Resonances in Alkali Negative-Ion Photodetachment and Electron Affinities of the Corresponding Neutrals*

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Two techniques of laser photodetachment spectroscopy have been utilized to provide the first accurate experimental determinations of alkali-atom electron affinities. Strong resonances corresponding to autodetaching states are found near the first ^2P levels of the neutral alkalis. These resonances are by far the narrowest observed to date in electron-atom systems.

The electron affinities of the alkali atoms have evoked considerable experimental and theoretical interest for a number of years. In spite of the wealth of theoretical predictions,[1] there have been no accurate experimental determinations of alkali electron affinities. Recent advances in negative-ion source technology have allowed alkali negative-ion photodetachment studies[2] with conventional light sources, but the accuracy of the resulting electron affinities was not sufficient to afford a real test of the theoretical computations. By substituting lasers for the conventional light sources, the accuracy of alkali-atom electron affinities can be improved by 1–2 orders of magnitude. Using such techniques, we have studied photodetachment of all alkali negative ions. In addition to accurate measurements of the electron affinities, strong resonances have been observed in the heavy alkalis at energies near that of the first excited state of the neutral atom.

Two different experimental techniques are employed in these measurements: fixed-frequency laser photoelectron spectroscopy[3] and tunable laser photodetachment[4] cross-section measurements. In both cases the alkali negative ions are produced in a commercial hot-cathode discharge source in which alkali halides are volatilized. Typical mass-analyzed alkali negative-ion beam currents are ~0.5 nA.

In the photoelectron spectroscopy apparatus,[3] the negative-ion beam is crossed with the intracavity beam of a 4880-Å argon-ion laser. Electrons photodetached into a small angle enter a hemispherical electron energy analyzer whose energy resolution is 50 meV full width at half-maximum (FWHM), and the resulting detached-electron energy spectrum is analyzed to determine the electron affinity. A least-squares fit to the 50-meV-wide detached-electron peak determines the centroid to 1 meV.

Photodetachment of the alkali negative ions was studied with this apparatus. The absolute electron energy scale was set using the K^- photodetached-electron peak as the reference. This choice is appropriate since the electron affinity of K is accurately determined below, and, in order to avoid errors associated with slight nonlinearities of the electron energy analyzer, one wishes to use a reference ion whose electron affinity is close to that of the ion being studied. The results of these measurements are given in Table I. In addition to their intrinsic interest, these electron affinity determinations are of crucial import in understanding the nature of the Cs^- and Rb^- resonances reported below.

In the other apparatus,[4] we measure the relative cross section for production of neutral atoms as a function of laser wavelength. A 2.5-keV alkali negative-ion beam is crossed with the

TABLE I. Measured electron affinities of the alkali atoms (eV). The quantity in parentheses is the uncertainty in the last digit.

	Photoelectron spectroscopy	Photodetachment cross-section thresholds
Li	0.620(7)	...
Na	0.548(4)	0.543(10)
K	Reference ion	0.5012(5)
Rb	0.486(3)	0.4859(15)
Cs	0.470(3)	0.472(3)

light beam from a flashlamp-pumped tunable dye laser; after interacting, the negative ions and the neutral atoms produced by laser photodetachment are electrostatically separated, and the atoms are detected with a secondary emission detector.

This latter technique is most suitable to determination of electron affinities by observation of the onset of neutral production at the photodetachment threshold. While this wavelength region in the alkalis is not accessible to current dye-laser systems, the region corresponding to the opening of the first excited ^2P-state exit channel is. If this threshold can be unambiguously identified, the electron affinity is then easily obtained by subtraction of the neutral excitation energy. Because the two outer electrons in the alkali negative ion are strongly correlated[1] (in the terminology of configuration interaction, there is a strong admixture of the p^2 configuration in the s^2 alkali-ion ground state), one might hope to see an observable effect at the threshold for producing neutrals in the ^2P state, even though the additional final-state channels ($np\epsilon s$) and ($np\epsilon d$) appear to correspond to two-electron transitions. Furthermore, since one of the additional channels has an outgoing electron with zero angular momentum, the general treatment[5] of threshold behavior predicts an infinite cross-section derivative at the channel opening.

Figure 1 shows the K^- photodetachment cross section in the wavelength region corresponding to the $^2P_{1/2,3/2}$ thresholds. The energy difference between the two sharp drops corresponds to the doublet splitting in $K(4^2P_{1/2,3/2})$. The minimum near 17 025 cm^{-1} is taken to be the opening of the $K(4^2P_{1/2})$ exit channel. Similar measurements on Na^- show a feature that looks like a Wigner cusp,[5] which is taken to be the opening of the $Na(3^2P)$ exit channel.

The Cs^- photodetachment cross section in the region near the opening of the 6^2P Cs final-state channels is dominated by two resonances, as shown in Fig. 2. The location of the $^2P_{1/2,3/2}$ channel openings and the associated uncertainties, as determined from the photoelectron spectroscopy study, are indicated by crosshatching. Several points should be noted concerning this cross section. First, the channel openings occur within 3 meV of the observed minima. Second, the photodetachment cross section appears to go to *zero* near the $^2P_{1/2}$ channel opening. At this minimum, the cross section has dropped more than 3 orders of magnitude in a wavelength range of 10 Å and the observed small cross section at the minimum appears to be solely a result of the finite linewidth (1 Å) of the laser. Third, the photodetachment cross section drops an order of magnitude, but does *not* go to zero, near the $^2P_{3/2}$ channel opening. The widths (FWHM) of these two features are ~1 and 3–4 meV, respectively.

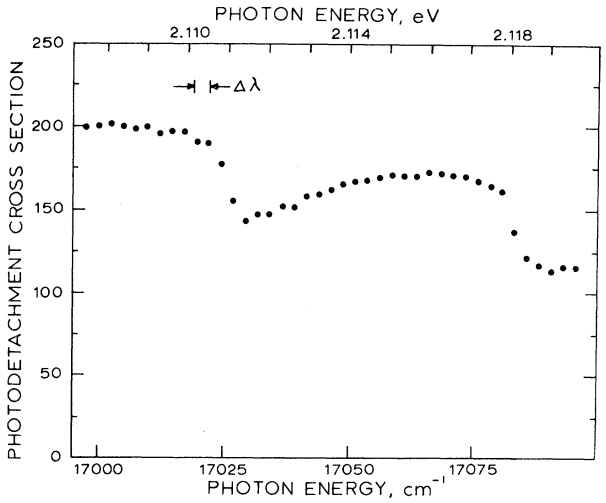

FIG. 1. K^- photodetachment cross section in the region of the opening of the $K(4^2P_{1/2,3/2})$ exit channels. The energy difference between the two sharp drops corresponds to the above doublet splitting in K.

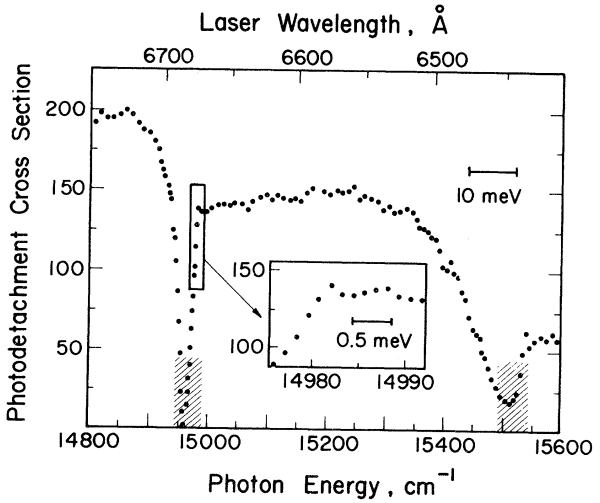

FIG. 2. Cs^- photodetachment cross section, 6800–6400 Å. The shaded regions indicate the confidence limits on the opening of the $Cs(6^2P_{1/2})$ and $Cs(6^2P_{3/2})$ exit channels, as determined by photoelectron spectroscopy.

Similar studies of Rb^- photodetachment near the $^2P_{1/2,3/2}$ channel openings give a result that is qualitatively similar to that found for Cs^-. Again, the photoelectron spectroscopy results show that the channel openings occur very near the cross-section minima. The principal difference between the two is that the resonances are an order of magnitude narrower in Rb^- than in Cs^-. Figure 3 shows a high-resolution (laser linewidth ~0.15 Å) measurement of the Rb^- photodetachment cross section near the $^2P_{1/2}$ channel opening. The small nonzero cross section at the minimum appears also to result from the finite linewidth of the laser. The width of this resonance (FWHM) is approximately 150 μeV, and that of the $^2P_{3/2}$ resonance is 1 meV. The $^2P_{1/2}$ channel opening, as determined by photoelectron spectroscopy, occurs 0.5 meV to the high-energy side of the minimum, and the error bars (± 3 meV) associated with this measurement extend off both sides of the figure.

The principal feature of these data which must be explained is the apparent vanishing of the cross sections near the $^2P_{1/2}$ threshold. On the sole basis of a new channel opening which competes with an already open channel, there is no *a priori* reason[5] to expect a zero in the cross section. A more tenable explanation is that there exists an autodetaching state of the alkali negative ion which lies just below each of the ^2P states in the heavy alkalis. This state must be optically connected to the negative-ion ground state, and it must couple with open continuum channels, giving rise to a Fano line shape[6] in the photodetachment cross section. *LS* coupling is clearly inappropriate in the vicinity of the ^2P channel openings, but it does not necessarily follow that there will be any significant coherent mixing of the ^1P and ^3P continuum states of the negative ion. The spin-orbit effect may be negligible for the ejected electron, in which case only one exit channel, the ^1P, will be significantly accessible at photon energies insufficient to excite the $^2P_{1/2}$ state of the neutral alkali. On the basis of this model it follows that a resonance profile will lead to a nearly vanishing cross section at some photon energy. This model would also require that the cross section not vanish near the $^2P_{3/2}$ threshold because at this energy there is another nonresonant continuum channel open. One would then expect to see the $^2P_{1/2}$ channel opening appearing as an either infinite or discontinuous derivative in the cross section with respect to energy, somewhere to the high-energy side of the minimum. The inset in Fig. 2, a high-resolution view of the Cs^- photodetachment cross section above the $^2P_{1/2}$-related minimum, shows a sharp discontinuity ~2.5 meV above the minimum. We interpret this discontinuity to be the $Cs(^2P_{1/2})$ channel opening. In the case of Rb^-, the autodetaching state would appear to be even closer to the ^2P threshold, and the $Rb(^2P_{1/2})$ channel opening must lie somewhere in the steeply rising region on the high-energy side of the minimum in Fig. 3. This same model suggests that such a "state" is responsible for the observed features in Na and K, but that the channel opening intervenes before the resonance is fully developed. The electron affinities obtained based on these interpretations of the observed features are given in Table I.

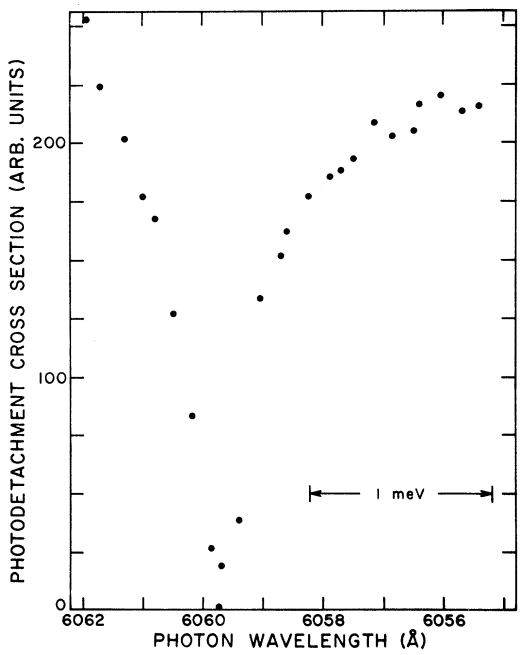

FIG. 3. Rb^- photodetachment cross section near the $Rb(5^2P_{1/2})$ channel opening. Photoelectron spectroscopy shows that the channel opens 0.5 meV above the cross section minimum with error bars (± 3 meV) which extend off the figure.

In an effort to identify the autoionizing state responsible for this structure we have performed some preliminary close-coupling photodetachment calculations.[7] While it is clear that the final state should be characterized in either intermediate or *jj* coupling, calculations performed in *LS* coupling may still be helpful in understanding the observed structure. In K^-, for example, such a calculation results in a cross section

that has the same general shape as the observed cross section in the energy region ± 100 meV around the ^2P threshold and predicts a sharp drop of approximately a factor of 2 within 8 meV near the ^2P thresholds. This result suggests that the spin-orbit interaction of the atomic electron is more important than that of the detached electron, but that both are negligible except in the region of the doublet.

Such calculations have also been done for Cs, using solutions of three-state ($6s$-$6p$-$5d$) coupled-equation expansion for both the initial and final states. The $^1P^\circ$ elastic-scattering phase shift was found to resonate strongly just below the $6p$ excitation threshold, rising by over $\pi/2$ in the last 150 meV, yielding a very sharp minimum in the photodetachment cross section near threshold. The final-state wave function was found to be dominated by the configuration $6p7s$ in this region with a strong admixture of $6p5d$, perhaps explaining the failure of the resonance to appear in earlier two-state ($6s$-$6p$) calculations.[8] This assignment is supported by detailed study of the total photodetachment matrix element, which reveals that the maximum in the sum of the elements connecting the ground state with the configuration $6p7s$ is associated with the zero in the sum of the remaining elements, in accord with the theory of Fano.[6] Similar calculations are underway for Rb^-, but, based on the Cs^- results, we make the tentative assignment $5p6s$ to the observed Rb^- resonances.

In summary we have measured the electron affinities of all of the alkalis using laser photodetachment techniques and have observed strong resonances resulting from autoionizing states in the heavy alkalis. These resonances are by far the narrowest ever observed in electron-atom system. The electron-affinity results are summarized in Table I.

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[1]See, e.g., A. Weiss, Phys. Rev. 166, 70 (1968); D. W. Norcross, following Letter [Phys. Rev. Lett. 32, 192 (1974)]; W. H. E. Schwarz, Chem. Phys. Lett. 10, 478 (1971).

[2]H. Kaiser, dissertation, Ruprecht-Karl-Universität, Heidelberg, 1973 (unpublished).

[3]M. W. Siegel, R. J. Celotta, J. L. Hall, J. Levine, and R. A. Bennett, Phys. Rev. A 6, 607 (1972).

[4]H. Hotop, T. A. Patterson, and W. C. Lineberger, Phys. Rev. A 8, 762 (1973).

[5]E. P. Wigner, Phys. Rev. 73, 1002 (1948).

[6]U. Fano, Phys. Rev. 124, 1866 (1961).

[7]D. L. Moores and D. W. Norcross, in *Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973,* edited by B. C. Cobic and M. V. Kurepa (Institute of Physics, Beograd, Yugoslavia, 1973), p. 595.

[8]P. G. Burke and J. F. B. Mitchell, J. Phys. B: Proc. Phys. Soc., London 6, L161 (1973).

Application of Scattering Theory to the Calculation of Alkali Negative-Ion Bound States*

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Binding energies of the ground ^1S states of the alkali negative ions are calculated using the coupled equations of scattering theory, based on semiempirical effective potentials for the neutral atoms. An additional true bound state with configuration ^3P lying just below the first excited state of the neutral atom is predicted for every species except Li^-.

A number of calculations have been made of the electron affinities of the alkali atoms, both *ab initio*[1-3] and based on semiempirical potentials for the neutral atom,[4-6] using both single-configuration[1,4] and multiconfiguration[2,3,5,6] negative-ion wave functions. Of these several sets of results, those of Weiss[2] and Schwarz[5] are in the best overall agreement with recent experimental results.[7] There has not yet been a calculation in good agreement with experiment for Cs^-. None of these calculations has predicted more than one true bound state (as opposed to autoionizing