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Ca^- and Its Elusive Properties*

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Abstract

The historical progression of theoretical and experimental information on the properties of the two electronic states of the Ca^- ion is reviewed. New results are described that have revealed a shape resonance and a Cooper minimum, and have yielded a much lower electron binding energy for the ground state Ca^- ^2P of only $18{\cdot}4\pm2{\cdot}5$ meV compared with the previous value of 43 ± 7 meV, and have also confirmed earlier observations of the metastable ^4P state. Some important uncertainties still exist and are noted.

1. Introduction

Ca^- has proven to be a formidable and seemingly moving target for both experimental and theoretical attempts to determine its properties. Initially, because of its $4s^2$ closed subshell electronic configuration, neutral Ca was believed unable to bind an extra electron to form the negative ion (Weiss 1968; Zollweg 1969), similar to the rare gases and the other alkaline earths. However, Heinecke and Baumann (1969) were able to form a beam of Ca^- in a Penning discharge ion source, with a lifetime exceeding 10^{-6} s. Later, Heinecke *et al.* (1974) measured relative photodetachment cross sections for the same ions. They were able to cover an extensive photon energy range $0{\cdot}5$–$3{\cdot}2$ eV using an arc continuum light source and a monochromator or filters for wavelength selection. In what must have been a difficult experiment, the energy resolution was fairly poor, but they obtained a good spectrum showing a broad minimum near 1 eV, a rise to a shoulder near 2 eV, and a narrow peak near 3 eV, as seen in Fig. 1. In trying to understand the data they excluded the possibility of either a 3d or 4p electron bound to the ground state forming a ^2D or ^2P state, because of arguments given previously (Weiss 1968; Zollweg 1969). They suggested instead either a 3d4s4p ^4F state or a $4s4p^2$ ^4P state bound to the first excited triplet state 4s4p ^3P, but were unable to explain the structure with these assignments. Later, Bunge *et al.* (1982), searching theoretically for metastable excited negative ion states, showed that the lowest Ca excited state, 4s4p ^3P, could bind another 4p electron to form the metastable $4s4p^2$ ^4P with a calculated binding of 550 meV. Autodetachment to the Ca ^1S ground state requires spin–orbit coupling, thus it was expected to be metastable, but no decay rates were calculated.

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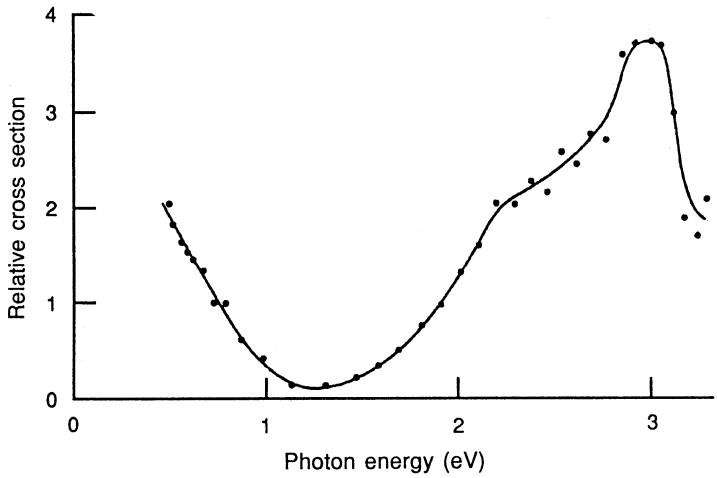

Fig. 1. Ca^- photodetachment data of Heinecke *et al.* (1974).

(1a) Early Searches for Metastable ^4P and Discovery of ^2P

We started a program in the early 1980s to explore properties of metastable negative ions, with the idea that higher excited resonances, which are generically the same as electron scattering resonances, would be much more easily probed by laser photodetachment of the metastable ion instead of the ground state ion, such as H^-. Negative ion resonances are very important in electron scattering phenomena, and most experimental knowledge of their location and importance has been obtained through electron scattering experiments. However, it is also possible to explore them by laser photodetachment, which is restricted by optical selection rules, but is capable of the high energy resolution required to reveal the detailed structure of such resonances and thus to test theoretical calculations. In atoms, these resonances occur near excited Rydberg states. The lowest resonance in H^- is 11 eV above the ground state of H^-, and has only been explored using 800 MeV relativistic H^- beams to Doppler-shift the 3–4 eV photons from tunable lasers upward to the required energies (Bryant *et al.* 1977). However, from He^- 1s2s2p ^4P, the prototype metastable negative ion, all of the higher He Rydberg states are within 4·4 eV and are thus much more easily accessible by tunable lasers. Since the 2^3S state is easily formed from He^+ beams by near-resonant electron capture in Cs vapour (Peterson and Lorents 1969),

$$He^+ + Cs \rightarrow He\,2^3S + Cs^+, \tag{1a}$$

it is relatively easy to form He^- in a second collision within the Cs vapour,

$$He\,^3S + Cs \rightarrow He^-\,^4P + Cs^+, \tag{1b}$$

as was first demonstrated by Donnally and Thoeming (1967). This technique can be generalised because in most species, the first metastable Rydberg states, which form the metastable negative ions, lie about 4 eV below the positive ion, or about the same as the ground state of Cs (ionisation potential = 3·9 eV). Thus this two-step charge transfer method can be used to form other metastable negative ions as well. Our experimental program started with photodetachment measurements on He^- (Hodges *et al.* 1981), and by 1984 we had observed Ca^- formation in collisions of 3 keV Ca^+ with Cs and found a slow decay rate for the ions of $\sim 10^4\ s^{-1}$. However the Ca^- beams were weak and the pressure of research on other metastable ions pre-empted further experiments.

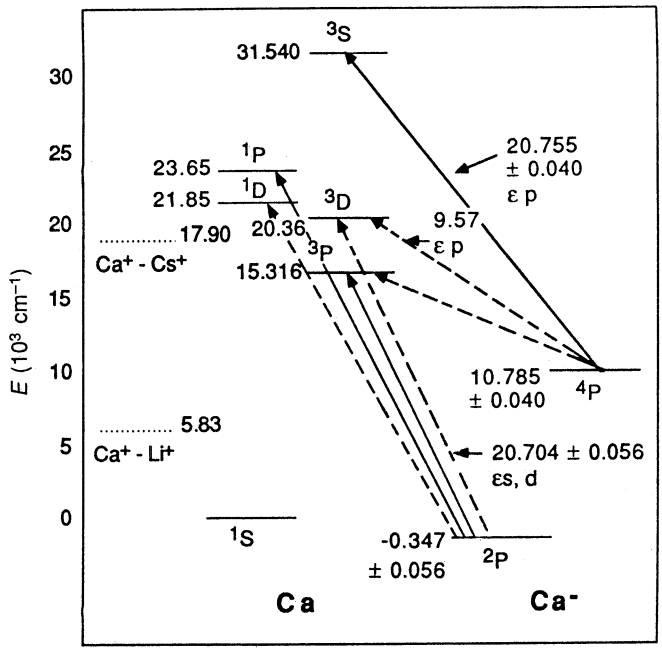

Fig. 2. Energies of various Ca and Ca^- states, and some electronic transitions (the dashed ones were not observed). The Ca^- ^2P energy indicated is the value of Pegg *et al.* (1987). Levels of resonant electron capture for Ca^+ in Cs and Li are also shown.

Next, Alton *et al.* (1986) produced Ca^- from higher energy 60–85 keV beams of Ca^+ in Li vapour, to begin a search for the metastable ^4P. They searched unsuccessfully for autodetached electrons and concluded that their Ca^- either was stable, despite the lack of theoretical evidence, or was a very long-lived metastable ($\tau \gg 10^{-6}$ s). Probably motivated by these results, Froese Fischer *et al.* (1987) made the first highly accurate multiconfiguration Hartree–Fock (MCHF) calculations on Ca^-, and found surprisingly that a stable $4s^24p\ ^2P$ state was bound below the Ca ground state by 45 meV. That result was strongly supported by laser photodetached electron energy measurements of Pegg *et al.* (1987), who found an electron affinity of 43±7 meV. This news was very exciting,

but seemed to not disagree with our earlier preliminary work, which was designed to produce the predicted metastable ^{4}P ion by two-step electron capture in Cs similar to reactions (1a) and (1b), featuring near-resonant production of Ca ^{3}P (the parent of ^{4}P) in the first step. In the reaction $Ca^+ + Cs \rightarrow Ca + Cs^+$, similar to reaction (1b), the energy level in Ca for a purely resonant (no energy change) electron capture is shown by the dotted line labeled Ca^+–Cs^+ in Fig. 2. This reaction is only 0·32 eV exothermic for ^{3}P products (and 0·31 eV endothermic to ^{3}D, which radiates to ^{3}P), but it is exothermic by 2·2 eV for ^{1}S ground state products. In contrast, the electron capture by Ca^+ in Li, used by Pegg *et al.*, favours ground state Ca (0·7 eV exothermic) over ^{3}P (1·2 eV endothermic). The resonant level is also shown in Fig. 2, by the dotted line labeled Ca^+–Li^+. Thus formation of Ca^- in Cs favours ^{4}P, but in Li it favours ^{2}P (although at the high beam velocities of Pegg *et al.* the near-resonant propensity of electron capture is relaxed and both states should be formed).

(1b) Confirmation of ^{4}P and Subsequent Dilemmas

Stimulated by the discovery of stable Ca^- ^{2}P, we resumed our search for the metastable ^{4}P, again using a 3 keV Ca^+ beam and a Cs vapour target. The experimental arrangement is shown in Fig. 3. A well-collimated, mass-analysed Ca^+ beam is directed through a Cs vapour oven, and into an interaction chamber (pressure $\sim 3\times10^{-7}$ Torr). It enters an electrostatic quadrupole deflector Q1, which separates the +, −, and 0 charge states that exit the oven, and deflects the Ca^- beam through 90°, onto an 8 cm drift path, and into a second quadrupole Q2, which deflects it into a current monitor. Any neutral Ca atoms that are formed along the Q1–Q2 drift path transit Q2 and strike the front surface of a quartz plate oriented at 45° to the beam and coated with a thin film conductor. Secondary electrons are ejected from the conducting surface and accelerated to a channeltron electron multiplier, whose output pulses are amplified and counted. For photodetachment measurements a laser beam is directed along the Q1–Q2 drift path. This arrangement is very useful because it offers a long beam interaction region and (as we shall see) also because the detection efficiency is not dependent on the photodetached electron energies. With the laser off, neutrals result from autodetachment or collisional detachment. The autodetached component is determined by leaking N_2 gas into the chamber and measuring the count rate versus pressure. The zero pressure intercept represents the autodetached component, permitting estimates of the autodetachment rate. For photodetachment measurements the laser beam is mechanically chopped and the laser-independent background is subtracted out.

We first reconfirmed slow autodetachment and measured a lifetime of 0·29±0·1 ms (Hanstorp *et al.* 1989). We then used photodetachment to determine the energy level of the Ca^- ^{4}P state, by finding the photon energy required to reach the threshold for an excited state of the Ca neutral product. With the level predicted to be 550 meV below ^{3}P, the most convenient threshold for our cw dye laser was that of the Ca^- ^{4}P → Ca 4s5s ^{3}S+kp transition shown in Fig. 2. The Wigner threshold law states that the cross section σ should increase as

$$\sigma \propto (E - E_0)^{l+1/2}, \tag{2}$$

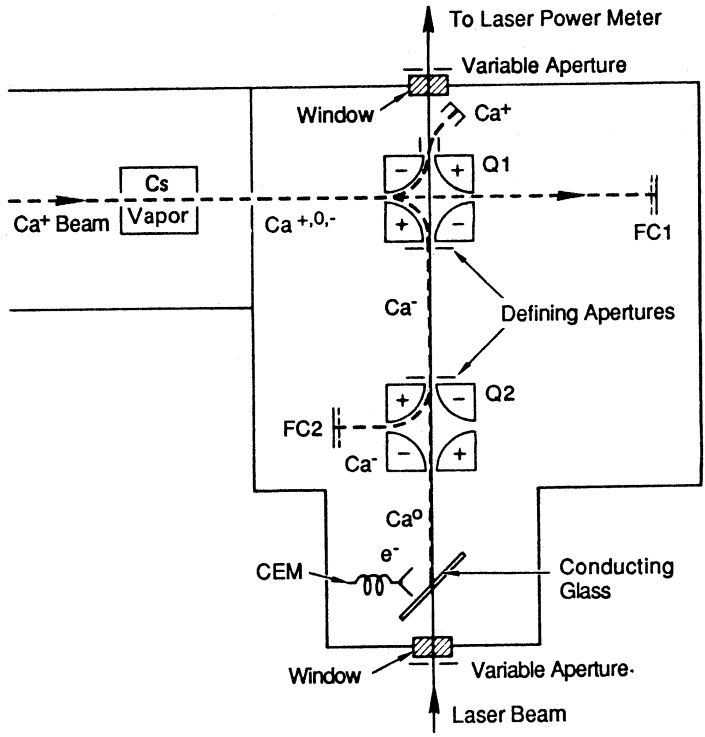

Fig. 3. Diagram of the experimental apparatus.

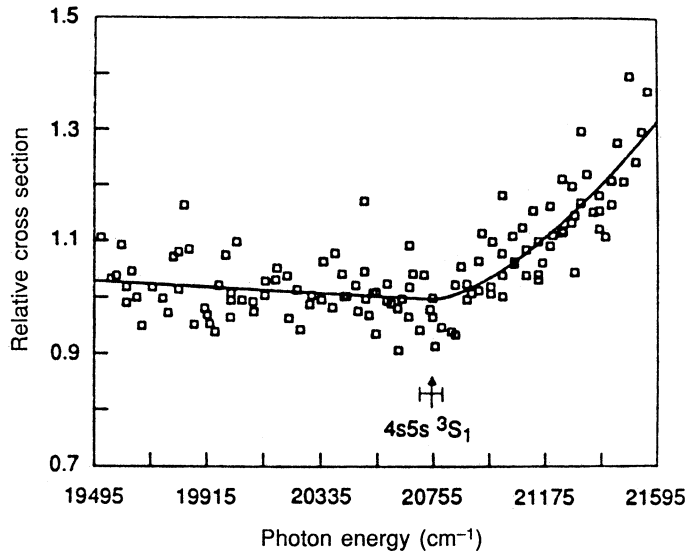

Fig. 4. Photodetachment data of Hanstorp *et al.* (1989) showing the $^4P \rightarrow 5s\ ^3S+kp$ threshold.

for photon energy E, above the threshold E_0. We found such a threshold at $E = 20765 \pm 40\,\mathrm{cm}^{-1}$, as seen in Fig. 4, yielding an electron affinity $\mathrm{EA}(^3\mathrm{P}) = 562{\pm}5$ meV (Hanstorp *et al.* 1989), probably in better agreement with the 550 meV predicted earlier by Bunge *et al.* (1982) than was expected. Inasmuch as we found evidence of only one decay rate, we suggested that, similar to He^-, the $J = \frac{5}{2}$ substate would have a slower decay rate than the $\frac{3}{2}$ or $\frac{1}{2}$, and that our ^{4}P ions were probably in the $J = \frac{5}{2}$ level. We later learned that this guess was faulty.

In addition to the ^{4}P component in the beam, which we had tried to emphasise in our production scheme, we also sought evidence of any ^{2}P ground state population that might have been formed. If there were any ^{2}P, an abrupt $(E - E_0)^{1/2}$ s-wave onset at the threshold of the $4s^24p\ ^2\mathrm{P} \rightarrow 4s3d\ ^3\mathrm{D}{+}ks$ transition (see Fig. 2) was expected at $20700{\pm}56\,\mathrm{cm}^{-1}$, determined from the $\mathrm{EA}(^1\mathrm{S}) = 43$ meV of Pegg *et al.* (1987). We reasoned that if ^{2}P ions were present, this structure would also appear in Fig. 4, and from its absence, we concluded that our beam contained less than 10% of ^{2}P (Hanstorp *et al.* 1989). This conclusion also proved to be incorrect.

(1c) Indication of Resonances from Electron Scattering Data

The next development came with the realisation of Johnston *et al.* (1989) that the existence of a stable ground state of Ca^- could shed light on some of their unpublished $\mathrm{e}^-{+}\mathrm{Ca}$ scattering data. From the energy derivative of the electron current transmitted through Ca vapour, they found evidence of a broad resonance at $1{\cdot}1{\pm}0{\cdot}15$ eV and a narrow one at $2{\cdot}8{\pm}0{\cdot}15$ eV, which compared favourably with the wide minimum and sharp maximum in the photodetachment data of Heinecke *et al.* (1974) shown in Fig. 1. The resonances were attributed to strongly mixed Ca^- ^{2}D resonant states of configurations $4s^23d$ and $4s4p^2$. This interpretation was supported by *ab initio* calculations. Because the Ca^- ions of Heinecke *et al.* (1974) were formed directly in a discharge, we can now say that they were undoubtedly exclusively in the ^{2}P ground state instead of an excited state as originally assumed; thus the comparison made by Johnston *et al.* (1989) was very appropriate.

(1d) Metastability of ^4P questioned, and Uncertainty arises about the Energy of ^2P

Next, some doubts about our experiment and conclusions (Hanstorp *et al.* 1989) were raised by T. Andersen (personal communication, 1990). He pointed out that the decay of the ^{4}P state in Be^- by spin–orbit coupling had been shown to be fast (Aspromallis *et al.* 1985) except for a spurious cancellation in two components of the interaction, which made only the $J = \frac{3}{2}$ substate decay slowly. Andersen argued that there was no reason to expect such an effect in Ca^- ^{4}P. In the subsequent reconsideration of our conclusions about the absence of ^{2}P ions in our beam, we recognised the possibility that the test that we had used for them, the $4s^24p\ ^2\mathrm{P} \rightarrow 4s3d\ ^3\mathrm{D}{+}ks$ transition, could be strongly suppressed because, for a single electron transition, it requires the transformation of the very diffuse p orbital in Ca^- into the compact 3d orbital in the neutral. We then decided to re-examine our beam by photodetachment near the threshold of the $4s4p\ ^3\mathrm{P}{+}kp$ continuum, which is a $4s \rightarrow 4p$ transition observed about 16 meV

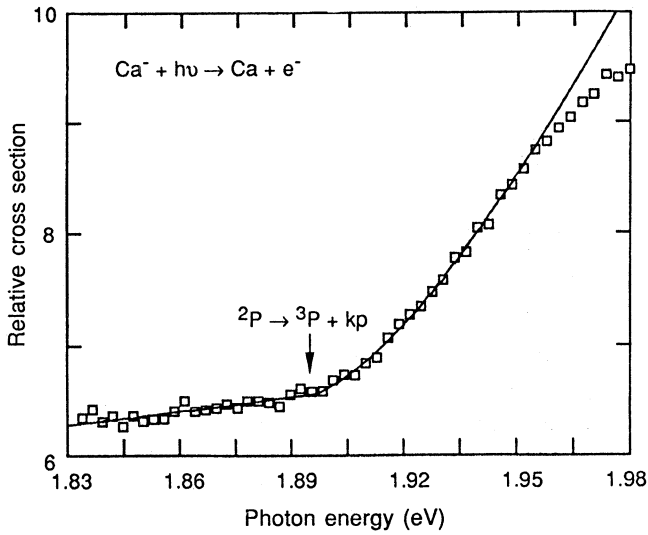

Fig. 5. Photodetachment cross sections near the $^2P \rightarrow {}^3P+kp$ threshold. A p-wave threshold law fit is also shown.

above the threshold in the work of Pegg *et al.* (1987). This p-wave threshold is at much lower photon energies than we had used previously, and was expected near 1·936 eV based on the value EA(^1S) = 43 meV. As Fig. 5 shows, we did indeed find a p-wave onset near that energy, indicating ^2P ions. However, we were startled when our preliminary fits to equation (2) gave $E_0 \sim 1{\cdot}903 \pm 0{\cdot}008$ eV, indicating an electron affinity closer to 11±8 meV than the accepted value of 43 meV! The onset was not very strong, and because of the fine-structure splittings in the ^3P state, the uncertainty was fairly large, but certainly smaller than the difference between the two experimental results.

We again made measurements near 2·6 eV, where we observed the same onset that we had seen previously and attributed to ^4P transitions (Hanstorp *et al.* 1989). These new data near 2·6 eV were in essential agreement with the previous results, but now some uncertainty was growing regarding their proper interpretation.

(1e) Possible Slow Decay of ^2P from Blackbody Photodetachment. Does Metastable ^4P Exist?

The new results on ^2P were unsettling enough, but became more so when we considered the possibility that if the electron affinity were as low as 11 meV, blackbody photodetachment might be fast enough in the apparatus at 300 K to have caused the slow decay that we had observed in our beam and attributed to slow autodetachment (Hanstorp *et al.* 1989). This concern was heightened by some crude estimates of the blackbody rates. Using cross sections that were estimated by scaling those calculated for He^- photodetachment (Hazi and Reed 1981; Saha and Compton 1990) to account for a reduced EA of about 11 meV, we found effective lifetimes compatible with the 0·3 ms we had observed earlier (Hanstorp *et al.* 1989), and about 1 ms if the EA were 40 meV. Was it possible

that we only had ^{2}P ions in the beam, and that the increase near 2·6 eV we had attributed to ^{4}P was really the beginning of the large peak seen by Heinecke *et al.* (1974) and the 2·8 eV resonance found by Johnston *et al.* (1989)?

These questions were reinforced when we learned that Brage and Fischer (1991) had calculated autodetachment decay rates for the $J = \frac{3}{2}$ and $\frac{5}{2}$ states of ^{4}P, and found rapid rates exceeding 10^9 s^{-1}. These results cast doubt on the very existence of metastable ^{4}P, and thus on the interpretation of our old data. It was obvious that new measurements were urgently needed at higher photon energies between 2·6 and 3 eV.

2. Recent Work

We have recently carried out extensive photodetachment measurements in the energy region 2·8–3·1 eV, common to the peak in the data of Heinecke *et al.* (1974) in Fig. 1 and the scattering resonance of Johnston *et al.* (1989). In addition, we have made measurements in the 1·1–1·7 eV region near the minimum in Fig. 1. More measurements were also taken between 1·8 and 2·2 eV near the ^{2}P → ^{3}P threshold. The combined results are very revealing.

Except for minor modifications, the apparatus is the same as in the early work (Hanstorp *et al.* 1989)—see Fig. 3. The experiment is improved because the laser is now scanned automatically and the data processing is also improved using an on-line computer. For this work, one change was made for photon energies above 2·7 eV, because a substantial photoelectron current was generated on the InO_2 conducting surface covering the quartz plate that was used to monitor the neutral current while also passing the laser beam. This current severely interfered with the photodetached neutral current measurements above 2·7 eV. The problem was greatly alleviated by the eventual use of a thin (~40–60 Å) gold coating. Although this coating absorbed or reflected about 40% of the laser light (the wavelength dependence of the loss was determined and included in the cross sections), the photoelectron yield was fairly low and accounted for by laser on–off measurements with the ion beam blocked, before and after each run.

(2a) Shape Resonance above Ca 4s4p ^1P and the Electron Affinity of Ca ^1S

The data above 1·1 eV are shown in Fig. 6. The striking new feature is the large, narrow peak near 3 eV. It is obviously the same as the peak found by Heinecke *et al.* (1974) (Fig. 1), but much narrower because of our improved energy resolution. Noticing its location, we considered its possible association with the ^{1}P threshold, and because of its asymmetry and lack of interference structure, it strongly suggested a shape resonance with which we had become familiar in our earlier work on He^- (Peterson *et al.* 1985). This new structure appeared to be a shape resonance above the 4s^{2}4p ^{2}P → 4s4p ^{1}P+kp threshold. Thus it would be a p-wave shape resonance, similar to the He^- case, for which we had derived an approximate form to fit the cross section $\sigma(E)$ in a single channel case. Equation (10) of Peterson *et al.* (1985) can be rearranged as

$$\sigma(E) \sim (E - E_0)^{3/2}[(E - E_R)^2 + (\Gamma/2)^2]^{-1}, \qquad (3)$$

where E_0 and E_R are the photon energies of the threshold and resonance, and $\Gamma/2$ is the resonance half-width (decay rate). Although derived specifically for

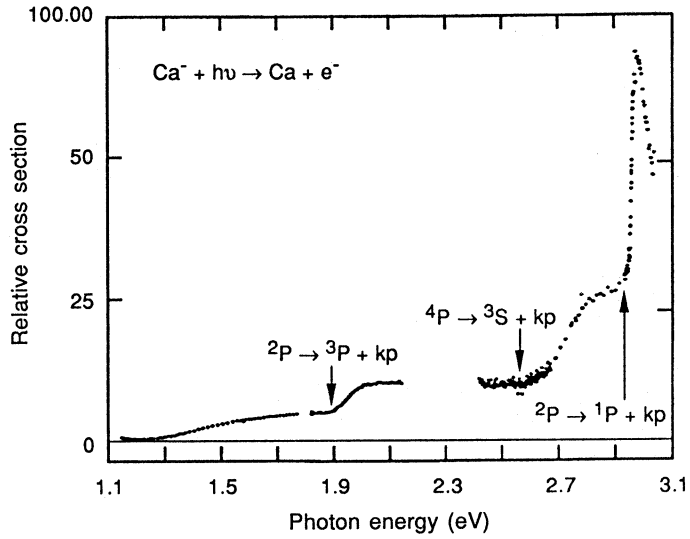

Fig. 6. Total photodetachment cross sections above 1·1 eV; arrows indicate various thresholds. Note the shape resonance near 2·9 eV.

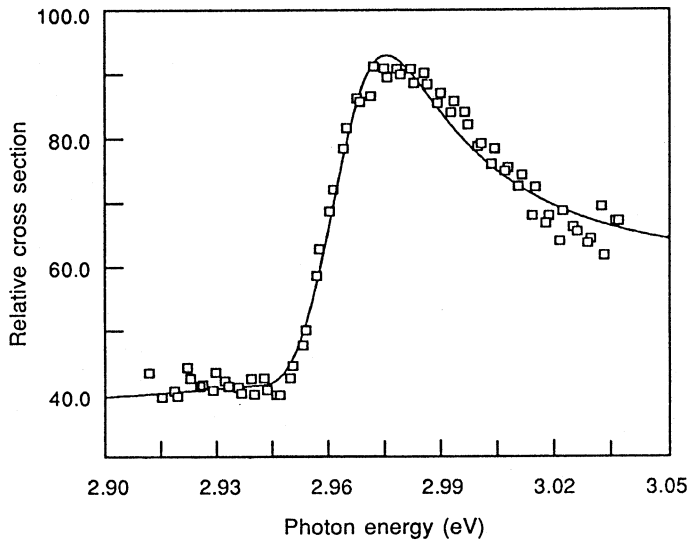

Fig. 7. Total photodetachment cross sections in the region of the shape resonance and a fit to all data using the modified threshold law to obtain E_R and $\Gamma/2$.

the near-threshold region, this formula can give a reasonable fit to the entire resonance to determine E_R and $\Gamma/2$. Then, with these parameters fixed, only near-threshold data are used to determine E_0 accurately.

In order to apply equation (3) properly, the various fine-structure (f.s.) transitions between initial and final states must be considered. The initial Ca^- is a doublet containing both $J = \frac{1}{2}$ and $\frac{3}{2}$ states separated by the interval ΔE_{fs}. The final neutral state is a singlet, $Ca(^1P)$. We neglect any f.s. splitting in the

resonance; it is probably small and in any case its effect on the threshold fitting for the determination of E_0 is negligible. Equation (3) can then be rewritten

$$\sigma(E) = \sigma_0 + AE + B\left(\frac{(E-E_0)^{3/2}}{(E-E_R)^2+(\Gamma/2)^2} + \frac{W[E-(E_0-\Delta E_{fs})]^{3/2}}{[E-(E_R-\Delta E_{fs})]^2+(\Gamma/2)^2)}\right), \quad (4)$$

where E_0 and E_R are relative to the ground state $Ca^-(^2P_{1/2})$, W is the population of $J=\frac{3}{2}$ relative to that of $J=\frac{1}{2}$, and B is a normalisation constant. The continuum contribution to the photodetachment cross section from both ^2P and ^4P populations in the Ca^- beam, seen below the threshold in Fig. 7, is approximated by the constant σ_0 plus a linearly energy-dependent term of slope A (determined from the cross section below threshold). The value of ΔE_{fs} has been calculated to be 6·9 meV by Dzuba *et al.* (1991) and 4·2 meV by Brage and Fischer (personal communication, 1991). In the following analysis, we have used the average of these, $\Delta E_{fs} = 5{\cdot}6$ meV. The calculated value of ΔE_{fs} is probably more certain than the calculated electron affinity because the correlation contributions, which determine the latter and are so difficult to determine, should be nearly identical for the two f.s. states. The populations are assumed to be given by the statistical weights of the initial $J=\frac{1}{2}$ and $\frac{3}{2}$ states, i.e. $W=2$, a reasonable assumption because of the small ΔE_{fs}.

In equation (4) E_R and $\Gamma/2$ were first obtained by a least squares fit to all data within 100 meV of the threshold. This fit, shown in Fig. 7, gave $E_R = 2{\cdot}9673$ eV and $\Gamma/2 = 17{\cdot}3$ meV. Next, with these parameters in (4) fixed, higher resolution

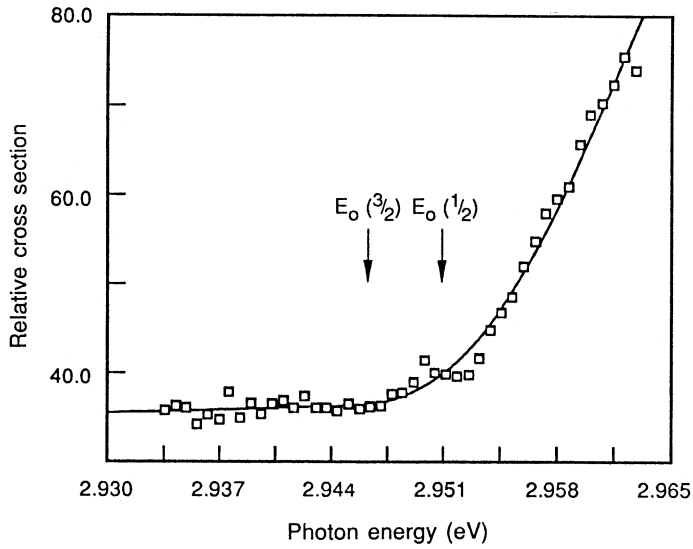

Fig. 8. Finely spaced data over a 30 meV range near the ^1P threshold, and a fit using equation (4) to obtain E_0.

data within only 15 meV of threshold were fitted, yielding an accurate value for $E_0 = 2{\cdot}9509$ eV, which is the energy of Ca ^{1}P relative to Ca^- $^2P_{1/2}$. The fit and E_0 are shown in Fig. 8. Combined with the uncertainties in ΔE_{fs} and the population W, this value of E_0 yields an electron affinity

$$EA(^1S) = 18{\cdot}4 \pm 2{\cdot}5 \text{ meV}$$

for the ground state of calcium. It agrees well with the more uncertain value of 15±6 meV obtained from the final analysis of the lower threshold, which will be discussed elsewhere by Walter *et al.* (1992). The agreement of the results obtained from two completely different thresholds gives great credence to the results.

The energy E_R of the resonance is higher than the $2{\cdot}8{\pm}0{\cdot}15$ eV obtained by Johnston *et al.* (1989) from their scattering data, however their energy resolution was much lower than ours and it is very difficult to obtain accurate values of the electron energy in the presence of metal vapours, which can give contact potentials of several tenths of an eV on other metal surfaces. The narrow width of 17 meV and lack of interference structure are consistent with its characterisation as a shape resonance located slightly above the ^{1}P state (Walter and Peterson 1992).

Table 1. Electron affinities for Ca(^{1}S) (in meV)

Reference	Method	EA
Experimental		
Present work	Photodetection threshold	18·4±2·5
Pegg *et al.* (1987)	Photoelectron spectroscopy	43±7
Theoretical		
Valence Correlation Only		
Froese Fischer *et al.* (1987)	MCHF	45
Froese Fischer (1989)	MCHF	62
Kim and Greene (1989)	R matrix	70
Gribakin *et al.* (1990)	Dyson equation	58
Cowan and Wilson (1991)	HFR	82
Core–Valence Correlation		
Johnson *et al.* (1989)	Dyson equation	56
Bauschlicher *et al.* (1989)	SOCI	22
Fuentealba *et al.* (1990)	CI+CV	0
Brage and Fischer (1992)	MCHF+CV	47

The discovery of the stable ^{2}P state (Froese Fischer *et al.* 1987; Pegg *et al.* 1987) stimulated a rash of theoretical activity that generated at least ten further calculations in the following four years using various techniques, and more work is under way at present. Most of the results are shown in Table 1. The results on the binding energy cover the range 0–100 meV, with most in the 40–60 meV range, so they are generally considerably higher than the measured 18 meV; only the 22 meV of Bauschlicher *et al.* (1989) is close. However, because these binding energies are only about 10^{-6} of the total electronic energy in the atom, higher accuracy is exceedingly difficult. Fuentealba *et al.* (1990) first pointed out that most calculations had ignored the effects of the polarisation of

the 3p core, which weakens the binding. In their calculations the binding dropped from 48 to 0 meV when core polarisation was included. The values in Table 1 are grouped according to whether they included this core–valence correlation.

(2b) Details of the $^2P \rightarrow {}^1S$+kd Interference Minimum near 1·1 eV

Johnston *et al.* (1989) concluded that the broad resonance in their scattering data, corresponding to the minimum near 1·1 eV in the data of Heinecke *et al.* (1974) shown in Fig. 1, resulted from a destructive interference between two strongly mixed ^{2}D states of $4s^23d$ and $4s4p^2$ configurations. Recent photodetachment calculations of Froese Fischer and Hansen (1991) have shown that this minimum, which is in the lowest (ks+kd) continuum above ^{1}S, results from a 'Cooper minimum' in the d-wave component, i.e. the optical dipole moment changes sign and the d-wave partial cross section goes to zero.

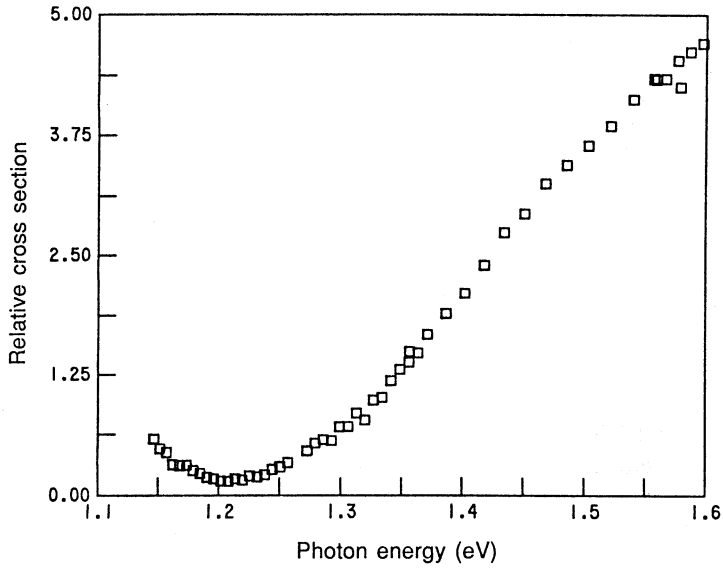

Fig. 9. Total cross sections near the d-wave Cooper minimum near 1·2 eV. Note the decreasing slope above 1·5 eV, as the interference weakens. The cross section at the minimum consists of weak contributions to the $^2P \rightarrow {}^1S$+ks continuum and from ^{4}P photodetachment.

We have now made accurate relative measurements in this energy region using a cw Ti–sapphire laser pumped by an Ar ion laser. The results are shown in Fig. 9. We find the minimum at 1·213±0·01 eV, from a parabolic fit. Froese Fischer and Hansen (1991) found values of the minimum between 1·35 and 1·45 eV for the *detached electron energy*, depending on the wavefunctions and type of calculation, but their wavefunctions also predicted a binding energy of 70 meV in the negative ion, which would place the photon energy still higher. Although their cross sections were adjusted in energy to have a threshold at 43 meV, in the light of our results, their initial wavefunctions were clearly too compact (tightly bound) which would result in higher energies for the photodetachment structures.

(2c) Verification of the Ca^- ^4P Metastability?

It can be seen in Fig. 6 that the shape resonance is not connected with the slower rise at 2·6 eV that we earlier attributed to the ^4P atoms in the beam. The cross section above that onset apparently reaches a maximum slightly above 2·8 eV, where the slope decreases, indicating the beginning of a broad peak, as expected for a p-wave cross section with no interfering channels or resonances. We have no explanation for this structure other than the original assignment to the $4s4p^2\ ^4P \rightarrow 4s5s\ ^3S+kp$ channel. Our best value for the binding of the metastable ^4P state below $^3P_0$ is 566±6 meV, compared with the predicted value of 550 meV from Bunge *et al.* (1982). What remains unknown is the ^4P decay rate.

Considering the possible blackbody photodetachment of the main ^2P component in our beam, we must conclude that the lifetime of the ^4P ions in the beam is unknown, except that we view them about 4 μs after their formation. We were naturally disturbed to learn of the predicted rapid autodetachment ($>10^9\ s^{-1}$) of the ^4P $J = \frac{3}{2}$ and $\frac{5}{2}$ states from the calculations of Brage and Froese Fischer (1991). However, very recent calculations by Brage *et al.* (1992) show that a cancellation of elements within the autodetachment interaction for the $J = \frac{1}{2}$ state greatly decreases its autodetachment rate compared with the other substates. The calculated rate results from the difference of two large numbers, and is probably difficult to obtain accurately. The most recent result for the lifetime is about 0·13 ms (Brage *et al.* 1992), which is too short considering our observations. Further experimental work on the ^4P decay rate is planned.

3. Summary and Conclusions

In recent work, we have managed to locate and identify a p-wave shape resonance in excited Ca^- located 16·3 meV above the the neutral ^1S state, with a half-width of 17·3 meV. A fit to the data using a modified threshold law to include the effects of a shape resonance (Peterson *et al.* 1985) established the photon energy of the ^1P threshold, from which the Ca ground state electron affinity $EA(^1S) = 18·4±2·5$ meV was determined. This value is confirmed by photodetachment measurements near the ^3P threshold, which yielded 15±6 meV. Other photodetachment measurements on ground state Ca^- gave a clear resolution of the d-wave interference minimum near 1·2 eV.

We have also reconfirmed and clarified a p-wave onset near 2·6 eV, which we can only ascribe to a metastable ^4P state component in the Ca^- beam, which was prepared so as to emphasise that state. Although some ^2P states are expected as direct products, the actual preponderance of ^2P probably results from the almost immediate decay of the initially dominant $J = \frac{3}{2}$ and $\frac{5}{2}$ ^4P states, yielding ^1S atoms, which can then capture electrons to form Ca^- ^2P.

From the lack of any observed photoexcitation of ^2P to 4s3d Ca $^{1,3}D$, we conclude that, above the first threshold to ^1S+ks, kd, the diffuse 4p electron in the Ca^- ground state is a spectator in higher final state excitations: only transitions from the 4s core occur. The ramifications of this behaviour will be discussed elsewhere (Walter *et al.* 1992).

Ca^- has indeed been a challenge to both theorists and experimentalists. The recent experimental work has apparently rendered the ^2P state more of a fixed

target for the theorists, and one that will require fine tuning of the theoretical techniques. With the fairly accurate determination of the binding energy of the ^2P state, and the additional definition of detailed structure caused by higher resonances and interferences, good opportunities exist for the development of detailed theoretical calculations on this complicated atomic system.

The most important remaining questions involve the blackbody photodetachment rate of the ground state, which requires good theoretical photodetachment cross sections, and the autodetachment decay rate of $^4P_{1/2}$, assuming that the other f.s. states decay so rapidly (Brage and Froese Fischer 1991) that they cannot be observed experimentally.

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