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Threshold photodetachment of Al^-: Electron affinity and fine structure

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Tunable infrared laser spectroscopy of $Al^-(3p^2\ ^3P_J)$ has yielded an improved value for the electron affinity of aluminum and experimental data on the previously unobserved fine structure of the ionic ground state. The electron affinity is determined to be 3491.0(4) cm^{-1} [432.83(5) meV], and the $J=0$-1 and $J=1$-2 splittings are found to be 22.7(3) and 45.7(2) cm^{-1}, respectively. The result for the electron affinity is in substantial disagreement with a very recent experimental investigation. Our work also indicates that isoelectronic extrapolations for the ionic fine structure were accurate within uncertainties, and is in good agreement with recent calculations of the electron affinity. [S1050-2947(97)50512-9]

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The study of atomic negative ions continues to be an active area of investigation [1] and many improvements in the knowledge of electron affinities and ionic fine structure have been obtained since the 1985 review of Hotop and Lineberger [2]. In part, the interest in atomic negative ions stems from the qualitatively different features resulting from the short range potential, and is due to the theoretical challenges posed by the relativistic and strong electron correlation effects. Nevertheless, negative ions are of practical interest as well, including in the ultrasensitive detection of atoms and isotopes through accelerator mass spectrometry [3]. The negative ion of aluminum has been the subject of substantial experimental and theoretical work. Utilizing laser photodetachment electron spectrometry, Feigerle *et al.* [4] measured the electron affinity (EA) of Al to be 442(10) meV, and found the $Al^-(^1D_2)$ level to lie 332(10) meV above ground-state Al^-, with a binding energy of 110(10) meV. The latter value for the $^1D_2$ level agreed with the result of electric-field dissociation by Oparin *et al.* [5], where a binding energy of $\approx$95 meV was obtained. As a result of subsequent refined calibrations [6], an improved value for the EA of Ref. [4] was suggested to be 441(10) meV [2]. Recently, Calabrese *et al.* [7] measured the electron affinity of Al to be $440.94(+0.66/-0.48)$ meV by utilizing a tunable F-center laser and a coaxial ion-laser beam apparatus. Although they were unable to investigate the actual threshold region and the associated fine structure, they compensated for lack of data in this region via extrapolating from higher photon energy data. In the past few years, calculations have been reported by Arnau *et al.* [8], who used a configuration-interaction (CI) method with pseudopotentials, Woon and Dunning [9], who employed a CI method with correlation-consistent basis sets, and Wijesundera [10], who utilized a multiconfiguration Dirac-Fock method. They obtained values of 450 meV [8], 437 meV [9], and 433 meV [10], respectively. The present Rapid Communication reports an accurate experimental determination of the electron affinity of aluminum. In addition, the fine-structure splittings of the $Al^-(3p^2\ ^3P_J)$ term have been measured, to our knowledge, for the first time.

An energy-level diagram of Al^- and the ground state of Al is shown in Fig. 1. The $Al^-(3p^2\ ^3P_J)$ ground state is expected to have fine-structure levels with splittings estimated from isoelectronic extrapolations, of 26(3) cm^{-1} for $J=0$-1 and 76(7) cm^{-1} for $J=0$-2 [2]. The ground state of Al is a $3p\ ^2P_J$ state with a fine-structure $J=1/2$-3/2 splitting of 112.061 cm^{-1} [11]. Our experimental approach to the determination of the EA of aluminum involves tunable infrared laser spectroscopy and keV-energy ion-beam technology. Details of the apparatus are described elsewhere [12,13]. Nanosecond-duration laser pulses in the 820–880-nm range were generated using a dye laser, pumped by the second harmonic of a 10-Hz Q-switched Nd:YAG (neodymium-doped yttrium aluminum garnet) laser. The dye laser output was converted into tunable infrared radiation via second Stokes generation using stimulated Raman scattering in a high-pressure hydrogen cell, with a measured Raman shift of 4155.20(2)cm^{-1}. The infrared light had a bandwidth of

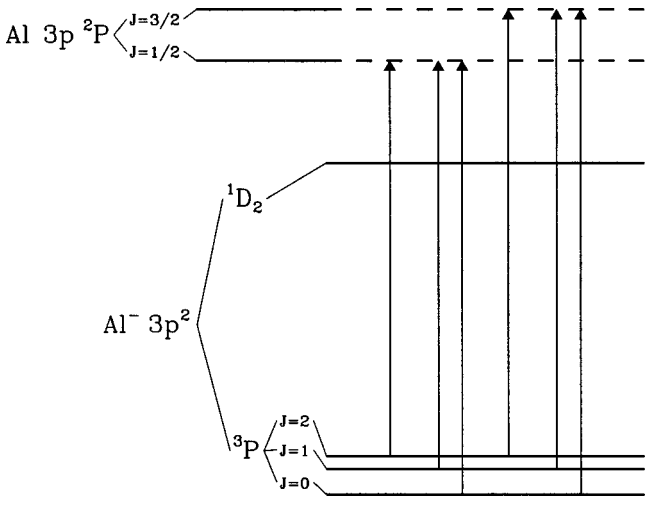

FIG. 1. Schematic energy-level diagram of Al^- and Al. Arrows indicate photodetachment thresholds in order of increasing photon energy. For clarity of presentation, fine-structure splittings are not shown to scale.

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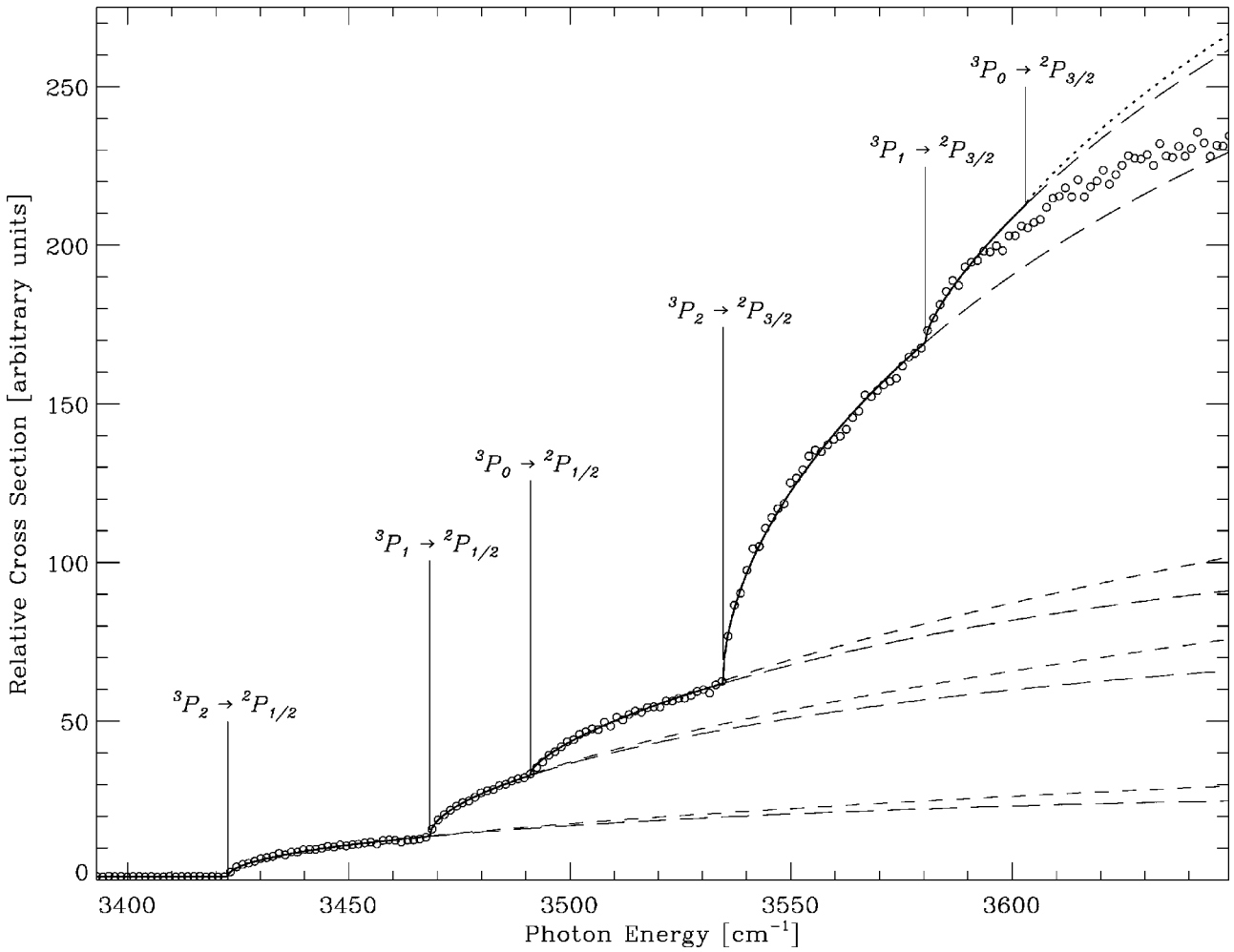

FIG. 2. Photodetachment yield versus laser wavelength. The overall result of a Wigner *s*-wave fit including the leading correction term is indicated by the solid line (and extrapolated with a dotted line). Individual thresholds are extrapolated with dashed lines: short dashes for a Wigner *s* wave (first three thresholds only), and long dashes for a Wigner *s* wave with leading correction. These two lines define the upper and lower limits of *s* wave thresholds within the ZCC model.

$\approx 0.1\ \mathrm{cm}^{-1}$ and pulse energies were ≈ 0.5 mJ at 3 μm. A 16-keV Al^- beam was extracted from a Cs sputter ion source. Ultrapure aluminum cathodes were utilized in order to greatly minimize the potential contamination from prolific Si^- impurity beams, although our mass resolution discriminates quite effectively against mass 28 at mass 27. The beam was then magnetically analyzed and deflected 30° into an ultrahigh-vacuum chamber. There it was further charge-state analyzed in an electric field before being crossed at 90° with a collimated infrared laser beam. The Al^- current at this stage was typically several nA. The charge states created in the interaction region were analyzed by a second set of electric-field deflection plates. The photodetached neutral atoms impinged on a discrete dynode electron multiplier for analog data acquisition via a gated integrator and boxcar averager. Calibrations of the dye laser setup were routinely performed using an optogalvanic cell, but rigorous comparisons of the wavelength of the second Stokes generated light with known ionic energy intervals have also been performed, including in the cases of Te^- [14] and Cs^- [2]. Various tests indicate that the second Stokes wavelength calibration is reliable to at least $0.2\ \mathrm{cm}^{-1}$.

We have conducted numerous infrared laser scans of the threshold region for Al^- photodetachment. The sum of several scans over the region of $3400-3650\ \mathrm{cm}^{-1}$ is shown in Fig. 2. The data correspond to approximately 1200 laser shots per wave number. Five nested thresholds are seen in the figure, corresponding to the following transitions (from low to high energy): $^3P_2 \rightarrow {}^2P_{1/2}$, $^3P_1 \rightarrow {}^2P_{1/2}$, $^3P_0 \rightarrow {}^2P_{1/2}$, $^3P_2 \rightarrow {}^2P_{3/2}$, and $^3P_1 \rightarrow {}^2P_{3/2}$. Wigner *s*-wave thresholds could be fitted very accurately to the data and the resulting threshold energies are summarized in Table I. The same threshold energies but a slightly closer fit to the data above

TABLE I. Results of the *s*-wave fits to the data.

Transition	Threshold Energy (cm^{-1})	Relative strength Measured	Calculated
$^3P_2 \rightarrow {}^2P_{1/2}$	3422.6(2)	5.0(3)	5
$^3P_1 \rightarrow {}^2P_{1/2}$	3468.3(2)	8.5(7)	9
$^3P_0 \rightarrow {}^2P_{1/2}$	3491.0(4)	4.8(9)	4
$^3P_2 \rightarrow {}^2P_{3/2}$	3534.8(2)	29(6)	25
$^3P_1 \rightarrow {}^2P_{3/2}$	3579.8(8)	8(2)	9
$^3P_0 \rightarrow {}^2P_{3/2}$			2

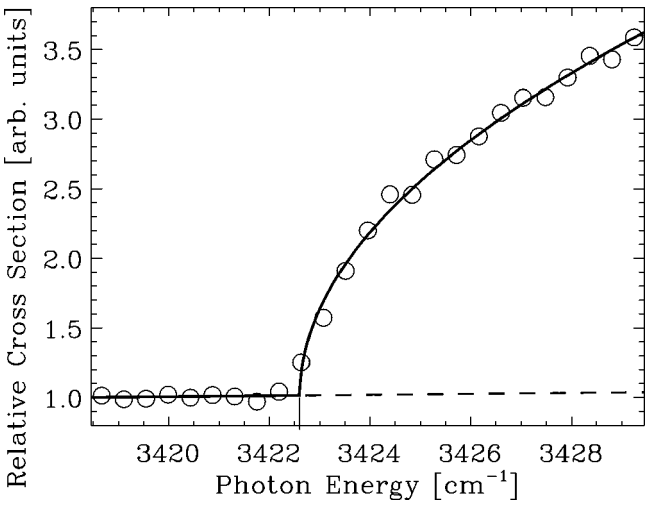

FIG. 3. High-resolution scan of the $^3P_2 \rightarrow {}^2P_{1/2}$ threshold region. The solid line represents a fitted *s* wave.

threshold were obtained by including in the fitting routine the leading correction term to the Wigner law, as derived by Farley [15] on the basis of the zero-core-contribution (ZCC) model of photodetachment [16]. The result of this fit is indicated by the solid line in Fig. 2. The sixth and last threshold ($^3P_0 \rightarrow {}^2P_{3/2}$) could not be resolved due to a weak transition strength combined with the fact that it appears on top of the other detachment signals. The fit to the data was therefore extrapolated beyond the sixth threshold (dotted line in Fig. 2) using its calculated transition strength [17] (see below). The increasing deviation between the fit and the data in this region seems to indicate a limitation of the ZCC model, which was also observed and discussed by Calabrese *et al.* [7] (it should be noted, however, that some equations in Ref. [7] contain typographical errors). The first three thresholds were also scanned at a very slow rate of 8000 laser shots per wave number in order to improve the accuracy of the fitted threshold values. As an example, the region of the first threshold is shown in Fig. 3, which also demonstrates the small but measureable signal resulting from photodetachment of the weakly populated $Al^-(^1D_2)$ level. The EA of Al is found from the $^3P_0 \rightarrow {}^2P_{1/2}$ threshold, and is determined to be 3491.0(4)cm^{-1} or 432.83(5) meV (using 8.065 541 0 cm^{-1}/meV [11]). The well-known fine-structure splitting of the Al ground state can be extracted from the difference of the thresholds for the $^3P_2 \rightarrow {}^2P_{1/2,3/2}$ transitions as well as $^3P_1 \rightarrow {}^2P_{1/2,3/2}$. This yields experimental values of 112.2(3) and 111.5(8) cm^{-1}, respectively, which are in excellent agreement with the tabulated value of 112.061 cm^{-1} [11]. The first three thresholds ($^3P_J \rightarrow {}^2P_{1/2}$) provide values of the fine-structure splittings of the ion: 22.7(3) cm^{-1} and 45.7(2) cm^{-1}, respectively, for $J=0$-1 and $J=1$-2 [and 68.4(3) cm^{-1} for $J=0$-2]. The next two thresholds ($^3P_{2,1} \rightarrow {}^2P_{3/2}$) enable a second determination of the $J=1$-2 splitting of 45.0(8) cm^{-1}. The quoted uncertainties of the values are largely associated with the fits to the nested thresholds. The respective magnitudes of our threshold signals are in good agreement with theory [17], assuming a statistical population of the ionic levels. The calculated values for the relative strengths of the transitions are shown in Table I, together with the experimental values. The errors in the experimental values account for the fact that the two different *s*-wave fits give slightly different values for the relative strengths of the thresholds.

Our experimental result [432.83(5) meV] for the electron affinity of Al is in agreement with the earlier measurement of Feigerle *et al.* [4,2] of 441(10) meV, but in definite disagreement with the very recent result of Calabrese *et al.* [7], who obtained 440.94($+0.66/-0.48$) meV. The photodetachment data of Ref. [7] have a signal-to-noise ratio of ≈ 10 while ours is ≈ 100. This difference in statistics should be reflected in the respective uncertainties of the final EA values, but the two results still differ by about 16 standard deviations, based on the lower error margin quoted in Ref. [7]. There are major differences between the experiments, which we will therefore outline briefly. Calabrese *et al.* conducted their photodetachment study with a cw *F*-center laser, with a stated resolution of $\approx 0.13\ cm^{-1}$, in a coaxial (3-keV) ion-laser beam configuration. Our laser resolution is very similar to theirs, and our average laser power very comparable. Our typical ion currents are two orders of magnitude higher than those of Ref. [7], but our interaction region is also two orders of magnitude shorter. More importantly, the setup of Ref. [7] was very prone to intracavity and extracavity water absorption lines, such that their laser power was reduced to near zero in several wavelength regions. We are much less susceptible to this problem since our infrared light is generated just before the interaction region, and the remaining infrared beam path is effectively purged with dry nitrogen gas. As Calabrese *et al.*, we still normalize the data to the laser power transmitted through the ultrahigh-vacuum region. The most striking difference, however, between the experiments is that Calabrese *et al.* were not able to make measurements at or below the threshold region due to an upper limit of 2820 nm on the wavelength scan for the KCl:Li color center laser crystal. Thus they were unable to truly exploit the narrow linewidth of the cw laser, and in contrast to our measurements, could not explore the multiple thresholds due to fine-structure splittings (the lower end of their scan range is 3585 cm^{-1}). Fitting a single *s* wave to their data Calabrese *et al.* obtain an approximate electron affinity of 3580.5(2.0) cm^{-1}, which coincides with our value for the $^3P_1 \rightarrow {}^2P_{3/2}$ threshold. Due to its small relative strength of 17%, it seems unlikely, however, that this threshold was observed alone, without substantial contributions from the first four thresholds (compare Fig. 2). Therefore, Calabrese *et al.* extrapolate their data to threshold via higher-order fits and weighted averages over the transitions between all possible levels of the ion and atom, using the appropriate theoretical frameworks [15–17]. We have tested their procedures by applying them to our data in the region above 3585 cm^{-1}. This yielded an electron affinity of 3480(15) cm^{-1}, which agrees with the value for the $^3P_0 \rightarrow {}^2P_{1/2}$ threshold within error margins. Hence, the extrapolation procedures seem valid. All in all, it appears that the low-energy data (first six points) of Ref. [7] for some reason rise too steeply with increasing photon energy if compared with our data for this energy region. The respective slopes differ by approximately a factor of 3. We conclude that some systematic error has probably arisen in the work of Calabrese *et al.*, in addition to the statistical errors incurred by the low signal-to-noise ratio and the necessary extrapolation to threshold.

Although much theoretical effort has been directed to calculations on even lighter species, aluminum is sufficiently light that advanced calculations are being attempted. There have been three recent theoretical works on the electron affinity of aluminum. Arnau *et al.* obtained 450 meV [8], Woon and Dunning [9] a value of 437 meV, and Wijesundera 433 meV [10]. All three numbers, which have uncertainties of the order of 10 meV, are in good agreement with experiment. Our experimental determination of the fine-structure splittings of Al^- indicates that the earlier values based on isoelectronic extrapolations [2], 26(3) cm^{-1} and 76(7) cm^{-1} for $J=0$-1 and $J=0$-2, respectively, were essentially valid within quoted uncertainties. The negative ion of aluminum has also been the subject of recent experimental and theoretical studies [18] in terms of the continuum far above the detachment threshold. As regards future studies of Al^-, a highly accurate value of the binding energy of the $^1D_2$ term might, in principle, be obtained via a multiphoton detachment scheme. However, the expected low transition probability of the $^3P \rightarrow {}^1D$ transition ($\sim 10^{-4}$ s^{-1}) [19] would seem to make a $1+1$ photon detachment scheme via an electric-dipole-forbidden bound-bound resonance rather unlikely [20]. Alternatively, one could use charge-exchange production techniques to maximize the population in the excited level, and employ resonant ionization spectroscopy [21] with detachment to an excited state of the aluminum atom. In contrast, single-photon detachment from $Al^-(^1D_2)$ would be technically very demanding from a nonlinear optical standpoint, requiring tunable midinfrared radiation.

In summary, we have measured the electron affinity of aluminum with an accuracy of 0.05 meV, and have resolved the fine structure of the ion. The measurement is in good agreement with recent calculations [8–10] but calls seriously into question the very recent experimental result of Calabrese *et al.* [7]. Several considerations would suggest that the present EA value be adopted. Perspectives for future work have also been briefly discussed.

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