Shape Resonance in Ca^- Photodetachment and the Electron Affinity of $Ca(^1S)$

C. W. Walter and J. R. Peterson
Molecular Physics Laboratory, SRI International, Menlo Park, California 94025
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It was only recently found that a stable negative ion Ca^- ^2P exists below the $Ca(^1S)$ ground state. An electron affinity of 43 ± 7 meV was obtained experimentally, and numerous theoretical calculations have now found values between 0 and 100 meV. We report the first photodetachment threshold measurements on Ca^-, which display a p-wave threshold above Ca $4s4p\ ^3P$ and a large p-wave shape resonance above Ca $4s4p\ ^1P$. Both threshold energies obtained from the data agree with a new electron affinity of 18.4 ± 2.5 meV for $Ca(^1S)$.

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Among the many subjects of *ab initio* calculations of atomic energy levels, Ca^- is proving to be among the most challenging. Prior to 1987 the ^1S ground states of alkaline-earth atoms, with closed ns^2 subshells, were predicted theoretically to have negative electron affinities, analogous to the rare gases. Then, Froese Fischer, Lagowski, and Vosko [1] found theoretically that Ca^- exists stably in a $4s^24p\ ^2P$ state, bound by about 45 meV below $Ca(^1S)$, in agreement with measurements of Pegg *et al.* [2], who had earlier found evidence of a stable Ca^- state and subsequently measured an electron affinity $EA(^1S)$ of 43 ± 7 meV [2]. In the following four years at least ten other calculations [3–12] have examined alkaline-earth negative ions, with most finding Ca EA's in the 40–80-meV range, but with no consistent agreement. Calculations of higher accuracy are extremely difficult because, as Bates [13] points out, 40 meV is only 2×10^{-6} of the total electronic energy in Ca. Until now, there have been no other experimental determinations.

In another vein, the first results on stable Ca^- [1,2] led Johnston, Gallup, and Burrow [14] to reexamine earlier data on electron transmission through Ca vapor. The energy-differential currents revealed a broad resonance at 1.1 ± 0.15 eV and a narrow resonance at 2.8 ± 0.15 eV which were assigned to strongly mixed $4s^23d\ ^2D$ and $4s4p^2\ ^2D$ states of Ca^-. The data were also compared with early low-resolution Ca^- photodetachment measurements by Heinicke *et al.* [15], which showed structures at similar energies: a broad minimum near 1 eV and a narrow maximum near 2.9 eV. It is now clear that the Ca^- beam in the experiments of Heinicke *et al.* [15], which was extracted directly from an ion source, was predominantly in the stable ^2P state; however, because of the existing belief that Ca^- was unstable, they had considered the ions to be in long-lived ($>10\ \mu s$) excited states of ^4F or ^4P configuration. In fact, a metastable $4s4p^2\ ^4P$ state was eventually predicted theoretically by Bunge *et al.* [16] to be quite strongly bound by 550 meV below Ca ^3P. These calculations on Ca^- ^4P were first substantiated by work in our laboratory, in which we determined the $EA(^2P) = 562 \pm 15$ meV and measured a decay lifetime of 0.29 ± 0.10 ms [17]. In an extension of the work on ^4P, we recently sought evidence of the ^2P state of Ca^- in our beam, by photodetachment near the $^2P \rightarrow 4s4p\ ^3P + kp$ threshold, expected near $h\nu = 1.93$ eV. We indeed found a p-wave threshold [18], but its location near 1.90 eV placed the $EA(^1S)$ value closer to 15 meV than to the 43 meV of Pegg *et al.* [2]. We again observed the p-wave threshold near 2.6 eV that we had attributed earlier to the ^4P state [17], but now we were concerned that this structure might instead be connected with the *doublet* resonance near 2.8 eV discussed by Johnston *et al.* [14]. It became clear that more measurements were needed at higher photon energies near 2.8 eV.

We report here on new photodetachment measurements in the region 2.8–3.1 eV. The data reveal a large p-wave shape resonance located near 3 eV. Analysis of this structure both characterizes the resonance and establishes the energy of the $Ca(^1P)$ threshold, from which we derive a new electron affinity of 18.4 ± 2.5 meV for ground-state $Ca(^1S)$.

Except for minor modifications, the experimental setup has been described before [17]. Ca^+ ions were extracted from a Colutron ion source, accelerated to 3 keV, focused, magnetically mass analyzed, and directed through a Cs-vapor charge-transfer cell and into a separately pumped interaction chamber (pressure $\sim 3 \times 10^{-7}$ Torr). The beam then entered an electrostatic quadrupole $Q1$ which separated the various charge states exiting the charge-transfer cell (Ca^+,Ca^0,Ca^-) and deflected the Ca^- ions 90°, onto an 8-cm drift path and into a second quadrupole $Q2$, which directed them into a current monitor. Between the two quadrupoles, the ion beam was merged coaxially with a laser beam from an Ar^+-laser-pumped cw dye laser (linewidth ~ 0.5 Å). Neutral Ca atoms formed along the $Q1$-$Q2$ drift path passed through $Q2$ and struck the front surface of a quartz plate coated with a thin (~ 40 Å) film of gold, from which secondary electrons were ejected and accelerated to a channeltron electron multiplier, whose output pulses were amplified and counted. The laser beam then passed through the coated quartz plate (about 40% was absorbed or reflected) and was monitored after it exited the vacuum.

Fast Ca neutrals could be formed along the $Q1$-$Q2$

drift path from Ca^- either by photodetachment or autodetachment, or by collisions with the background gas. The photon-dependent component was determined by mechanically chopping the laser beam, and using a CAMAC-based gated two-channel counter to provide the on-off difference and sums of the channeltron output. The laser was scanned under computer control and the photodetachment signal was recorded as a function of laser frequency. At the higher photon energies above 2.8 eV, an additional laser-produced signal resulted from photoelectrons ejected from the gold surface of the quartz plate. This component was evaluated by scanning the laser with the ion beam off, before and after each photodetachment scan, and was subsequently subtracted from the data. The relative photodetachment cross sections were determined by normalizing the measured detachment signal to the transmitted laser power and the negative ion beam current. In order to obtain a consistent laser-ion beam overlap for each measurement, the laser beam was centered on two apertures placed external to the vacuum chamber at the entrance and exit windows. Using this procedure, the relative cross sections showed satisfactory internal consistency over a wide range of photon energies obtained with several different dyes used in the tunable laser.

We have now also used a tunable cw Ti:sapphire laser to cover almost continuously an extensive photon energy range from 1.13 to 3.04 eV. Most of the data are shown in Fig. 1; the complete results will be published separately [19]. We concentrate here on the narrow region 2.9–3.04 eV, for which Stilbene 1 dye was used in the dye laser.

We draw attention to the cross section near the ^1P threshold in Fig. 1. A large sharp peak occurs near 3.0 eV, atop a slowly increasing background from detachment to lower-energy continua, including the $^4P \rightarrow {}^3S + kp$ channel studied earlier [17] using the same Ca^- beam as produced in this work. The data near 3 eV are shown in greater detail in Fig. 2. The peak has the form characteristic of an electronic shape resonance, similar to the $He^-(1s2p^2\,{}^4P)$ shape resonance that was well resolved in our earlier work [20]. In shape resonances, the excited electron is temporarily bound above the parent state by the centrifugal potential barrier caused by its own orbital angular momentum $l>0$, and decays into that continuum. Thus it gives only a positive contribution to the total cross section, and will appear asymmetrical if close to threshold. In contrast, Feshbach states lie below the parent neutral state and decay by configuration interaction with the continuum of one or more lower neutral states. Thus they decay slower and are narrower than shape types, and also exhibit destructive as well as constructive interference with the underlying continua, as described by Fano [21].

The 3.0-eV peak has the asymmetric, noninterference structure of a shape resonance, and its energy suggests a p-wave shape resonance above the $4s^24p\,{}^2P \rightarrow 4s4p\,{}^1P + kp$ threshold $E_0({}^1P)$. This interpretation will be justified by the following data analysis.

In the absence of resonances or interactions with lower continua, the photodetachment cross section just above an opening channel with continuum electron of angular momentum l and linear momentum k follows the Wigner threshold law $\sigma \sim k^{2l+1}$. However, as observed in He^- by Peterson, Bae, and Huestis [20], the Wigner law fails quickly above the threshold in the presence of a shape resonance. They derived a modified threshold formula to include the effects of a p-wave shape resonance [20]. An approximate form, their Eq. (10), can be expressed as

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

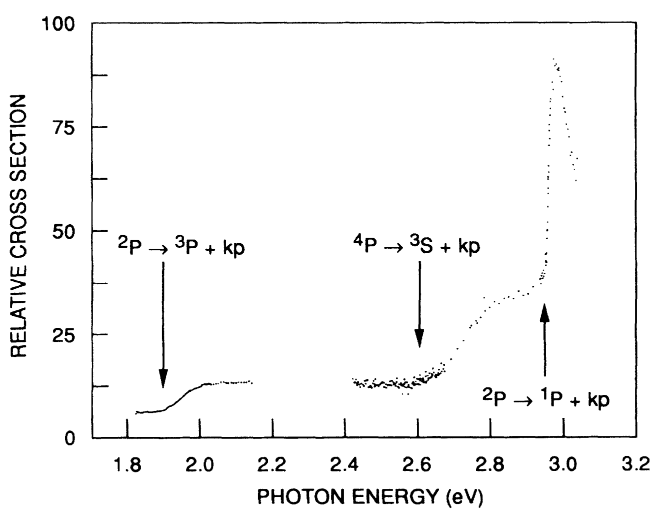

FIG. 1. Total photodetachment cross sections above 1.8 eV; arrows indicate various thresholds from ^2P and ^4P Ca^- beam components. Note the shape resonance near 2.9 eV.

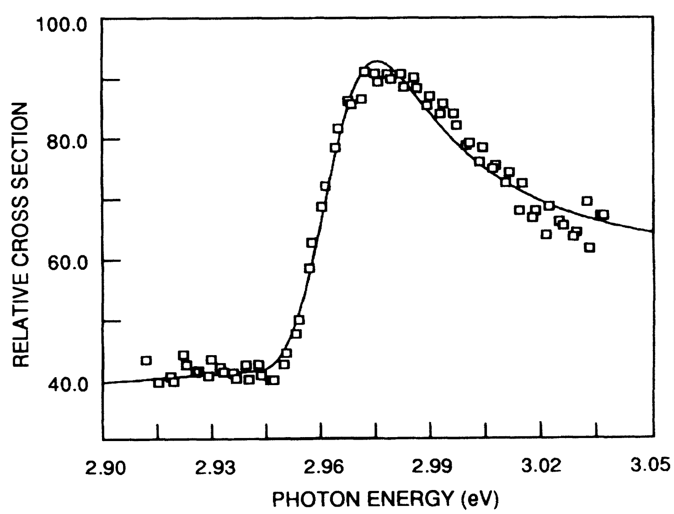

FIG. 2. Data in the region of the shape resonance, and a fit to them using the modified threshold law, Eq. (2), to obtain E_R and $\Gamma/2$.

where E is the photon energy, E_0 is the threshold of the opening state, E_R is the resonance energy, and $\Gamma/2$ is the half-width [(inverse lifetime)/$\hbar$]. It can be seen that this approximate form is simply a Wigner threshold numerator with a dispersion-type resonance denominator. Although derived specifically for near-threshold data, this formula can give a reasonable fit to the entire resonance [20] to determine E_R and $\Gamma/2$. With these fixed, only near-threshold data are then used to determine E_0.

In order to apply Eq. (1), the various fine-structure (fs) transitions between initial and final states must be considered. Here the initial Ca^- state is a doublet consisting of $^2P_{1/2}$, the ground state, and $^2P_{3/2}$, separated by the interval ΔE_{fs}. The final state of Ca is a singlet, Ca(^1P). We neglect any fs splitting in the resonance; it is probably small and its effect on the determination of E_0 is negligible. Equation (1) can then be rewritten as

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

where E_0 and E_R are relative to the $Ca^-(^2P_{1/2})$ ground state, W is the population of $J=\frac{3}{2}$ relative to that of $J=\frac{1}{2}$, and B is a normalization constant. The continuum contribution to the photodetachment cross section from both ^2P and ^4P components in the Ca^- beam is approximated by the constant σ_0 plus a linearly energy-dependent term of slope A (determined from the cross section below threshold). ΔE_{fs} in $Ca^-(^2P)$ has been calculated to be 6.9 meV by Dzuba *et al.* [22], and 4.2 meV by Brage and Froese Fischer [23]. These fs interval calculations should be much more reliable than those for the absolute electron affinity because the correlation contributions (difficult to calculate) should be nearly identical for the $^2P_{1/2}$ and $^2P_{3/2}$ state energies. In the analysis that follows, we take $\Delta E_{fs}=5.6$ meV, the average of these values. The populations of the fs levels are assumed to be given by the statistical weights of the initial $J=\frac{1}{2}$ and $\frac{3}{2}$ states, i.e., $W=2$. This assumption seems reasonable because of the small energy separation.

The values of E_R and $\Gamma/2$ in Eq. (2) were established by a least-squares fit to all the data within 100 meV of the threshold. This fit, shown as the solid line in Fig. 2, gave $E_R=2.9673$ eV and $\Gamma/2=0.0173$ eV. Next, the resonance parameters were fixed at these values and the higher-resolution data within only 15 meV of threshold were fitted to yield $E_0=2.9509$ eV, which represents the threshold for the $Ca^-(^2P_{1/2})\rightarrow Ca(^1P)+kp$ transition. Equation (2) provides a satisfactory fit to the entire resonance, and a very good fit to the threshold data, as seen in Fig. 3. Note that the slow onset of the p-wave behavior obscures the two fs thresholds, which are contained in Eq. (2) and the fit shown in Fig. 3. Extension of the measurements to higher photon energies was prevented by our inability to operate the dye laser at shorter wavelengths.

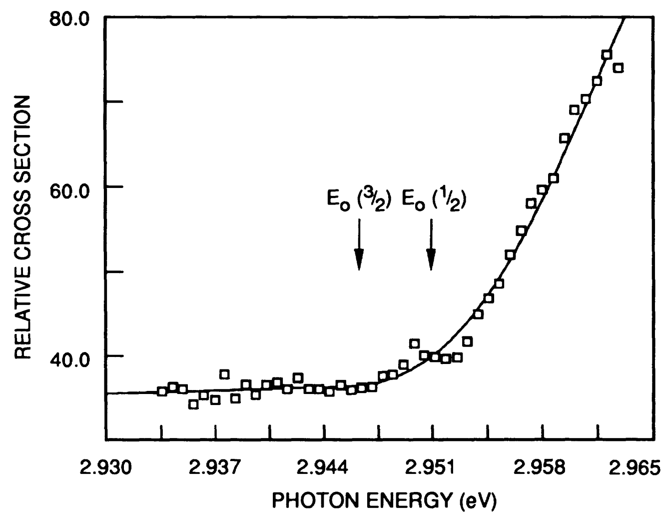

FIG. 3. Finely spaced data over a 30-meV range near the ^1P threshold, and a fit using Eq. (2) to obtain E_0. $E_0(\frac{1}{2},\frac{3}{2})$ indicate the thresholds for $^2P_{1/2,3/2}\rightarrow {}^1P+kp$.

The fit to all the data fixes E_R at 16.3 meV above E_0, and $\Gamma/2=17.3$ meV. Such nearly equal magnitudes of $\Gamma/2$ and E_R-E_0 were also observed in the $^4P^e$ shape resonance in He^- [20], and this characteristic probably typifies shape resonances in general [14,20]. The similarity here supports our interpretation of the resonance as associated with (located above) the ^1P state instead of the ^3P state, as suggested by Johnston, Gallup, and Burrow [14]. If the shape resonance were attached to the lower ^3P state at 1.89 eV, E_R-E_0 would be 1.08 eV and $\Gamma/2$, the half-width, would be much broader than 17 meV.

From the measured threshold energy $E_0(^1P)$ we determine EA(^1S) via the relation

$$\mathrm{EA}(^1S)=E_0(^1P)-E(^1P), \tag{3}$$

where $E(^1P)=2.9325$ eV is the spectroscopically established energy of Ca ^1P relative to ^1S. Using $E_0=2.9509$ eV, we obtain EA(^1S)$=18.4\pm2.5$ meV. We believe that the uncertainty is reasonably conservative. It results primarily from determining the slope and magnitude of the continuum and from the uncertainty in ΔE_{fs} (the fit itself yields an uncertainty ~ 1.0 meV). This value of EA(^1S) agrees with the less certain value of 15 ± 6 meV obtained from analysis [19] of the lower ^3P threshold data seen in Fig. 1. The large uncertainty here results from the less distinct onset and the large fs splittings in the Ca ^3P state. Thus data from two separate thresholds agree with the value EA(^1S)$=18.4\pm2.5$ meV, in disagreement with the 43 ± 7 meV obtained by Pegg *et al.* [2]. We have sought an explanation for the difference (in consultation with Pegg and Compton). We have found none, but we note that low-energy electron measurements are inherently difficult. The agreement of our determination from the two separate thresholds estab-

TABLE I. Electron affinities for Ca(^1S) in meV. MCHF denotes multiconfiguration Hartree-Fock; DFT, density functional theory; HFR, relativistic Hartree-Fock; SOCI, second-order configuration interaction.

Reference	Method	EA
Experimental		
Present work (1991)	Photodetachment threshold	18.4 ± 2.5
Pegg *et al.* (1987) [2]	Photoelectron spectroscopy	43 ± 7
Theoretical		
Valence correlation only		
Froese Fischer *et al.* (1987) [1]	MCHF	45
Froese Fischer (1989) [3]	MCHF	62
Vosko *et al.* (1989) [4]	DFT	130
Kim and Greene (1989) [5]	*R* matrix	70
Gribakin *et al.* (1989) [8]	Dyson equation	63
Gribakin *et al.* (1990) [9]	Dyson equation	58
Cowan and Wilson (1991) [11]	HFR	82
Core-valence (CV) correlation		
Johnson *et al.* (1989) [6]	Dyson equation	56
Bauschlicher *et al.* (1989) [7]	SOCI	22
Fuentealba *et al.* (1990) [10]	CI+CV	0
Brage and Fischer (1991) [12]	MCHF+CV	47

lishes strong confidence in it.

The experimentally determined electron affinities and a summary of theoretical values are tabulated in Table I. The uncertainty in the calculations is manifested in the lack of agreement among them and, as mentioned above, reflects the difficulty in obtaining an uncertainty of even 50 meV in the calculations when it is only $\sim 10^{-6}$ of the total energy. Nevertheless, such accuracy is a challenge to the calculations, and will doubtless be achieved when all of the correlation, relativistic, and core polarization effects are adequately accounted for, along with the use of suitably large wave-function basis sets. In addition, the location and width of the shape resonance, and the resultant photodetachment cross sections are important quantities that can also be calculated for comparison with the present experimental results.

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