. PHY-8713309, and travel grants from the Swedish Natural Science Research Council and the University of Göteborg.

---

[a]Permanent address: Chalmers University, Göteborg, Sweden.

[b]Permanent address: Queens University, Belfast, Northern Ireland.

[1]A. W. Weiss, Phys. Rev. **166**, 70 (1968); D. R. Beck, C. A. Nicolaides, and G. Aspromalis, Phys. Rev. A **24**, 3252 (1981); D. R. Beck, Phys. Rev. A **30**, 3305 (1984).

[2]C. F. Bunge, M. Galán, R. Jäuregui, and A. V. Bunge, Nucl. Instrum. Methods Phys. Res. **202**, 299 (1982).

[3]Y. K. Bae and J. R. Peterson, Phys. Rev. A **30**, 2145 (1984).

[4]T. J. Kvale, G. D. Alton, R. N. Compton, D. J. Pegg, and J. S. Thompson, Phys. Rev. Lett. **55**, 484 (1985).

[5]E. Heinicke, H. J. Kaiser, R. Rackwitz, and D. Feldman, Phys. Lett. **50A**, 265 (1974); J. Heinemier and P. Hvelplund, Nucl. Instrum. Methods **148**, 425 (1975).

[6]D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).

[7]C. Froese Fischer, J. B. Lagowski, and S. H. Vosko, Phys. Rev. Lett. **59**, 2263 (1987).

[8]Y. K. Bae and J. R. Peterson (unpublished).

[9]C. E. Moore, in *Atomic Energy Levels,* edited by C. C. Keiths, NBS Circular No. 467 (U.S. GPO, Washington, DC, 1971).

[10]I^- was obtained from the Ca^- current to the Faraday cup with secondary electrons suppressed. I_0^0 came from the extrapolated CEM (zero-pressure) count rate. The detection efficiency of the CEM was taken to be 100% after reaching a maximum count rate that was independent of draw-off and acceleration potentials. The secondary emission coefficient of the conducting layer on the glass plate was deduced to be > 1 after a series of tests including measurements of threshold for photoemission (2.5–3.0 eV).

[11]D. R. Beck (private communication).

[12]J. R. Peterson, Y. K. Bae, and D. L. Huestis, Phys. Rev. Lett. **55**, 692 (1985).

[13]E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[14]Estimated by energy scaling from similar triplet transitions in Mg and Ba.