State-Selective Depletion Spectroscopy of Negative Ions: First Observation of the ^4P State in Ca$^-$ and Sr$^-$

P. Kristensen, C. A. Brodie,* U. V. Pedersen, V. V. Petrunin,† and T. Andersen
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

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A new nonlinear laser technique, yielding accurate and detailed information about the photodetachment process, is applied to the study of excited states in atomic negative ions. The method has facilitated the first experimental observation of the controversial ^4P state in the Ca$^-$ ion and the homologous state in the Sr$^-$ ion and also provided comprehensive information about their binding energies, fine-structure intervals, and autodetachment lifetimes, together with the absolute strengths of the intercombination transitions to the ^2P ground states. [S0031-9007(97)02770-1]

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Acquiring reliable information about the structure and dynamics of negative ions, especially of weakly bound systems like the alkaline-earth ions, has proven to be a challenge in atomic physics. Previously, the most accurate and trustworthy data were obtained from photodetachment studies based either on observation of the neutral atom yield or on electron spectroscopy. Absolute cross-section measurements are, however, difficult to perform with these methods, since accurate information about both the ion density and the number of produced atoms is required. In addition, the sensitivity and resolution obtainable with these methods were not sufficient to gain the much needed structural information about weakly bound ions which constitute the test field for the ongoing theoretical and computational development. Recently, a new nonlinear spectroscopic technique was introduced which allowed the determination of structural information for long-lived or stable states, by measuring the relative photodetachment yield detected by state-selective resonant ionization of the produced atoms [1].

In this Letter, we present a new and markedly different nonlinear laser technique, based on the measurement of the photodetachment depletion of a specific long-lived or stable negative-ion state. This method allows photodetachment studies of individual fine-structure components of the negative ion yielding partial absolute ϵl-wave cross sections (i.e., ϵs, ϵd wave) in the vicinity of an autoionizing state. The applicability and potential of this technique are demonstrated by studies of the photodetachment cross section of the Ca$^-$ ^2P ground-state levels in the vicinity of the first excited $4s4p^2\ ^4P$ state, together with similar studies of the Sr$^-$ ion. The new technique has facilitated the first unambiguous observation of the ^4P states, and also made possible a comprehensive study of these autodetaching ions, yielding information about their structural and dynamic properties.

The $4s4p^2\ ^4P$ state has played a very important role in the process leading to the present understanding of the Ca$^-$ ion, the most studied negative ion for the last ten years (for a review, see Ref. [2]). It is, however, doubtful whether the Ca$^-$ ^4P ion has ever been observed [2–9]. Prior to 1987, when the stable Ca$^-$ ion was discovered [10], the existence of this ion was assumed to be due to the $4s4p^2\ ^4P$ state which was predicted to be a long-lived metastable state, with a lifetime exceeding several μs and bound by 550 meV with respect to the Ca $4s4p\ ^3P$ state [3]. In 1989, Hanstorp *et al.* [4] reported the observation of an excited state in Ca$^-$ with a lifetime of $290 \pm 100\ \mu$s and attributed this to the decay of the metastable ^4P state. It was also claimed [4] that the Ca$^-$ beam did not contain stable ground-state ions, but only metastable ^4P ions, and thus a variation in the photodetachment cross section was attributed to the opening of the Ca$^-$ $4s4p^2\ ^4P + \hbar\omega \rightarrow$ Ca $4s5s\ ^3S + \epsilon l$ channel from which a binding energy of 562(5) meV was deduced for the ^4P state. However, the long lifetime was in contradiction with calculations [5,7], yielding lifetimes for the ^4P state of less than $\sim 0.1\ \mu$s. Haugen *et al.* [8] also showed experimentally that a beam of Ca$^-$ ions in the ground state would decay with a lifetime of $490 \pm 20\ \mu$s due to photodetachment by room temperature blackbody radiation. Recently, calculations of the binding energy for the Ca$^-$ ^4P state have yielded values which are in good agreement with each other [9], but which differ significantly from the experimental value. Thus it is very doubtful whether the ^4P state in Ca$^-$ has been observed so far [11]. The study of the Sr$^-$ ion has been less intensive until now, and only the existence of the ground state is established [12,13].

The experiments were carried out using a collinearly overlapped negative-ion/laser-beam setup previously described [1,11,14]. A 40 kV Ca$^-$ or Sr$^-$ beam is overlapped by three pulsed nanosecond laser beams in a 1 m long interaction region. As illustrated in Fig. 1, the first laser pulse λ_{detach} is used to explore the detachment cross section in the energy region around the ^4P autoionizing state. The λ_{probe} (532 nm) pulse is applied, with a small time delay after the first laser pulse ($\tau \approx 10$ ns), to probe the remaining population in the ground-state levels by detachment to the $nsnp\ ^3P_{J=0,1,2}$ levels of the parent atom ($n = 4$ for Ca, $n = 5$ for Sr). Detachment from the $ns^2np\ ^2P_{1/2}$ level populates the ^3P state predominantly

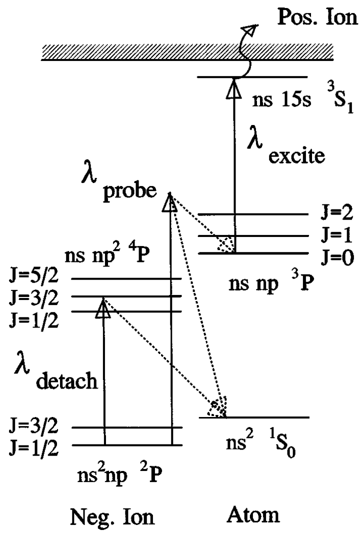

FIG. 1. Schematic energy-level diagram of the negative ion (Ca^-, $n = 4$, Sr^-, $n = 5$) and the corresponding parent atom (Ca or Sr).

in the $J = 0, 1$ levels since detachment to the $J = 2$ level can occur only if the spin of the np electron, upon removal of one of the ns electrons, changes direction with respect to the direction of the angular momentum. On the other hand, detachment from the $^2P_{3/2}$ level leads to formation of the ^3P state mainly in the $J = 1, 2$ levels. Thus, the populations of $J = 0$ and $J = 2$ are proportional to the $J = 1/2$ and $J = 3/2$ populations in the ^2P ground state just prior to the application of the λ_{probe} laser beam. The populations of the ^3P_J levels are monitored separately via resonant excitation by the λ_{excite} pulse to the $ns15s$ $^3S_1$ Rydberg level, followed by state-selective field ionization [1]. This detection scheme provides independent measurements of the absolute photodetachment cross section for the two ^2P fine-structure components by monitoring the decrease in the population of each of these levels after the interaction with the λ_{detach} beam.

In Fig. 2, the Ca^+ ion signal is shown as a function of the wavelength of the λ_{detach} laser in the region around the Ca^- $^2P_{3/2} \rightarrow {}^4P_{5/2}$ transition. Since the ^4P autodetaching levels are energy degenerate with the $^1S + \epsilon l$ continuum, the photodetachment cross section will display a Fano interference pattern [15]. Photodetachment of the $^2P_{J,M}$ levels can, in the electric-dipole approximation with linearly polarized light, proceed via

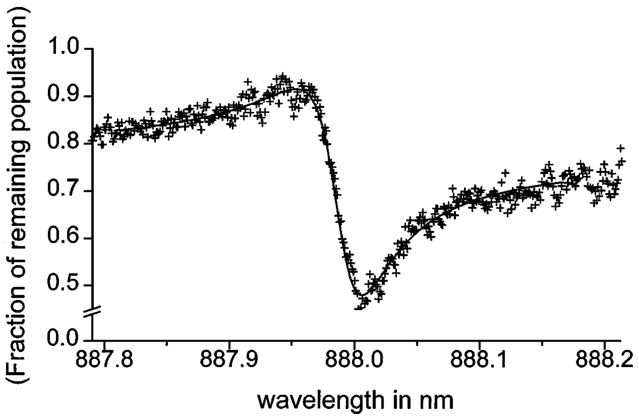

FIG. 2. The positive-ion signal vs wavelength in vacuum for the Ca^- $^2P_{3/2} \rightarrow {}^4P_{5/2}$ transition. The data have been normalized to the signal level when blocking the first laser. The solid line is a fit to the data (see Table I)

$$^2P_{1/2,M} + \hbar\omega \rightarrow {}^1S_0 + \epsilon s[^2S_{1/2,M}], \quad \epsilon d[^2D_{3/2,M}] \tag{1}$$

and

$$^2P_{3/2,M} + \hbar\omega \rightarrow {}^1S_0 + \epsilon s[^2S_{1/2,M}], \quad \epsilon d[^2D_{3/2,M}, {}^2D_{5/2,M}], \tag{2}$$

where M, the magnetic quantum number, is conserved due to the polarization. The cross sections for photodetachment via the individual channels $\sigma(L, J, M, L', J', M')$ are related through $3j$ and $6j$ symbols by

$$\begin{aligned} \sigma(L, J, M, L', J', M') = {} & \begin{pmatrix} J & 1 & J' \\ -M & 0 & M' \end{pmatrix}^2 \\ & \times \begin{Bmatrix} J & 1 & J' \\ L' & 1/2 & L \end{Bmatrix}^2 (2J + 1) \\ & \times (2J' + 1)\sigma(L, L'), \end{aligned} \tag{3}$$

where (L, J, M) and (L', J', M') are the quantum numbers for the initial and final states (detachment channel), respectively. Excitation of the intermediate autodetaching $^4P_{J'',M''}$ state can only interfere with a detachment channel provided that $J'' = J'$ and $M'' = M' = M$. Thus, the population of a specific initial level is

$$\begin{aligned} \sum_M \frac{N(J, M)}{N^0(J, M)} = \sum_M \exp\Big[& - \int S\sigma(L, J, M, L', J'', M)\phi(t)\, dt \\ & - \sum_{J' \neq J''} \int \sigma(L, J, M, L', J', M)\phi(t)\, dt \Big]. \end{aligned} \tag{4}$$

The exponent is a sum of the contribution from the interfering and the noninterfering channel. According to Fano [15], the shape of the interference structure S can be expressed in the following parametric form:

$$S(\hbar\omega) = \frac{(\frac{E_r - \hbar\omega}{\Gamma} + q)^2}{(\frac{E_r - \hbar\omega}{\Gamma})^2 + 1}, \tag{5}$$

where E_r is the energy of the autodetaching resonance relative to the initial ^2P_J level, Γ the autodetachment decay rate, and q the Fano (or asymmetry) parameter. The photon flux is given by $\phi(t) = I(t)/\hbar\omega$, $I(t)$ being the intensity of the laser pulse as a function of time, and $\hbar\omega$ the photon energy. $\sum_M [N(^2P_{J,M})/N^0(^2P_{J,M})]/(2J + 1)$ is obtained by normalizing the positive ion signal to the signal level when blocking the $\lambda_{\mathrm{detach}}$ laser. The finite bandwidth of the laser was modeled by folding the cross section in Eq. (5) with a Gaussian profile of the same width as that of the laser. The parameters obtained by fitting the scans for each of the transitions are presented in Table I. The transition energies are corrected for the Doppler shift which was deduced by recording the resonances with the $\lambda_{\mathrm{detach}}$ laser beam co- and counterpropagating the ion beam. The cross sections are obtained assuming a uniform spatial laser intensity. For the transitions to the Ca$^-$ $^4P_{1/2}$ level, the value of the height of the Fano profile ($\Delta\sigma = \sigma_{\max} - \sigma_{\min}$) and the total background $[\sum_{L'} \sigma(L, L')]$ are given instead of q and the cross sections $\sigma(L, L')$ since the width of the resonance is determined by that of the laser. Consequently, the data were fitted with a Gaussian instead of a Fano profile. The strength of an optical $^2P \rightarrow {}^4P$ transition is given as the Einstein coefficient $A_{if} = \Delta\sigma\Gamma(2\pi)^2 g_i/g_f\lambda^2$, where g_i and g_f are the statistical weights of the initial and final states. For a Fano profile $\Delta\sigma = (1 + q^2)\sigma(L, J, M, L', J', M')$ [16]. All the ^4P levels can be expected to have quite long radiative lifetimes $\tau^{\mathrm{rad}} = (\sum A_{if})^{-1}$ since the transitions to the ground state require a spin flip. Using the values from Table I, the radiative lifetimes of the Ca$^-$ $^4P_{1/2}$ and the Sr$^-$ $^4P_{1/2}$ levels were determined to be 900 and 30 μs, respectively.

The autodetachment lifetime is given by the width of the resonance as $\tau^{\mathrm{auto}} = (2\pi\Gamma)^{-1}$. For Ca$^-$ ^4P, these have previously been predicted by Brage and Fischer [5], yielding $\tau_{3/2}^{\mathrm{auto}} = 822$ and $\tau_{5/2}^{\mathrm{auto}} = 86.5$ ps, which is about 1 order of magnitude larger than the experimental values in Table I. The widths of the resonances corresponding to the Ca$^-$ $4s^24p$ $^2P_{1/2,3/2} \rightarrow 4s4p^2$ $^4P_{1/2}$ transitions are limited by the bandwidth of the laser, indicating a lifetime for the $^4P_{1/2}$ level longer than 100 ps. An upper limit for this lifetime was determined by a pump-probe technique. Population was transferred from the $^2P_{3/2}$ to the $^4P_{1/2}$ level by the $\lambda_{\mathrm{detach}}$ laser and subsequently probed, as a function of time, by a second laser pulse ($\lambda \sim 1064$ nm) detaching the $^4P_{1/2}$ population to the Ca $^3P_0$ level which finally was monitored by the resonance-ionization method described earlier. The first laser was attenuated so that only a very limited part of the ions were photodetached by this laser after being excited to the $^4P_{1/2}$ level. Since the positive ion signal could be observed only when the two laser pulses were overlapping, the lifetime for the $^4P_{1/2}$ level must be less than the 10 ns duration of the two lasers pulses. This signifies that the $^4P_{1/2}$ autodetachment lifetime is in the range 0.1–10 ns, much shorter than the 137 ns predicted by Miecznik *et al.* [7].

The total cross sections for the s- or d-wave emission can be obtained from Eq. (3) and the data in Table I. A quantitative comparison between the present cross sections and the calculated values for Ca$^-$ [17]

TABLE I. The parameters obtained by fitting the data: E_r is the photon energy for the transition, τ^{auto} the autodetachment lifetime, A_{ij} the Einstein coefficient, q the Fano asymmetry parameter, and $\sigma_s = \sigma(1,0)$ and $\sigma_d = \sigma(1,2)$ the values for $\sigma(L, L')$ defined in Eq. (3) (total cross sections are 1/9 of the values quoted for σ_s and σ_d).

	E_r (cm^{-1})	τ^{auto} (ps)	A_{ij} [a] (10^3 s^{-1})	q	σ_s [a] (Mb)	σ_d [a] (Mb)
Ca$^-$						
1/2-1/2	11 199.19(8)	>100[b]	0.2		(see note[c])	
1/2-3/2	11 231.10(8)	57(15)	0.3	1.7	65	110
3/2-1/2	11 159.96(8)	>100[b]	0.9		(see note[d])	
3/2-3/2	11 191.85(8)	70(15)	0.4	4.2	60	95
3/2-5/2	11 244.62(8)	9(2)	6.0	1.9	64	113
Sr$^-$						
1/2-1/2	10 629.94(16)	12(4)	4.5	−4.8	52	266
1/2-3/2	10 751.04(16)	8(2)	2.1	1.0	57	220
3/2-1/2	10 469.36(16)	13(4)	33	−3.0	45	200
3/2-3/2	10 590.59(16)	7(2)	5.8	3.3	52	226
3/2-5/2	10 786.04(16)	1.7(3)	51	1.6	52	258

[a] The relative uncertainties for A_{ij}, σ_s, and σ_d are ~15%. The accuracy of the absolute values are estimated to be ~30% mainly limited by the uncertainty in the determination of the photon flux.

[b] The widths of these resonances were determined by the bandwidth of the laser.

[c] $\Delta\sigma = 16$ Mb, $\sigma_s + \sigma_d = 170$ Mb; see text.

[d] $\Delta\sigma = 33$ Mb, $\sigma_s + \sigma_d = 130$ Mb; see text.

TABLE II. Binding energy and fine-structure splittings of the ^4P state, and fine-structure splitting of the ^2P ground state in meV.

	Binding energy		ΔE	
	^4P	$^2P_{3/2\text{-}1/2}$	$^4P_{3/2\text{-}1/2}$	$^4P_{5/2\text{-}3/2}$
Ca^-	521.84(10)	4.865(14)	3.955(14)	6.543(14)
Sr^-	532.38(3)	19.89(3)	15.01(3)	24.23(3)

is, however, unjustified: at the photon energy where the Ca^- ^4P state is observed, the theoretical calculations predict [17] the appearance of a Cooper minimum, but this feature has previously been reported to appear at somewhat lower photon energies [2,18]. The agreement between the present measured cross sections and the values calculated for Ca^- and Sr^- by Gribakin *et al.* [19] from the velocity form of the dipole matrix element may be considered fortuitous, since the cross sections calculated in the length and the velocity form differ considerably.

The fine-structure splittings of both the ground and excited states are shown in Table II. The ground-state values confirm recent experimentally reported fine-structure splittings for Ca^- [11] and Sr^- [12], but improve the accuracy by a factor of 7 and 2, respectively. The ^4P fine-structure splittings are markedly larger than the values predicted by Cowan and Wilson [20], whereas the $\Delta E_{5/2\text{-}1/2} = 10.498(20)$ meV splitting for the Ca^- ion is in good agreement with the 11.4 meV calculated by Fischer *et al.* [9]. The binding energies in Table II represent the center-of-gravity energy of the $nsnp^2$ ^4P states with respect to the center-of-gravity energy of the $nsnp$ ^3P states. These values were obtained using the known electron affinities and energy splittings [11,12,21]. The binding energy for the Ca^- ^4P state $\Delta E = 521.84(10)$ meV is significantly smaller than the 550 meV calculated by Bunge and Galán [3] and the experimental value of 562 meV reported by Hanstorp *et al.* [4]. Our value is in good agreement with the recent calculations by Fischer *et al.* [9] who reported 515.8 meV, and 517 ± 10 meV, and with Cowan and Wilson's calculation [20] yielding 520 meV. The Sr^- ^4P binding energy of 532.38(3) meV is also in good agreement with the calculated value of 540 meV obtained by Cowan and Wilson [20]. They reported the binding energies of the $^4P_{1/2}$ levels with respect to the $^3P_0$ levels, but the necessary corrections for allowing comparison have been performed.

The short lifetimes observed for all three fine-structure levels of the ^4P state in Ca^- finally dismiss the previous claims by Hanstorp *et al.* [4] for observing the quartet state. The increase in the photodetachment cross section, observed at $20\,765 \pm 40$ cm^{-1} and considered [2,6] as an indication for observation of Ca^- ^4P, can now also be dismissed as representing the onset of the ($^4P + \hbar\omega \rightarrow 4s5s\ ^3S + \epsilon p$) detachment channel.

In summary, a new spectroscopic technique has been developed by which the partial absolute photodetachment cross sections can be measured by observing the residual population of the specific fine-structure levels of the ground state of the negative ion. Observation of the variations in the cross section allows a determination of the binding energies, fine-structure intervals, and autodetachment lifetimes of the excited state in the negative ion. The present study of the Ca^- and Sr^- ions indicates that the state-selective depletion technique may be a valuable tool to elucidate the structural properties of more complex negative ions such as the rare earth ions for which hardly any reliable information has been achieved so far.

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*Also at McMaster University, Hamilton, Ontario, Canada.

†Permanent address: Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia.

[1] V. V. Petrunin *et al.*, Phys. Rev. Lett. **75**, 1911 (1995).
[2] J. R. Peterson, Aust. J. Phys. **45**, 293 (1992).
[3] C. F. Bunge and M. Galán, Nucl. Inst. Meth. Phys. Res. **202**, 299 (1982).
[4] D. Hanstorp, P. Devynck, W. G. Graham, and J. R. Peterson, Phys. Rev. Lett. **63**, 368 (1989).
[5] T. Brage and C. F. Fischer, Phys. Rev. A **44**, 72 (1991).
[6] C. W. Walter and J. R. Peterson, Phys. Rev. Lett. **68**, 2281 (1992).
[7] G. Miecznik, T. Brage, and C. F. Fischer, J. Phys. B **25**, 4217 (1992).
[8] H. K. Haugen *et al.*, Phys. Rev. A **46**, R1 (1992).
[9] C. F. Fischer, J. E. Hansen, and H. W. Hart, Phys. Rev. A **51**, 1999 (1995).
[10] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).
[11] V. V. Petrunin, H. H. Andersen, P. Balling, and T. Andersen, Phys. Rev. Lett. **76**, 744 (1996).
[12] H. H. Andersen, V. V. Petrunin, P. Kristensen, and T. Andersen, Phys. Rev. A (to be published).
[13] D. Berkovits *et al.*, Phys. Rev. Lett. **75**, 414 (1995).
[14] P. Kristensen, U. V. Pedersen, V. V. Petrunin, T. Andersen, and K. T. Chung, Phys. Rev. A **55**, 978 (1997).
[15] U. Fano, Phys. Rev. **124**, 1866 (1961).
[16] E. Lindroth, Phys. Rev. A **52**, 2737 (1995); (private communication).
[17] C. F. Fischer and J. E. Hansen, Phys. Rev. A **44**, 1559 (1991).
[18] E. Heinicke, H. J. Kaiser, R. Rackwitz, and D. Feldmann, Phys. Lett. **50A**, 265 (1974).
[19] G. F. Gribakin, B. V. Gul'tsev, V. K. Ivanov, and M. Y. Kuchiev, J. Phys. B **23**, 4505 (1990).
[20] R. D. Cowan and M. Wilson, Phys. Scr. **43**, 244 (1991).
[21] A. A. Radzig and B. M. Smirnov, in *Reference Data on Atoms, Molecules, and Ions*, edited by J. P. Toennies (Springer-Verlag, Berlin, 1985), 1st ed.