Near-threshold photodetachment of the Li^- ion

J. Dellwo, Y. Liu, and D. J. Pegg*
Department of Physics, University of Tennessee, Knoxville, Tennessee 37996

G. D. Alton
Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
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The method of threshold-photodetachment spectroscopy has been used to measure the electron affinity of Li. Changes in the partial cross sections for the resolved $h\nu+Li^-(2\,^1S)\rightarrow Li(2\,^2S)+e^-(\epsilon p)$ ($^2S\epsilon p$) and $h\nu+Li^-(2\,^1S)\rightarrow Li(2\,^2P)+e^-(\epsilon s)$ ($^2P\epsilon s$) channels were separately investigated in the vicinity of the $2\,^2P$ threshold. The near-threshold data in the $^2P\epsilon s$ channel were fitted to a Wigner law to determine a threshold photon energy of $19\,884.8\pm1.6$ cm^{-1}. An electron affinity of 4980.9 ± 1.6 cm^{-1} (617.6 ± 0.2 meV) is obtained upon subtraction of the well-known $2\,^2P$ excitation energy. The position of the Wigner cusp in the $^2S\epsilon p$ channel was measured to be $19\,882.4\pm4.0$ cm^{-1}, in agreement with the more precise $^2P\epsilon s$-channel threshold energy.

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INTRODUCTION

Calculations of the structure of negative ions pose a challenge to theory. Electron affinities (numerically equal to the binding energy of the least-tightly-bound electron) are much smaller than ionization energies of atoms and positive ions and are comparable in magnitude to electron-correlation energies. As a consequence of this sensitivity to correlation, a calculation of an electron affinity has become an effective way of testing the appropriateness of various atomic-structure models. Beyond the bound three-body prototype system H^-, the alkali-metal-element anions are the most tractable to theory. *Ab initio* calculations on Li^-, for example, have taken account of the interactions between all four electrons in this system while semiempirical calculations have treated the Li^- ion as an effective three-body system in the frozen-core approximation. In this model the two highly correlated valence electrons orbit a positive charge that is screened by two otherwise inert core electrons. There have been fewer experimental determinations of the electron affinity of Li but the more recent values have a higher precision than the best current theoretical values.

The most direct, and potentially the most accurate, method of measuring the electron affinity of an atom is to record the onset of photoelectron or residual atom production in the photodetachment process. Using this method, often called threshold-photodetachment spectroscopy (TPS), the precision of the measurement is, in principle, limited only by the optical resolution that is intrinsically high when a laser is used as the light source. In addition, the Wigner threshold law [1] fitted to the data in the near-threshold region can frequently be used to accurately determine the photon energy at threshold. The TPS method has been successfully applied to the first detachment threshold (the residual atom being left in the ground state) and higher detachment thresholds (the residual atom being left in an excited state). In the latter case, the excitation energy of the atom must be subtracted from the measured photon threshold energy to determine the electron affinity. In this paper we report on measurements of the electron affinity of Li using TPS. Our data were taken in the vicinity of the $2\,^2P$ threshold.

EXPERIMENTAL PROCEDURE

The crossed-beam apparatus used in the present work has been previously described in detail by Pegg [2]. In the experiment a monoenergetic 65-keV beam of Li^- ions was crossed perpendicularly by a beam of monochromatic photons from a pulsed dye laser. Photoelectrons ejected from the interaction region, in the direction of motion of the ions, were collected and energy analyzed using an electron spectrometer. Photoelectron angular distributions were measured by keeping the collection direction fixed in the forward direction while rotating the electric vector of the plane-polarized laser beam using a double Fresnel rhomb. Near-threshold photoelectrons associated with the $^2P\epsilon s$ channel had sufficiently low velocities relative to the ion beam velocity that they were all collected in the forward direction in the laboratory frame, irrespective of their angle of emission in the ion frame.

A typical photoelectron spectrum is shown in Fig. 1. The peaks are associated with photodetachment via the following processes: $h\nu+Li^-(2\,^1S)\rightarrow Li(2\,^2S)+e^-(\epsilon p)$ and $h\nu+Li^-(2\,^1S)\rightarrow Li(2\,^2P)+e^-(\epsilon s)$. These two channels are labeled $^2S\epsilon p$ and $^2P\epsilon s$, respectively. The $^2P\epsilon d$ channel is suppressed near threshold by the centrifugal barrier. By resolving the two channels we were able to investigate unambiguously the threshold dependence of the partial cross sections for each channel. Figure 2 indicates the energy dependence of the measured partial cross sections for the elastic $^2S\epsilon p$ (top) and inelastic $^2P\epsilon s$ (bottom) channels in the vicinity of the 2^2P threshold. The individual fine-structure thresholds associated with the

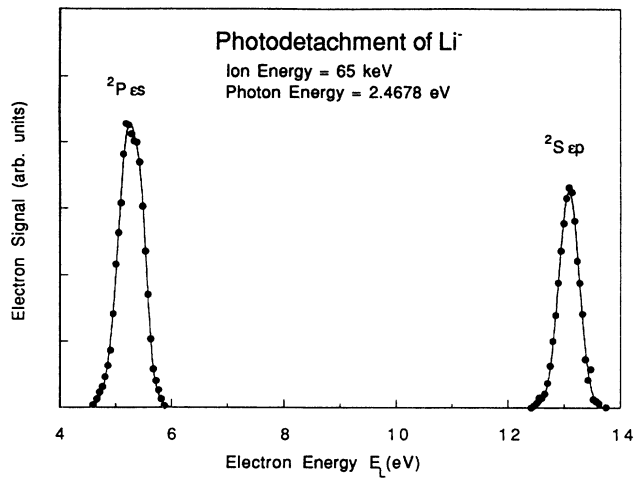

FIG. 1. Spectrum of photoelectrons detached from a fast beam of Li^- ions by visible radiation from a pulsed laser. The lower-energy and higher-energy peaks are associated with photodetachment via the $^2P\epsilon s$ and $^2S\epsilon p$ channels, respectively. In the ion frame the $^2P\epsilon s$ threshold electrons have an energy of only 2 meV. This is kinematically "amplified" to just over 5 eV in the laboratory frame.

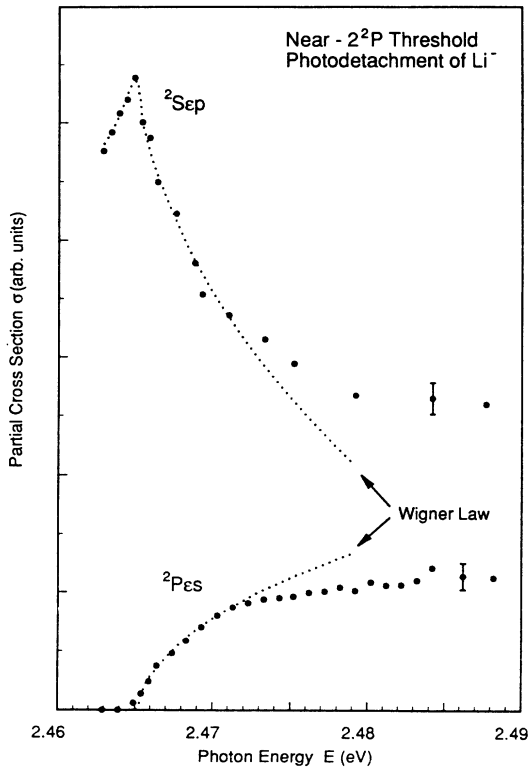

FIG. 2. Relative partial cross sections for the $^2S\epsilon p$ and $^2P\epsilon s$ channels in the vicinity of the $2\,^2P$ threshold. The dots represent the smoothed data and the dashed lines represent the best-fit Wigner-threshold-law curves convoluted with the instrumental function (a Gaussian of 1.5 meV full width at half maximum).

$^2P_{1/2,3/2}$ levels, which are 0.04 meV apart, were unresolved in the present experiment since the optical resolution was 1.5 meV. In the case of the $^2P\epsilon s$ channel, the Wigner law governing the near-threshold behavior takes the form $\sigma = A(E - E_0)^{1/2}$ where E_0 is the photon energy at threshold and A is a normalization constant. The sharp opening (infinite slope at $E = E_0$) of the $^2S\epsilon p$ channel is accompanied by an equally sharp drop in the partial cross section for the $^2S\epsilon p$ channel. This anomalous threshold behavior is the result of strong coupling between the two channels brought about by extensive configuration mixing in the final-state wave functions. The structure in the $^2S\epsilon p$ cross section at threshold is called a Wigner cusp. Near the cusp the $^2S\epsilon p$ partial cross section is expected therefore to follow a Wigner law of the form $\sigma = \sigma_0[1 - B(E - E_0)^{1/2}]$ where σ_0 and E_0 are the cross section and photon energy, respectively, corresponding to the cusp, and B is a normalization constant.

RESULTS AND DISCUSSION

The data in the $^2S\epsilon p$ and $^2P\epsilon s$ channels have been fitted separately to the predicted Wigner threshold law and in both cases the fit was found to be good over a range of ~ 6 meV beyond threshold. Figure 3 shows the near-threshold data for the $^2P\epsilon s$ channel. The range of validity is considerably larger than the 25-μ eV range reported by Mead, Lykke, and Lineberger [3] for the $6\,^2P$ threshold region in Cs^-. The extended range in the case of Li^- is probably due to the smaller dipole polarizability and the absence of the strong Feshbach resonance that falls just below the $6\,^2P$ threshold in Cs^-. In the present measurement the fitting of the near-threshold data in the $^2P\epsilon s$ channel to the Wigner law yielded the threshold photon energy of $19\,884.8 \pm 1.6$ cm^{-1}. The quoted uncertainty includes contributions from curve fitting and measurement of the wavelength of the radiation. The $2\,^2S$-$2\,^2P$ transition energy of $14\,903.8$ cm^{-1} has been measured by

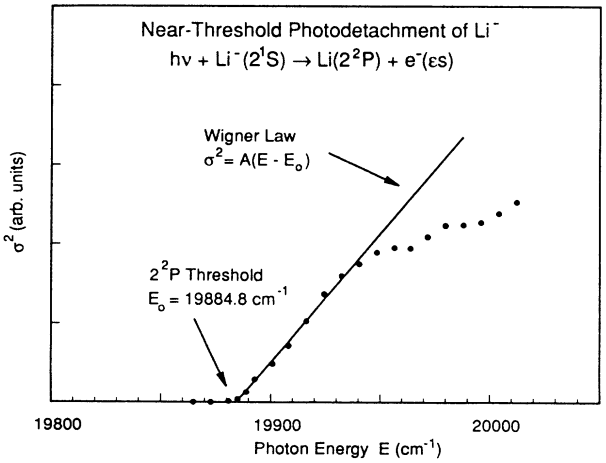

FIG. 3. Square of the relative cross section for photodetaching Li^- via the $^2P\epsilon s$ channel in the vicinity of the $2\,^2P$ threshold. The dots represent the smoothed data and the solid line represents the best fit of the Wigner threshold law to the data.

TABLE I. Experimental values for the electron affinity of Li (in meV).

Reference	Result	Method
This work	617.6±0.2	TPS
Feldmann (Ref. [5])	618.2±0.5	TPS
Bae and Peterson (Ref. [6])	617.3±0.7	TPS
Kaiser *et al.* (Ref. [7])	611±20	PES
Patterson *et al.* (Ref. [8])	620±7	PES

optical spectroscopy [4] to better than 0.02 cm^{-1}. Subtraction of the 2^2P excitation energy from the measured threshold photon energy yields an electron affinity of 4980.9±1.6 cm^{-1}. This value corresponds to 617.6±0.2 meV [assuming a conversion factor of 8065.5410(24) cm^{-1}/eV]. The less-precise measurement of the position of the Wigner cusp in the $^2S\epsilon p$ channel of 19 882.4±4.0 cm^{-1} agrees well with the measured $^2P\epsilon s$ threshold energy. This cusp energy corresponds to an electron affinity of 4978.5±4.0 cm^{-1}(617.3±0.5 meV).

In Table I the present result is compared with other experimental values of the electron affinity of Li. There is agreement, within the quoted uncertainty limits, with both the high-precision TPS results and the lower-precision photoelectron spectroscopy (PES) results. The three TPS results were obtained under quite different experimental conditions. The crossed-beam experiment of Feldmann [5] involved measurements in the infrared region of the spectrum in the vicinity of the $2\,^2S$ threshold. The particles detected were the atoms produced in the photodetachment process. The experiment of Bae and Peterson [6] and the present experiment both involved measurements in the visible region in the vicinity of the $2\,^2P$ threshold. The major difference between the latter two experiments was in the mode of detection and the geometry of the beams. In their merged-beam experiment, Bae and Peterson [6] detected the photoproduced atoms, thus limiting their measurements in the post-threshold region to total cross sections. In our crossed-beam experiment we detected photoelectrons which enabled us to resolve the two competing channels and make separate measurements of the threshold behavior in each channel. Overall, one could argue that it is perhaps preferable to work in the vicinity of the $2\,^2P$ threshold rather than the $2\,^2S$ threshold because of the presence of the sharper onset of production of the photoproducts and, to some extent, the relative ease of accurately measuring wavelengths in the visible. These two advantages appear to more than compensate for the uncertainty in the excitation energy of the $2\,^2P$ state, which is negligibly small.

TABLE II. Theoretical values for the electron affinity of Li (in meV).

Reference	Result
Weiss (Ref. [9])	616
Schwartz (Ref. [10])	620
Fung and Matese (Ref. [11])	613
Grün (Ref. [12])	591
Victor and Laughlin (Ref. [13])	614
Norcross (Ref. [14])	614
Kancerevicius (Ref. [15])	602
Stewart *et al.* (Ref. [16])	596
Sims *et al.* (Ref. [17])	609±7
Cooper and Gerratt (Ref. [18])	611
Lin (Ref. [19])	594
Kaldor (Ref. [20])	610
Christensen-Dalsgaard (Ref. [21])	596±48
Canuto *et al.* (Ref. [22])	608
Ågren *et al.* (Ref. [23])	615
Moccia and Spizzo (Ref. [24])	617.5 (618.7)
Graham *et al.* (Ref. [25])	619

Table II shows a sample of theoretical values for the electron affinity of Li. Overall the agreement between experiment and theory is good. Most of the calculated results tend to be somewhat lower than the experimental TPS values. It is difficult to assess whether there is any real discrepancy, however, since uncertainties are rarely quoted on calculated values. One exception is the *ab initio* configuration-interaction calculation of Sims *et al.* [17], which involves both core and valence electrons. The authors estimate an accuracy of ~1% on the result of this calculation which is about an order of magnitude less accurate than the best experimental values. Very recently a calculation has been made by Chung [26]. This value, 617.4±0.2 meV, is in excellent agreement with the current experimental results and is of comparable accuracy.

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*Also at Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

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