Alkali-metal negative ions. II. Laser photoelectron spectrometry*

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Photodetachment of alkali-metal negative ions by an Ar-ion laser (4880 Å) has been studied in a crossed-beam geometry. Energy analysis of the photodetached electrons yields the following electron affinities: EA(Li)=(0.620 ± 0.007) eV, EA(Na)=(0.548 ± 0.004) eV, EA(Rb)=(0.486 ± 0.003) eV, and EA(Cs)=(0.470 ± 0.003) eV. These values are obtained relative to an independent measurement of the potassium electron affinity: EA(K)=(0.5012 ± 0.0005). In addition, the angular distribution anisotropy parameter β has been measured at 4880 Å for photodetachment processes leaving the neutral in its ground state and in its first excited state. Relative photodetachment cross sections for these two processes are presented for K, Rb, and Cs.

I. INTRODUCTION

The alkali-metal atoms, by virtue of their hydrogenic nature, have been the subjects of extensive theoretical and experimental study for many years, and it has been known for quite some time that the alkali metals form stable negative ions. The study of negative ions is of great importance in understanding terrestrial and stellar atmospheres, as well as low-temperature plasmas, since the photodetachment process accounts for much of the continuum absorption seen in the visible and infrared spectra of stars and hot gases. A knowledge of atomic and molecular affinities is also necessary to the understanding of a vast number of chemical reactions involving negative ions. However, despite its importance, the attainment of reliable negative-ion data has, until recently, eluded many theoretical and experimental attempts. Electron affinities are probably the least well known of all basic atomic properties.

The alkali-metal negative ions deserve a prominent role in such investigations for several reasons. Because their core electrons can be treated as being relatively inert, they are more tractable to direct theoretical solution than perhaps any other system with the exception of H⁻. Moreover, the electron affinities of many atoms have been determined to date only through the use of isoelectronic extrapolation and interpolation techniques. The alkali metals, positioned at one end of the Periodic Table, are useful as benchmarks for a number of these methods. Accurate alkali-metal electron affinities are therefore essential in obtaining affinities of other elements by such means. Reference to most of the early experimental and theoretical work on the electron affinities of the

alkali-metal atoms can be found in the papers of Moiseiwitsch,[1] Berry,[2] Steiner,[3] and Schwarz.[4] The difficulties associated with forming these ions in sufficient quantity, as well as other experimental problems have in the past resulted in few and rather inaccurate determinations, with wide discrepancies in the values reported by different groups. Different experimental approaches have involved studies of the plasma produced by exploding wires,[5] surface ionization,[6] and charge exchange measurements.[7] The electron affinities were usually determined indirectly by detailed analysis of the data, resulting in large experimental uncertainties.

Theoretical determinations of the alkali-metal affinities include many attempts to semiempirically extrapolate the known spectral data on the neutrals and positively charged ions to the case of negatively charged ions.[8–10] The accuracy of early *ab initio* calculations,[11] employing variational techniques and Hartree-Fock wave functions, was poor because electron correlation effects were not adequately taken into account. Since the correlation energies are of the same order as the electron affinity, they must be properly included in calculations.[12]

More recent calculations have used configuration-interaction methods in an attempt to build correlation effects into the problem. Weiss[12] has performed such a calculation (using an *ab initio* variational approach) for Li⁻, Na⁻, and K⁻. Schwarz[4] has done a configuration-interaction calculation using a model potential approach on all of the alkali metals. Victor and Laughlin have performed a similar calculation of the electron affinity of lithium.[13] Bardsley *et al.*[14] have applied pseudopotential techniques to the alkali-metal affinity

problem as well. The latest theoretical calculation of alkali-metal electron affinities has been performed by Norcross.[15] The technique is multiconfigurational and approaches the problem from a scattering theory viewpoint. Using semiempirical model potentials for the neutral atoms, the close-coupling formalism developed for electron-alkali-metal atom scattering is solved with all channels closed—thereby establishing an eigenvalue problem for the alkali-metal negative ion, whose solution provides the electron affinity. Close-coupling calculations of photodetachment cross sections, and of photoelectron angular distributions are being performed as well by Moores and Norcross.[16]

In this paper, we present unambiguous and accurate experimental determinations of alkali-metal atom electron affinities. The measurements are obtained by laser photodetachment of an alkali-metal negative-ion beam and subsequent energy analysis of the photodetached electrons. In addition, electron angular distribution measurements yield values for the anisotropy parameter β for all energetically accessible channels. By correcting the observed electron peak intensities for their anisotropic angular distributions, we determine the photodetachment partial cross section ratio $\sigma(^2P)/\sigma(^2S)$, where $\sigma(n)$ is the cross section for leaving the neutral in the n state.

II. EXPERIMENTAL TECHNIQUES

The experimental technique used in obtaining the present data has been described in detail previously.[17] Negative alkali-metal ion beams are produced in a low-pressure discharge source by volatilizing alkali-metal halides. The salts used are LiBr, NaI, KBr, CsCl, and RbI. The resultant beam is accelerated to 680 eV, and subsequently mass analyzed by a Wien filter. Upon entering the interaction region (see Fig. 1) the ion beam is crossed with the focused linearly polarized intracavity beam of an argon-ion laser operating continuously at 4880 Å. Typical beam currents entering the Faraday cup are 0.2–1.0 nA. Photoelectrons detached into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed and then detected by a conventional particle multiplier and associated electronics. The monochromator operates at a fixed transmission energy and has a resolution of ~50 meV, full width at half-maximum (FWHM). The complete energy spectrum of the photodetached electrons is digitally accumulated with a multichannel analyzer by sweeping the voltage on the interaction region. The centers of the peaks so obtained can be determined to ± 1 meV by means of a computer least-squares-fitting routine.

A rotatable half-wave plate positioned inside the laser cavity allows one to vary the plane of polarization of the light. By measuring the electron count rate at a fixed energy, as a function of the angle between the polarization vector and the electron momentum vector, one obtains the angular distribution of photoelectrons.

III. DATA ANALYSIS

An energy-level diagram for a typical alkali metal is shown in Fig. 2. The ground state of the neg-
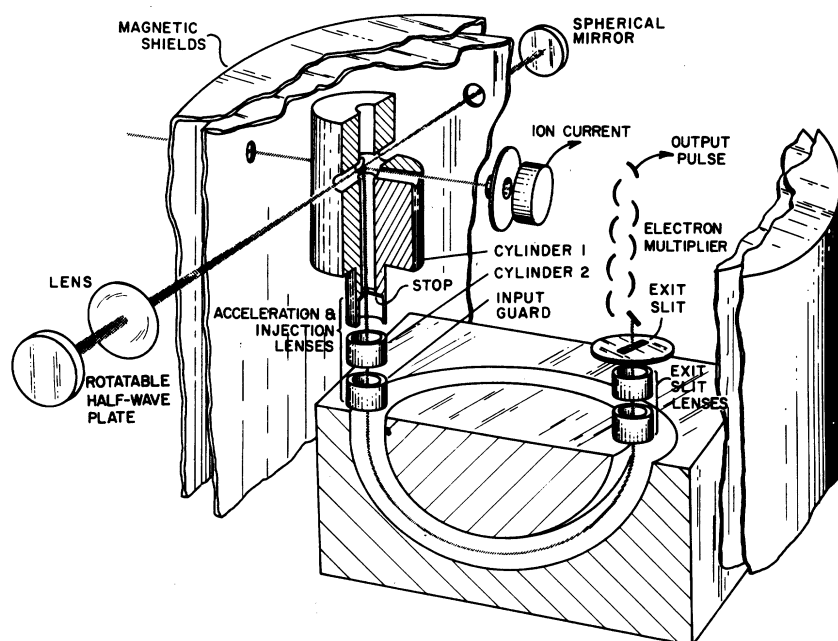

FIG. 1. View of interaction chamber showing crossed-beam geometry, hemispherical electron energy analyzer, and associated optics.

ative ion is $^1S_0$. The available photon energy of 2.540 eV means that for most of the alkali metals, both the ground state and the first excited state of the neutral are energetically accessible. We therefore expect, in principle, to see three peaks in the photoelectron energy spectrum. One group of electrons corresponds to the neutral being left in the ground $^2S_{1/2}$ state. The position of this peak is used in determining the electron affinity. Two groups of low-energy electrons should also be seen—corresponding to the final neutral states being $^2P_{1/2}$ and $^2P_{3/2}$. These three transitions are allowed one-electron dipole processes, the latter two being enhanced by the strong configuration mixing in the negative-ion ground state.

A typical alkali-metal negative-ion photoelectron energy spectra is represented by the Cs^- data shown in Fig. 3. The observed transitions are

$$A^-(ns^2\,{}^1S_0)+h\nu \rightarrow A(ns\,^2S_{1/2})+e^-,$$

$$A^-(ns^2\,{}^1S_0)+h\nu \rightarrow A(np\,^2P_{1/2,\,3/2})+e^-.$$
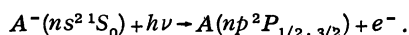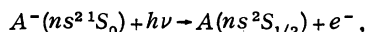
The peaks are labeled according to the final state of the neutral. In the case of Cs^-, the two fine-structure peaks are resolvable. The energy spacing between the ^2S and ^2P peaks should correspond to the appropriate energy separation between the neutral states. However, as has been noted previously,[17] the energy monochromator used in this experiment possesses a small aberration which results in a measured energy spacing between peaks that is slightly smaller than the actual spacing. This "compression" of the energy scale was first observed when the spacings between different vibrational peaks in the spectra of NO^- and O_2^- were measured and compared to spectroscopic data.[17] Diagnostic tests have shown the factor (previously determined to be about 3%) to be constant in time as long as the laser focus is not
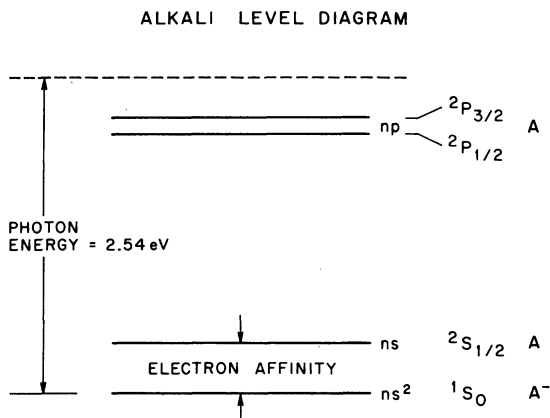
moved. Accurate determination of this compression factor by examining the peak spacing of a molecular spectrum is complicated by the small energy intervals between vibrational peaks as well as possible problems associated with unresolvable rotational structure. The alkali-metal spectrum affords a much simpler way to determine this "compression" effect. The spacing between the ^2S and ^2P peaks is large (~ 1.5 eV) and the peak shapes are not complicated by any structure effects. Comparing the measured separation between data peaks to the known values, we arrive at a compression factor of $(1.8 \pm 0.5)\%$ at our present operating configuration. Other tests have shown that this factor is essentially independent of transmission energy. The reason for this effect is still not well understood. A small residual magnetic field in the interaction region would walk the beam across the virtual entrance slit to the analyzer and can contribute to such a distortion of the energy scale. Since the effect is small and measurable, the data can be easily compensated for this aberration.

By applying conservation of energy and momentum to our detachment geometry we obtain an expression for the electron affinity EA:

$$EA = h\nu - \Omega - (m/M)W + E_{cp},$$

where $h\nu$ is the incident photon energy (2.540 eV), Ω is laboratory energy of the photoelectron leaving the neutral alkali metal in its ground state, m/M is the ratio of electron to ion mass, W is the kinetic energy of the ion, and E_{cp} is a contact potential-energy difference between the interaction region and the electron energy analyzer. The third term is a kinematic correction which arises in the
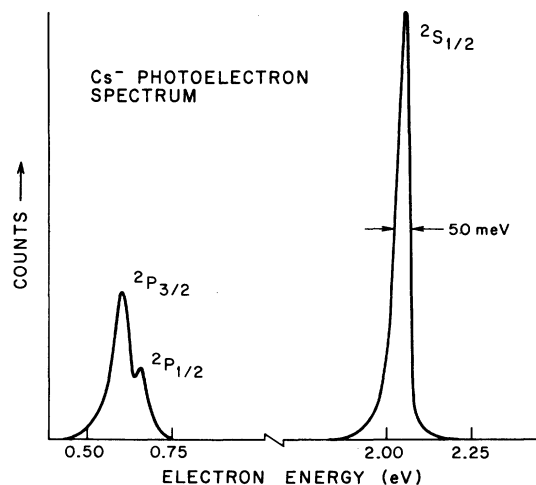

ALKALI LEVEL DIAGRAM

FIG. 2. Schematic energy-level diagram of alkali-metal negative ion A^- and neutral A.

FIG. 3. Cs^- photoelectron energy spectrum, following absorption of a 4880-Å (2.540-eV) photon.

transformation between center-of-mass and laboratory coordinates. The contact potential is unknown and possibly time varying with the chemical nature of the ion beam. Accordingly, all energy measurements obtained in this experiment are therefore calibrated against a reference atom produced simultaneously in the ion source, and whose affinity is accurately known. For the present studies, the calibration ion was chosen to be K$^-$ and the affinity was taken to be (0.5012 ± 0.0005) eV as measured by Patterson et $al.$[18] using a dye-laser photodetachment technique.

The unknown affinity is determined by measuring energy differences between appropriate peaks (corresponding to negative-ion ground state → neutral ground-state transitions) of the K$^-$ spectrum and the unknown ion spectrum, and applying the following expression

$$EA(X) = EA(K) + (\Omega_{K^-} - \Omega_{X^-}) + mW(1/M_K - 1/M_X).$$

In order to avoid problems due to slow drifts in the contact potential with time, electron spectra are accumulated simultaneously for the unknown and calibration ion. This is accomplished by rapidly switching the Wien filter between the two masses and accumulating the corresponding count rates in separate quadrants of a multichannel analyzer. A slightly asymmetric Gaussian line shape[17] is then least-squares fitted to the data, allowing the centroids of the peaks to be measured to ~1 meV.

IV. RESULTS AND DISCUSSION

A. Electron affinities

Electron affinities of the alkali-metal atoms obtained in the manner described above are summarized in Table I. The error limits result from the uncertainty in the peak location, as well as systematic errors due to energy-scale calibration and day-to-day reproducibility. The uncertainty in the determination of the peak locations due to counting statistics and the computer fitting routine is ±1 meV in all cases. The energy-scale calibration adds at most ±1-meV uncertainty to the Na, Rb, and Cs results, and ~±3-meV uncertainty to the Li result. Systematic errors associated with the kinematic term account for the remaining uncertainty.

A comparison of the present affinity results to other experimental determinations is also made in Table I. The two most recent experiments have involved photodetachment techniques. Feldman et $al.$[19] have made affinity determinations from the position of the photodetachment cross section threshold using a crossed-beam technique and a high-pressure xenon arc lamp as a light source. Patterson et $al.$[18] have performed high-resolution photodetachment studies in a crossed-beam geometry using a tunable dye-laser light source. The alkali-metal negative ion photodetachment onset is inaccessible to them and the electron affinities are determined by interpreting the structure seen in the region corresponding to the $^2P_{1/2,3/2}$ thresholds. The other electron affinity determinations shown in Table I were obtained by interpretation of data from experiments using a number of techniques, as shown. All results are listed chronologically with the most recent work towards the top. Agreement of the present results with the two most recent experimental determinations is excellent. Comparison of our results with the current theoretical work of Norcross also shows excellent agreement with his preliminary calculations.[15, 20]

TABLE I. Experimentally determined values of the alkali-metal electron affinities (in eV).

Li	Na	K	Rb	Cs	Method	Reference
0.620 ± 0.007	0.548 ± 0.004		0.486 ± 0.003	0.470 ± 0.003	photodetached electron spectrometry	Present work
	0.543 ± 0.010	0.5012 ± 0.0005	0.4859 ± 0.0015	0.472 ± 0.003	photodetachment	18
0.61 ± 0.05	0.53 ± 0.05	0.50 ± 0.05	0.48 ± 0.05	0.47 ± 0.05	photodetachment	19
0.56 ± 0.4					charge exchange	7
$0.65 - 1.05$					surface ionization	6
~0.6					exploding wire	5
		>0.35	>0.20	>0.19	photoionization	29
	0.35	0.3	0.27	0.23	charge exchange	30
	$0.41^{+0.06}_{-0.02}$	$0.22^{+0.08}_{-0.06}$	0.16 ± 0.06	$0.13^{+0.07}_{-0.06}$	charge exchange	31
0.4 ± 0.2	0.3 ± 0.2	0.5 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	electron impact	32

Now that the alkali-metal electron affinities are well determined, they can be used as benchmarks in obtaining other atomic affinities by means of interpolation procedures. In particular, Charkin and Dyatkina,[21] and Zollweg[8] have shown that the energy difference between the $d^k s^2$ and $d^k s$ ($k = 0, \ldots, 10$) configurations increases almost linearly with k in the case of neutral and positively ionized species. Extending this to the negative ions, one can estimate the electron affinities of the atoms in the three long rows of the Periodic Table since those for K, Rb, and Cs, on the one end, and those for Cu, Ag, and Au, on the other end, are well known. These values essentially fix the slope of the line representing the $d^k s^2 \rightarrow d^k s$ energy differences. Data for Cu, Ag, and Au have been obtained by Hotop, Bennett, and Lineberger,[22] and by Hotop and Lineberger.[23] Using their values, the new alkali-metal results, and the Zollweg procedure, we obtain the values in Table II. Affinities determined by Clementi's Hartree-Fock-type calculations[11] are also shown in Table II for comparison. Very few experimental determinations exist for these atoms. Scheer[24] has performed surface ionization measurements and determined the electron affinities of Mo(1.0 ± 0.2 eV), Ta(0.8 ± 0.3 eV), W(0.5 ± 0.3 eV), and Re(0.15 ± 0.10 eV). A photodetachment determination of the Pt affinity (2.128 ± 0.002 eV) has been obtained by Hotop and Lineberger.[23] All except Ta are in reasonable agreement with the interpolated results. It is hoped that in the near future, more experimental affinity determinations will make possible a definitive test of such interpolation procedures.

B. Photoelectron angular distributions

Studies of the angular distribution of the photodetached electrons provide a sensitive probe of nega-tive-ion structure by yielding information about the states involved in the photodetachment process. For linearly polarized light, the angular distribution takes the form[25,26]

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{total}}{4\pi} [1 + \beta P_2(\cos\theta)]$$

for electric dipole processes, where $P_2(\cos\theta) = \frac{1}{2}(3\cos\theta - 1)$ and θ is the angle between the polarization vector of the light and the direction of the ejected electron. β is called the anisotropy parameter, and it depends in a detailed way on the ejected electron's orbital momentum, as well as appropriate phase shifts and radial matrix elements.[25] The requirement of a non-negative cross section implies that $-1 \leq \beta \leq 2$. The limiting cases $\beta = 2$ and -1 result in $\cos^2\theta$ and $\sin^2\theta$ distributions, respectively.

In the process

$$X^-(ns^2\ {}^1S_0) + h\nu \rightarrow X(ns\ {}^2S_{1/2}) + e^-(l=1),$$
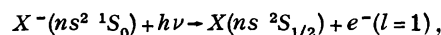
a bound s electron is detached into a p wave and a pure $\cos^2\theta$ distribution ($\beta = 2$) is expected. Configuration-interaction calculations[12,15] show that there is significant p^2 character to the negative-ion ground state. Consequently, dipole transitions leaving the neutral in the ^2P excited states proceed via both s and d wave outgoing electron channels. Hence, we have

$$X^-(ns^2\ {}^1S_0) + h\nu \rightarrow X(np\ {}^2P_{1/2, 3/2}) + e^-(l=0, 2).$$
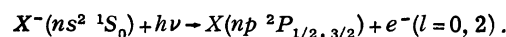
As a result, interference effects between the two outgoing waves make the value of β depend on the details of the photodetachment process, as well as photon energy.

The angular distribution of photoelectrons was measured for each of the observed energy peaks using 4880-Å light. Details of the measurement techniques have been given elsewhere.[17] The anisotropy parameter β is obtained by a least-

TABLE II. Electron affinities of the elements in the three long series (in eV).

Reference	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
11	0.92	···	−0.14	0.40	0.94	0.98	−1.07	0.58	0.94	1.28	1.80
Present work (method of Ref. 8)	[0.50]	−1.95	−0.78	−0.09	0.53	0.86	−1.18	0.15	0.65	1.13	[1.23]
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Present work (method of Ref. 8)	[0.49]	−1.68	−0.71	0.13	0.81	0.90	0.66	1.06	1.14	0.41	[1.30]
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
Present work (method of Ref. 8)	[0.47]	−0.47	0.51	−0.73	0.00	1.02	0.12	1.12	1.59	2.13	[2.31]

squares fit of the raw data to a functional form which contains correction terms to account for imperfections in the half-wave plate, as well as a small (~1%) depolarization of the laser light. The experimentally determined β's at 4880 Å are given in Table III. Electrons corresponding to the neutral being left in the ground state all have $\beta = 2$ within experimental uncertainty. This result indicates that LS coupling supplies an adequate representation of the photodetachment process at our photon energy (2.540 eV).

Close-coupling photodetachment calculations for the alkali metals are currently being performed by Moores and Norcross.[16] Theoretical comparison can then be made with the β's corresponding to detachment leaving the neutral in the ^2P excited state. Preliminary three-state results indicate that agreement is quite good for K[-], but gets worse as we move to the heavier alkali metals.[27]

In the electron energy spectrum of Cs[-], we resolve electrons leaving the neutral in each of the two fine-structure states and measure corresponding β's:

$$\beta = 0.70 \pm 0.02 \text{ for } Cs(^2P_{3/2}),$$

$$\beta = 0.52 \pm 0.03 \text{ for } Cs(^2P_{1/2}).$$

The value given in Table III for Cs is a statistically weighted average of the above two numbers. The difference between the two fine-structure numbers is a measure of the energy dependence of β as well as an indication of possible spin-orbit effects between the outgoing electron and the atom. Measurements of β's at different wavelengths (resulting in different electron energies) would be necessary to disentangle these two effects.

C. Partial cross-section ratios

After correction for the anisotropic angular distribution, the relative areas of the photoelectron energy peaks can be related to the partial photodetachment cross section at a fixed wavelength for the associated transitions. In particular, for the alkali metals we obtain the ratio of cross sections $\sigma(^2P)/\sigma(^2S)$ where $\sigma(n)$ is the partial photodetachment cross section corresponding to the final neutral state being "n."

Since all the relative intensity measurements were made with the laser polarization along the electron collection angle, we have for any peak

$$I_i \propto \sigma(i)(1 + \beta_i),$$

where I_i is the area of the ith peak, $\sigma(i)$ is the photodetachment cross section for the corresponding transition at the appropriate photon energy ($h\nu = 2.540$ eV), and β_i is the appropriate anisotropy parameter. Hence, the ratio of cross sections can be determined from

$$\frac{\sigma(m)}{\sigma(n)} = \frac{I_m}{I_n}\left(\frac{1 + \beta_n}{1 + \beta_m}\right).$$

Values of $\sigma(^2P)/\sigma(^2S)$ for the heavier alkali metals are

0.99 for K ,

0.74 for Rb,

0.96 for Cs .

The ^2P state in the lighter alkali metals is energetically inaccessible in this experiment. For Cs, we also obtain $\sigma(^2P_{3/2})/\sigma(^2P_{1/2}) = 2.25$.

Statistical errors contribute ~3–4% uncertainty to the above numbers. A much greater source of error may lie in the assumption of constant analyzer transmission as a function of electron energy. Previous measurements of molecular photodetachment spectra in which Franck-Condon factors were calculated,[17,28] indicate that the transmission is probably flat to better than 20% over the energy range investigated. The total error in the partial cross-section ratios is therefore estimated to be 20–25%.

Preliminary results of close-coupling photodetachment calculations being currently performed by Moores and Norcross show quite reasonable agreement with the above ratios.[27]

V. SUMMARY

We have studied all the alkali-metal negative ions by means of fixed-frequency laser photoelectron spectrometry. The measured electron

TABLE III. Anisotropy parameters β (at 4880 Å).

Final state of neutral	Li	Na	K	Rb	Cs
2_S	1.99 ± 0.02	2.01 ± 0.02	2.00 ± 0.02	2.01 ± 0.02	1.99 ± 0.02
2_P	$\cdots$	$\cdots$	-0.64 ± 0.02	-0.42 ± 0.03	0.64 ± 0.04

affinities agree extremely well with recent theoretical calculations and other photodetachment experiments. These results have been utilized to predict the electron affinities of the atoms of the three long rows of the Periodic Table. The results of angular distribution and partial cross-section ratio measurements are also in good agreement with preliminary theoretical results.

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