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Resonant multicolor spectroscopy in the photodetachment continuum: Observation of the metastable ^4S state in the negative calcium ion

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We report the observation of the predicted metastable $4p^3\ ^4S$ state in the Ca^- ion utilizing a spectroscopic technique based on nonlinear resonant multicolor absorption via an autodetaching state. The binding energy of the ^4S state is determined to be 586.86(10) meV with respect to the parent $Ca(4p^2\ ^3P)$ state, a value less than 3 meV from the predicted one. The lifetime of the ^4S state is determined to be larger than 7 ps.

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Negative atomic ions have attracted considerable interest among theoretical and experimental physicists for quite some time due to their special properties, such as the short-range potential or the strong influence of the electron-electron interaction. It is now well established that for many negative ions the ground state cannot be approximated adequately by a single configuration. The binding of an extra electron to the neutral atom is greatly influenced by the strength of the dielectronic repulsion compared to the nuclear attraction leading to significant changes in the filling of electronic orbitals. This is particularly important for the stable negative calcium ion, which can be formed by adding a $4p$ electron to the neutral $4s^2$ core, but not a $3d$ electron, as might be expected from extrapolation from neutral systems. In addition, the binding energy of the outer electron can be rather small, orders of magnitude below the binding energies of neutral atoms. Minor effects such as relativistic, core-core, and core-valence interactions therefore have relatively large consequences.

So far, the interest in negative ions has mostly been focused on the properties of the ground state for which a recent review is available [1]. The present knowledge about excited states is far less, and for many ions hardly any information is available. Due to the low binding energies, bound singly excited states are very rare in negative ions, but their existence has recently been proven in the Os^- ion [2]. Singly excited states will usually appear as very broad resonances in the continuum above the detachment limit. The experimental studies have focused more on the doubly excited states, many of which can be explored by one-photon absorption from the ground state. This has been the case in particular for the negative ions H^- [3,4] (and references therein), He^- [5,6], or the alkali-metal negative ions [7–10] (and references therein).

Doubly excited states with the same parity as the ground state of the negative ion have been more difficult to study by photon-absorption techniques, since more photons should be absorbed than are required to liberate an electron. The corresponding excess-photon absorption (EPA) phenomena, also known as above-threshold ionization in atoms, are normally associated with the application of strong laser fields having intensities of 10^{10} W/cm^2 or more. Intermediate autoionization or autodetaching states have been shown to enhance the EPA probability considerably [11–13]. It has recently been demonstrated [14] that excess-photon absorption via an autodetaching state could be applied to gain spectroscopic information about the autodetaching state. A very sensitive detection technique, such as resonant ionization [15], must be utilized to monitor the population of an excited atomic state that should be populated exclusively by two-photon detachment of the negative ion. With this technique the positions and lifetimes of the autodetaching $6s6p^2\ ^2P_{1/2}$ level in Ba^- and the $5s5p^2\ ^4P_J$ levels in Sr^- were obtained [14].

In the present study, we have taken advantage of a further development of the EPA technique to gain information about excited states in the negative calcium ion having the same parity as its $4s^24p$ ground state. This is in contrast to the studies of the Sr^- and Ba^- ions mentioned above, in which the spectroscopic information was obtained for states having opposite parity to the ground state and could thus be reached by one photon. The present investigation is focused on the detection and characterization of the $4p^3\ ^4S_{3/2}$ state in Ca^-, populated by two-photon absorption from the $4s^24p\ ^2P$ ground state via the intermediate $4s4p^2\ ^4P$ autodetaching state. Pioneering work on two-photon excitation of a resonance in a negative atomic ion has been reported for the lowest singlet D state in H^-, but in that experiment [16] the two photons originated from the same laser field. The H^- ions interacted with laser pulses as short as several picoseconds and with a field intensity of 3×10^{10} W/cm^2. In the present study, which takes advantage of the intermediate resonance and a more sensitive detection technique, the experiments are performed with nanosecond pulses at field intensities 6–8 orders of magnitude lower.

The Ca^- ion is known to possess the stable $4s^24p\ ^2P$ ground state with a binding energy of 24.55(10) meV for the $J=1/2$ component [15], and a fine-structure splitting [17] of 4.865(14) meV (for a recent review, see [18]). In addition, one of the two predicated metastable states, the $4s4p^2\ ^4P$ state, has finally been established [17], whereas the energetically higher-lying metastable state $4p^3\ ^4S$ so far has only

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been predicted to exist [19,20], but never observed. The ^4P state is metastable both with respect to Coulomb autoionization and radiative decay due to the spin conservation selection rule. The ^4S state is, as already pointed out by Bunge *et al.* [19], metastable towards Coulomb autoionization due to the parity conservation rule, but the ^4S state can decay via an allowed dipole transition to the metastable ^4P state. Its binding energy was predicted to be 626.2 meV with respect to the Ca($4p^2\ ^3P$) state, or 592.1 meV with respect to the Ca($4p3d\ ^3D$) state. Very recently van der Hart [20] calculated that the binding-energy values given by Bunge *et al.* would be reduced by 36.6 meV, enlarging the basis set used and including dielectronic core polarization. Van der Hart predicted the binding energy for the $4p^3\ ^4S$ state with respect to the Ca($4p3d\ ^3D$) state to be 555.5 meV.

The detection and characterization (position, lifetime) of the metastable $Ca^-(^4S)$ state is of interest since it will allow a test of the very elaborate calculation by van der Hart [20]. In addition it will increase our knowledge about the Ca^- ion, which has attracted great interest [18], experimentally as well as theoretically, for more than a decade.

The structure of the excited states is expected to be similar for the negative alkaline-earth ions Be^-, Mg^-, and Ca^-. The homologous $Be^-(2p^3\ ^4S)$ ion was observed more than a decade ago by Gaardsted and Andersen [21], who could detect the $2p^3\ ^4S \rightarrow 2s2p^2\ ^4P$ optical decay and determine the lifetime of the ^4S state using beam-foil spectroscopy. Subsequent laser-based studies [18,22] have yielded more precise energy values for these metastable states. Beam-foil spectroscopy was also applied to search for the homologous transition in Mg^- [23] and Ca^- [24], but without success. Until now, neither the $Mg^-(3p^3\ ^4S)$ nor the $Ca^-(4p^3\ ^4S)$ state have been observed.

The principle of the present experiment is based on a modification of the method used in the original experiments [14], introducing excess-photon absorption via autodetaching states for spectroscopic purposes. The original method relies on the absorption of two photons from the same laser field, and is suitable for spectroscopic studies of the autoionizing state reached with the first photon. In the present experiment the two photons absorbed have different energies. The first photon (λ_1) is used to reach one of the $Ca^-(4s4p^2\ ^4P)$ fine-structure levels, whereas the second photon (λ_2) completes the excitation of the Ca^- ion to the $4p^3\ ^4S$ state (see Fig. 1). This excitation scheme demands an alternative detection scheme. The collinear resonant-ionization method [25] is applied as before [14] to monitor the population of an excited Ca-atom state, which is populated exclusively by the two-photon detachment of the negative ion. Since the λ_1 photon energy is in the range 1.36–1.38 eV ($\lambda_1 = 888 - 897$ nm), only Ca-atomic states with energies above 2.8 eV, but below ~4.1–4.2 eV, are considered suitable candidates for monitoring the two-photon absorption process of present interest. The $Ca^-(4p^3\ ^4S)$ state is expected to be located within the upper energy region (~4.1–4.2 eV). The Ca($4s4p\ ^1P_1$) state fulfills these criteria and was selected for monitoring; it cannot be populated by one-photon detachment with any of the laser fields applied (see below). The $^1P_1$ state can, however, be populated by spin-forbidden autodetachment of the $Ca^-(4p^3\ ^4S)$ state. The neutral atom detection is performed by transferring the $4s4p\ ^1P_1$ population via the $4s4d\ ^1D_2$ level to the $4s13p\ ^1P_1$ level by means of two photons ($\lambda_3 = 734$ nm and $\lambda_4 = 896$ nm), followed by electric-field ionization (see Fig. 1). Since the lifetimes and energies of the $Ca^-(^4P)$ levels have been established [17], with lifetimes ranging from 9 ps for $J = 5/2$ to larger than 100 ps for $J = 1/2$, the time delay between λ_1 and λ_2 has to be very short. The maximum EPA signal was in fact obtained by allowing the λ_2 pulse (which is less powerful and destructive for the negative ion) to precede the λ_1 pulse by ~1 ns. The lifetimes of the neutral Ca states are known to be 4.6 ns for the $4s4p\ ^1P_1$ state and 80 ns for $4s4d\ ^1D_2$, which demands the application of the λ_3 and λ_4 photon pulses a few ns after λ_1 and λ_2.

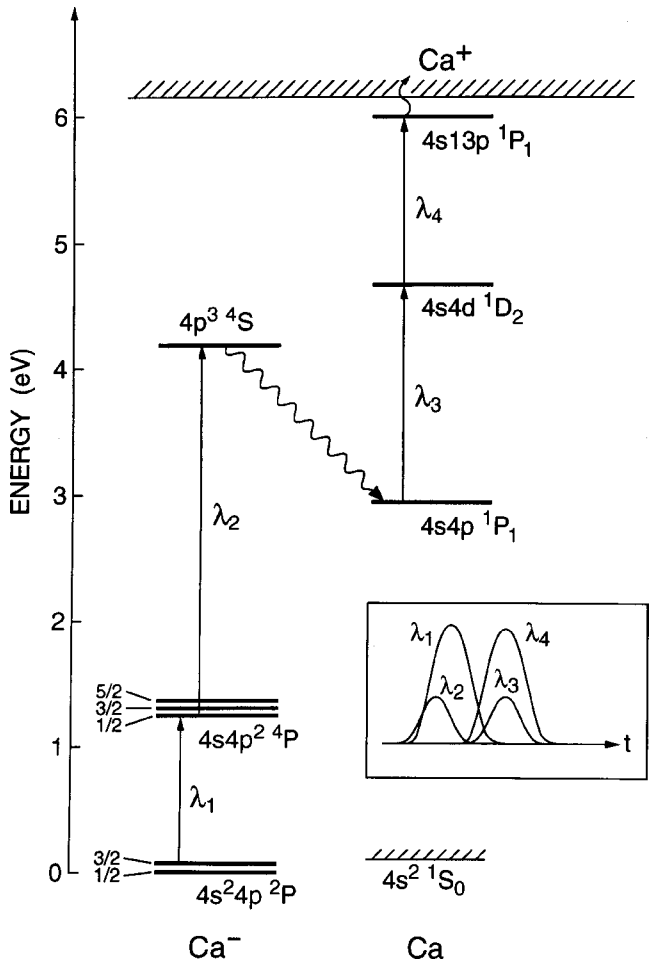

FIG. 1. Schematic energy-level diagram of the negative calcium ion and the corresponding parent atom for the EPA experiments.

The experiments were conducted using a collinear fast negative-ion/laser-beam setup, which has been described earlier [15]. A 28-keV Ca^- beam was produced from the corresponding positive-ion beam by charge exchange in an alkali-metal vapor. Following charge-state analysis, the Ca^- beam was overlapped collinearly with collimated beams from four different pulsed (~6 ns) lasers in a 1-m-long field-free interaction region. The geometry applied favors high spectral resolution as well as high sensitivity due to the rela-

tively large number of Ca^- ions involved in the interaction.

The laser system consists of four tunable dye lasers, commercial or homebuilt, pumped by the second or third harmonic of a Nd:YAG Spectra Physics GCR-170 pump laser (where YAG denotes yttrium aluminum garnet) with a repetition rate of 10 Hz. The bandwidth of the applied dye laser ranged from 3 to 8 GHz with a homebuilt (8-GHz) dye laser used for λ_1 and a commercial OPPO laser (3 GHz) used for λ_2. The measurements were performed with laser intensities of $\sim 10^5$ W/cm^2 for λ_1, and with intensities ranging from 4×10^2 W/cm^2 to 4×10^4 W/cm^2 for λ_2. It was possible to observe the EPA signal with laser intensities below the saturation limit for nonresonant one-photon detachment. The use of the low laser intensities is possible since the excess-photon absorption signal can be detected with very high sensitivity and almost zero background. We also satisfy the conditions for no displacement of the absorption signal due to laser intensity and saturation effects. Calibration of the photon energies for the OPPO laser and the other dye lasers was performed by measuring reference transitions ($4s4p\ ^3P-4p^2\ ^3P$ and $4s4p\ ^3P-4s4d\ ^3D$) in the fast neutral Ca beam.

After the exit aperture of the interaction region, a transverse electric field is applied by the use of a pair of cylindrical electrodes. They field ionize and subsequently deflect the Rydberg atoms onto a positive ion detector, which is situated approximately 25 cm after the field-ionization region at an angle of 11° from the incident ion direction. Depending on the degree of excitation, the Rydberg atoms are ionized at different positions in the nonuniform electric field and are thus deflected at different angles. This procedure provides a method of selectively detecting the population of a specific Ca Rydberg level and an effective discrimination against a background induced by collisions with rest gas particles [26].

The positive-ion yield was measured as a function of the photon energy of the λ_2 laser in the energy region where the $Ca^-(4p^3\ ^4S)$ state is expected to be localized (4.1–4.2 eV, above the Ca^- ground state). The detailed investigations have been performed with the $J=3/2$ level in the ground state as the starting point, but utilizing all three J levels of the $4s4p^2\ ^4P$ state as the intermediate autodetaching level. Figure 2 shows the production of Ca^+ ions in the wavelength region around 439 nm for λ_2, with $4s4p^2\ ^4P_{1/2}$ being used as the intermediate level. The detachment data were analyzed by means of a Lorentz function, yielding information about the energy and half width of the resonance. The three excitation channels ($J=3/2\rightarrow J=1/2$, 3/2, or 5/2) yielded identical results, within the experimental uncertainties, for the position of the $Ca^-(4p^3\ ^4S)$ state. The measured position was independent of the intensities used and it could still be observed with 10^5 W/cm^2 for λ_1 and 4×10^2 W/cm^2 for λ_2. As expected, a higher laser intensity was needed for the λ_1 laser than for the λ_2 laser to make the two-photon signal observable, since the λ_1 laser drives the spin-forbidden $^2P-\ ^4P$ transition in Ca^-, whereas λ_2 drives the allowed $^4P-\ ^4S$ transition. For both lasers involved, the power dependence of the two-photon signal was strongly sublinear. A similar observation was done in Ref. [14] and explained as the result of the competition between the two-photon signal and the rapid one-photon target depletion.

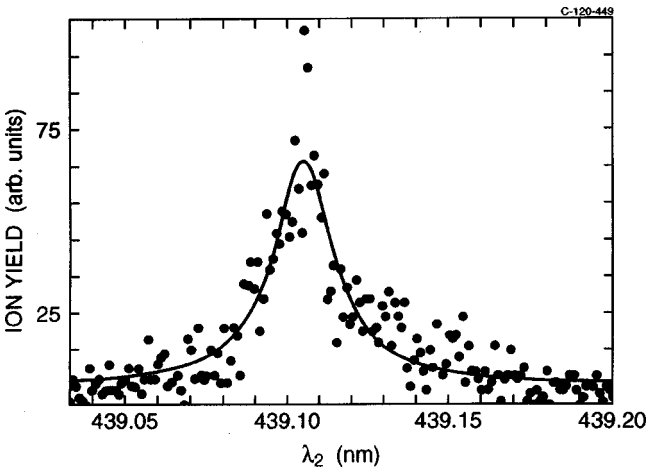

FIG. 2. The Ca^+ photo-ion yield, reflecting population of the $Ca(4s4p\ ^1P_1)$ level by the two-photon detachment process, with the λ_2 laser being scanned in the region of the $4s4p^2\ ^4P_{1/2}-4p^3\ ^4S$ transition in Ca^-.

Taking a small Doppler shift and the conversion of the observed wavelengths from air to vacuum into account yielded the energy of the $Ca^-(4p^3\ ^4S)$ state to be 4.18752(10) eV above the ground state of the neutral Ca atom. The main contribution to the 0.10 meV uncertainty in the location of the ^4S state originates from the uncertainty in the binding energy of the Ca^- ground state [18]. Considering the energy difference between the $Ca^-(4p^3\ ^4S)$ state and its parent $Ca(4p^2\ ^3P)$ state, the binding energy is determined to be 586.86(10) meV, with the value expressed relative to the weighted energy value of the three ^3P fine-structure levels. The binding-energy value is very close to the value predicted by van der Hart [20], whose calculations yielded a binding energy of 589.6 meV with respect to the $Ca(4p^2\ ^3P)$ state or 555.5 meV with respect to the lower-lying $4s3d\ ^3D$ state. The binding energy for the $4p^3\ ^4S$ state is larger than for the lower-lying $4s4p^2\ ^4P$ state, which had a binding energy of 521.84(10) meV [18] with respect to the $Ca(4s4p\ ^3P)$ state. The binding energies for the Ca^- ion are significantly larger, nearly a factor of 2 than the values reported for the homologous Be^- ion [18]. The binding energy for $Be^-(2p^3\ ^4S)$ was also larger than for $Be^-(2s2p^2\ ^4P)$.

Information about the lifetime of the $Ca^-(4p^3\ ^4S)$ state may be gained from the width of the Lorentz signal, obtained in experiments performed with low laser intensities to avoid saturation effects. To reduce the influence of the lifetime of the intermediate ^4P level on the width of the Lorentz signal, the $J=1/2$ level was selected as the intermediate level to benefit from the fact that this level has the longest lifetime of the three possible J levels with a lifetime in the interval 0.1–10 ns [18]. The width of the $^4P_{1/2}-\ ^4S_{3/2}$ signal was measured to be 0.55(16) cm^{-1}, which is equivalent to 9.6(2.6) ps. This value, however, should be considered a lower limit for the lifetime of the $^4S_{3/2}$ state since the contribution from the bandwidth of the λ_1 laser can be signifi-

cant, and in addition, the influence from the lifetime of the $^4P_{1/2}$ level is assumed to be negligible. Since the contribution from λ_1 to the width of the $^4P_{1/2}-{}^4S_{3/2}$ signal may be quite large, the lifetime of the $^4S_{3/2}$ level is probably longer than the 9.6(2.6) ps measured. The bandwidth of the home-built λ_1 laser does not exceed 0.3 cm^{-1} according to previous measurements, and it is then possible to estimate an upper limit for the lifetime of the ^4S state to be 40 ps. The $Ca^-(^4S_{3/2})$ lifetime is, however, very much shorter than for the homologous $Be^-(^4S)$ ion for which the lifetime was reported to be 1.25(10) ns [21]. The much shorter lifetime for $Ca^-(^4S)$ than for $Be^-(^4S)$ shows that the dominant decay mechanism for the Ca^- ion is via electron emission, whereas it is photon emission for the $Be^-(^4S)$ ion. These lifetimes can also explain why it has been possible to observe the optical decay channel for Be^- [21], but not for Ca^- [24]. The unsuccessful search [23,24] for the Mg^- ion, via observation of the optical transition $^4S\rightarrow{}^4P$, may also be due to a short $Mg^-(^4S)$ lifetime.

Investigations of the two-photon detachment signal can yield information about the character of the excitation process. Should the excitation process be considered as two sequential one-photon absorption processes or as a two-photon absorption process? Detuning the λ_1 laser away from the exact resonance position for the $J=3/2\rightarrow J=5/2$ transition had the consequence that the λ_2 signal was displaced in the opposite direction, still leaving the total energy of the two-photon excitation unchanged, which indicates that the excitation process should be considered as a direct two-photon absorption process and not two sequential one-photon processes.

The present investigation has demonstrated that it is possible to gain spectroscopic information about excited negative-ion states with the same parity as the ground state of the negative ion by means of two-color excess-photon absorption via an autodetaching intermediate state. The method could immediately be utilized to gain information about the $Sr^-(5p^3\,{}^4S)$ state and thereby test the prediction of van der Hart [20] for this state, since the energies and lifetimes of the intermediate state $Sr^-(5s5p^2\,{}^4P)$ levels have been established [17]. The EPA technique is, however, of general use and may be a powerful tool in further exploration of the structure and dynamics of excited states in atomic negative ions. The experiments performed have also illustrated how it is possible in the case of target-depletion competition between higher- and lower-order processes to encounter an apparent sublinear power dependence of the higher-order signal, making it observable even at extremely low-field intensities.

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[1] T. Andersen, H. K. Haugen, and H. Hotop, J. Phys. Chem. Ref. Data **28**, 1511 (1999).
[2] R. C. Bilodeau and H. K. Haugen, Phys. Rev. Lett. **85**, 534 (2000).
[3] H. C. Bryant and M. Halka, in *Coulomb Interactions in Nuclear and Atomic Few-Body Collisions*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1996).
[4] P. Balling *et al.*, Phys. Rev. A **61**, 022702 (2000).
[5] I. Yu. Kiyan, U. Berzinsh, D. Hanstorp, and D. J. Pegg, Phys. Rev. Lett. **81**, 2874 (1998).
[6] C.-N. Liu and A. F. Starace, Phys. Rev. A **60**, 4647 (1999).
[7] U. Berzinsh *et al.*, Phys. Rev. Lett. **74**, 4795 (1995).
[8] G. Haeffler, I. Yu. Kiyan, D. Hanstorp, B. J. Davies, and D. J. Pegg, Phys. Rev. A **59**, 3655 (1999).
[9] I. Yu. Kiyan, U. Berzinsh, J. Sandström, D. Hanstorp, and D. J. Pegg, Phys. Rev. Lett. **84**, 5979 (2000).
[10] C.-N. Liu and A. F. Starace, Phys. Rev. A **58**, 4997 (1998).
[11] S. Chin, D. Feldman, J. Krautwald,and K. Welge, J. Phys. B **14**, 2353 (1981).
[12] H. Stapelfeldt and H. K. Haugen, Phys. Rev. Lett. **69**, 2638 (1992).
[13] H. Stapelfeldt, P. Kristensen, U. Ljungblad, T. Andersen, and H. K. Haugen, Phys. Rev. A **50**, 1618 (1994).
[14] V. V. Petrunin, C. A. Brodie, P. Kristensen, U. V. Pedersen, and T. Andersen, J. Phys. B **31**, L415 (1998).
[15] V. V. Petrunin, J. D. Voldstad, P. Balling, P. Kristensen, T. Andersen, and H. K. Haugen, Phys. Rev. Lett. **75**, 1911 (1995).
[16] A. Stintz *et al.*, Phys. Rev. Lett. **75**, 2924 (1995).
[17] P. Kristensen, C. A. Brodie, U. V. Pedersen, V. V. Petrunin, and T. Andersen, Phys. Rev. Lett. **78**, 2329 (1997).
[18] T. Andersen, H. H. Andersen, P. Balling, P. Kristensen,and V. V. Petrunin, J. Phys. B **30**, 3317 (1997).
[19] C. F. Bunge, M. Galán, R. Jáuregui, and A. V. Bunge, Nucl. Instrum. Methods Phys. Res. **202**, 299 (1982).
[20] H. W. van der Hart , Phys. Rev. A **59**, 1125 (1999).
[21] J. O. Gaardsted and T. Andersen, J. Phys. B **22**, L57 (1989).
[22] H. H. Andersen, P. Balling, V. V. Petrunin, and T. Andersen, J. Phys. B **29**, L415 (1996).
[23] T. Andersen, J. O. Gaardsted, L. E. Sørensen, and T. Brage, Phys. Rev. A **42**, 2728 (1990).
[24] L. Eg Sørensen, M.Sc. thesis, University of Aarhus, 1990 (unpublished).
[25] S. A. Aseyev, Yu A. Kudryavtsev, V. S. Letokhov, and V. V. Petrunin, Opt. Lett. **16**, 514 (1991), and references therein.
[26] Yu. A. Kudryavtsev and V. V. Petrunin, Zh. Eksp. Teor. Fiz. **94**, 76 (1988) [Sov. Phys. JETP **67**, 691 (1988)].