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Photodetachment cross sections for Li^-

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Cross sections and asymmetry parameters associated with the process of photodetaching an electron from the Li^- ion via the process $h\nu + Li^- \rightarrow Li(2\,^2S) + e^-(\epsilon p)$ have been measured at several photon energies including the region in the vicinity of the opening of the channel: $h\nu + Li^- \rightarrow Li(2\,^2P) + e^-(\epsilon s)$. Strong coupling between these channels produces anomalous behavior in the $^2S\epsilon p$ channel cross section. The measured cross sections are slightly lower than the theoretical predictions, but are in essential agreement within the combined uncertainties in the two values. A search has also been made for a $^1P^\circ$ excited state of Li^- in the vicinity of the $2\,^2P$ threshold. The saturation characteristics of the photodetachment of Li^- and D^- ions have been investigated over a range of laser powers.

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INTRODUCTION

To calculate photoionization and photodetachment cross sections it is necessary to select appropriate wave functions to represent the initial (bound) and final (continuum) states that are coupled via the electric dipole interaction. Following photodetachment, the detached electron moves in the field of a neutral atom and the long-range interaction between the two products arises from polarization and exchange effects. As a result, a comparison of measured and calculated photodetachment cross sections affords a sensitive test of the ability of the chosen wave functions to account for electron correlation. In contrast, photoionization cross-section calculations are less sensitive to correlation since the long-range interaction between the ejected electron and the residual ion is dominated by Coulomb forces.

The Li^- ion, with just two electrons outside a closed core, is tractable to theory. Even so, there have been no calculations of cross sections for photodetaching an electron from Li^- in which the initial and final states are both treated in an *ab initio* manner. The earliest accurate calculation was made by Moores and Norcross [1]. These authors used the wave function generated in an *ab initio* configuration-interaction calculation by Weiss [2] to represent the bound state. The continuum state was represented by a close-coupled scattering wave function. The procedure involved accounting for polarization via semiempirical model potentials. The approach is justifiable since electron scattering and photodetachment are related processes via the "half-collision" concept. A more recent calculation by Moccia and Spizzo [3] uses a K-matrix method implemented with L^2 basis functions. Model potentials were used in both the initial and final state of the latter calculation. The most recent calculation is by Burkov, Letyaev, and Strakhova [4], who adopt an R-matrix approach. All three calculations are sufficiently accurate, however, to predict the cusplike structure in the cross section for the process $h\nu + Li^- \rightarrow Li(2\,^2S) + e^-(\epsilon p)$ at the threshold for the process $h\nu + Li^- \rightarrow Li(2\,^2P) + e^-(\epsilon s)$. In the remainder of the paper, these two channels will be labeled $^2S\epsilon p$ and $^2P\epsilon s$, respectively. The $^2P\epsilon d$ channel is suppressed near threshold by the centrifugal barrier. The accuracy for these calculations is estimated to be about 10%. We report here on an investigation of the photodetachment of Li^- over the spectral range 1.87–2.50 eV using energy- and angle-resolved photoelectron spectroscopy. This technique has permitted us to resolve the $^2S\epsilon p$ and $^2P\epsilon s$ channels that compete beyond the $2\,^2P$ threshold. The primary motivation for the present experimental work was to test, at a comparable level of accuracy, the calculated values of the photodetachment cross sections for Li^-. A secondary aim of the work was to search for the possible presence of a $^1P^\circ$ doubly excited state of the Li^- ion in the vicinity of the $2\,^2P$ threshold.

There have been two previous measurements of the total photodetachment cross section for Li^-. Kaiser *et al.* [5] performed a survey experiment over the wide photon energy range 0.5–3.0 eV. The optical resolution of this early nonlaser experiment was rather poor and consequently the accuracy of the total cross section results is quoted at ~30%. Later, Bae and Peterson [6] used a laser light source to determine the total cross section over the narrow energy range 2.40–2.55 eV. This range includes the $2\,^2P$ threshold beyond which the $^2P\epsilon s$, d channels, as well as the $^2S\epsilon p$ channel, are energetically accessible. The channels were, however, unresolved in the experiment in which the detected particles were the residual neutral atoms produced in the photodetachment process rather than the photoelectrons associated with the individual channels. The optical resolution of the experiment was high and the quoted accuracy on the cross-section measurements was ~15%. The present experiment encompasses the spectral range 1.87–2.50 eV over which the cross sections vary considerably. Within this range we have chosen three discrete photon energies to sample the $^2S\epsilon p$ partial cross section as the threshold for the opening of the $^2P\epsilon s$ channel is approached and crossed. In addition, in the vicinity of the threshold we have made detailed relative measurements of the partial cross sections for both channels. Of special interest here is the opening of the $^2P\epsilon s$ channel and the manner in which this opening affects, via strong configuration interaction, the partial cross section for the $^2S\epsilon p$ channel, both in the near pre-threshold and post-threshold regions. The channel mixing, which is associated with the polarization of the Li atom by the detached electron, produces anomalous behavior in the $^2S\epsilon p$ channel at the threshold for opening of the s-wave channel. In the near post-threshold region the $^2S\epsilon p$ cross section is expected to fall sharply as a result of the interaction with the $^2P\epsilon s$ channel which, according to the Wigner law [7] for s-wave detachment, opens with an infinite slope. In the near pre-threshold region the cross section for the $^2S\epsilon p$ channel rises sharply due to the interaction with the $^2P\epsilon s$ channel via virtual transitions [8]. The strong interaction with the $^2P\epsilon s$ channel in the near pre- and post-threshold regions produces a cusplike structure in the $^2S\epsilon p$ cross section at threshold. This cusp, called a Wigner cusp, has been previously observed in the total-cross-section measurements of Bae and Peterson [6]. We have also measured the asymmetry parameter β, which characterizes the angular distribution of the photoelectrons associated with the $^2S\epsilon p$ channel, both in the pre- and post-threshold regions.

EXPERIMENTAL PROCEDURE

The crossed-beam apparatus used in this work has been described previously [9]. A fast, monoenergetic beam of negative ions, produced from an accelerated beam of positive ions by charge exchange (sequential two-electron capture), is crossed perpendicularly by a monochromatic beam of photons from a flashlamp-pumped pulsed dye laser. Photoelectrons ejected from the interaction region, in the same direction as the ions, are energy analyzed and detected using a spherical-sector electrostatic spectrometer. A typical spectrum is shown in Fig. 1. The angular distributions of the photoelectrons can be studied by keeping collection fixed in the forward direction and rotating, using a double Fresnel rhomb, the electric-field vector of the plane-polarized laser radiation. The photoelectron signal is normalized to variations in both the photon flux and the ion beam intensity. Stray external magnetic fields in the experimental region are reduced by the use of three, mutually perpendicular, Helmholtz coils. Synchronous detection, based on the time structure of the laser, is employed to discriminate against background electrons that are primarily associated with the collision-

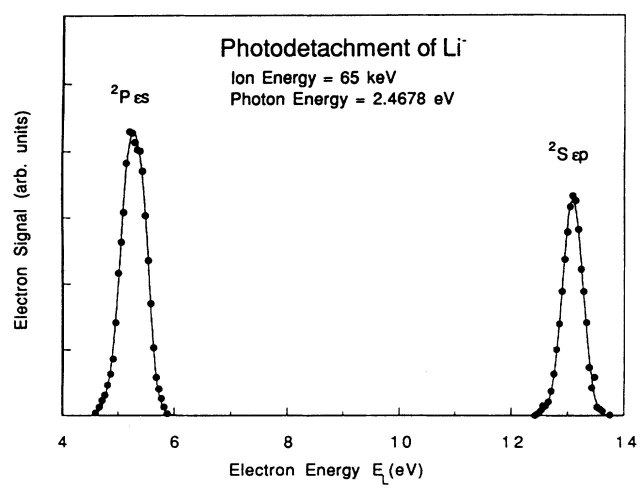

FIG. 1. Spectrum of photoelectrons detached from a fast beam of Li^- ions by visible radiation from a pulsed laser. The lower-energy and higher-energy peaks are associated with photodetachment via the $^2P\epsilon s$ and $^2S\epsilon p$ channels, respectively. In the ion frame the $^2P\epsilon s$ channel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

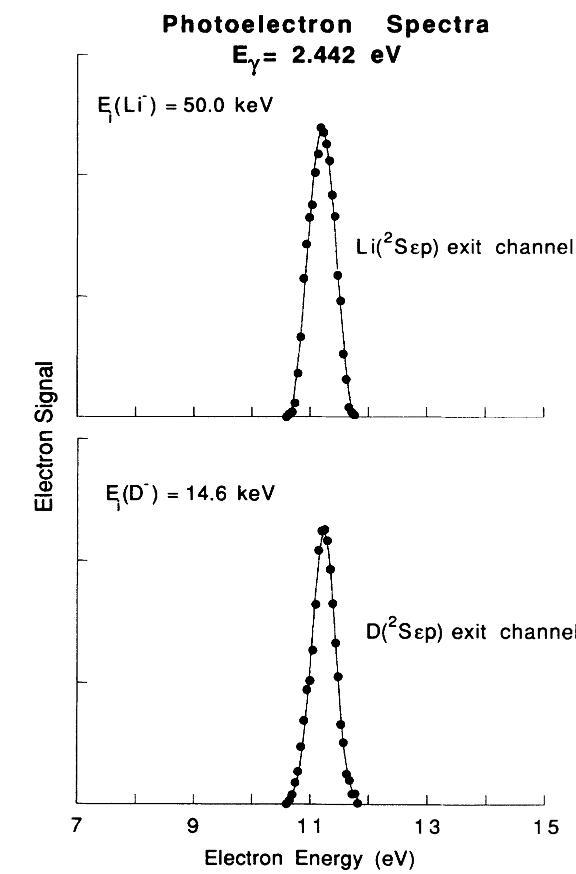

FIG. 2. An illustration of the use of kinematic line shifting to eliminate the dependence of the cross-section ratio on the efficiencies for collection and detection of the detached electrons from each beam. At this photon energy, the ion frame energies of the detached electrons from the Li^- and D^- beams are 1.824 and 1.688 eV, respectively. By the choice of the ion beam energies E_i shown in the figure, the energies of the detached electrons in the laboratory frame are made to coincide at ~ 11 eV.

al detachment of the beam ions.

The experimental method consists of measuring the yields of the detached photoelectrons for a fixed integration time, using energy- and angle-resolved spectroscopy. The angle-dependent photoelectron yields were determined by fitting the spectral peaks to Gaussian functions. In the present experiment the difficult task of making an absolute measurement of the photodetachment cross section has been circumvented by measuring instead the cross section for Li^- relative to that for a reference ion. In this calibration procedure the reference ion was chosen to be D^-, whose photodetachment cross section is known from theory to better than 3%. Strict collimation of the beams ensured that the overlap of each ion beam with the laser beam in the interaction region remained essentially unchanged for the relative measurement. Long-term changes in the photoelectron yields have been observed and are attributed to small changes in the beam overlap arising from variations in the spatial profile of the laser beam caused by dye degradation. The ratio $R=\sigma(Li^-)/\sigma(D^-)$ was determined by use of the relation $R=Ygf$. In this expression Y represents the measured ratio of the yields of photoelectrons from the Li^- and D^- beams (normalized to the same photon flux and ion beam density), g is a kinematic factor that takes account of the different ion-frame solid angles of emission for the two beams, and f is the ratio of photoelectron angular distributions (in the present experiment, $f=1$ at all photon energies). The velocities of the ions in the two beams were measured to $\sim 0.1\%$ by an *in situ* analysis of the photoelectron spectra from the Li^- and D^- beams as compared to the spectra resulting from the photodetachment of He^- ion beams of corresponding energies [9].

The fact that the photoelectrons are detached from fast moving ions has been exploited in order to eliminate the dependence of the measured electron yields on collection and detection efficiencies. The combination of relatively high ion beam energies (20–80 keV) and forward-directed electron emission allows us considerable latitude in kinematically shifting the ion-frame electron energies to any chosen value in the laboratory reference frame. In this experiment, the kinetic energies of the Li^- and D^- ion beams were carefully selected so that the energies of the detached electrons from each beam, although different in the ion frame, were made to coincide in the laboratory frame. This procedure circumvents the need to determine the relative efficiencies and thus enhances considerably the precision of the cross-section-ratio measurement. The technique is illustrated in Fig. 2.

RESULTS

The cross-section ratios $\sigma(Li^-)/\sigma(D^-)$ were measured to be 1.98 ± 0.15, 1.84 ± 0.11, and 2.97 ± 0.28 at photon energies of 1.871, 2.077, and 2.442 eV, respectively. An absolute scale for the measurements was established by normalizing the ratios to the theoretical cross sections $\sigma(H^-)$, which are known to better than 3%. The calculation of Stewart [10] was used for this purpose. The present values of $\sigma(Li^-)$ are compared in Table I, to the theoretical predictions of Refs. [1] and [3]. The experimental results tend to be somewhat lower than the theoretical results but the difference is small if the combined uncertainties in the two numbers are taken into account. The estimated uncertainties for theory and experiment are comparable, i.e., $\sim 10\%$. The quoted uncertainty in the ratio measurements has a nonstatistical origin. It is primarily due to scatter in the individual data sets resulting from small changes in the overlap of the laser and ion beams. This range error, which is about 10%, sets the limit on the precision of our cross-section measurements.

TABLE I. Cross sections for the photodetachment for Li^- (in Mb). Calculations in velocity (V) and length (L) gauges.

Photon energy (eV)	Ref. [1]	Ref. [3]	Present expt.
1.871	79 (V)	81 (V)	73.5 ± 6.0
	76 (L)	79 (L)	
2.077	75 (V)	76 (V)	63.5 ± 5.7
	74 (L)	75 (L)	
2.442	98 (V)	98 (V)	89.8 ± 9.5
	102 (L)	95 (L)	

A detailed study of the $2\,^2P$ threshold region is shown in Fig. 3. Here the error bar on the data point at a photon energy of 2.442 eV indicates the uncertainty in the absolute scale for the $^2S\epsilon p$ channel partial cross section. All other measurements for this channel have been made relative to the data point at 2.442 eV. The expected Wigner cusp is observed at threshold, but it appears to be preceded by a small but reproducible dip in the cross section. This structure is not predicted in the calculations of Moccia and Spizzo [3] that also appear in Fig. 3. It is tempting, but inconclusive, to say that this structure might be associated with a resonance that is either smeared out in energy due to insufficient resolution (in the present experiment the resolution was 1.5 meV) or that is unable to fully develop due to the close vicinity of the cusp. Feshbach resonances have been observed by Patterson *et al.*, [11] just below the ^2P channel openings in the photodetachment of the heavy alkali-metal anions which have substantial dipole polarizabilities. The attractive long-range dipole potential resulting from the polarization of the excited alkali atom by the departing electron is, in these cases, able to support a quasi-bound-state that manifests itself as a resonance in the cross section. No resonance structure was observed, however, in the case of Na^-. We attempted to verify whether the dip observed in the present case of Li^- showed other characteristics of a resonance by measuring the asymmetry parameter β over a small range of photon energies around it. The value of β would be expected to change sharply from the nonresonant value of $\beta=2$ in the vicinity of a resonance. No changes were observed. From the theoretical viewpoint, the question as to whether an excited Li atom in the $2\,^2P$ state can or cannot support a Feshbach resonance does not seem to have been conclusively answered to date. Since the ground state of Li^- is ^2S, the electric dipole accessible excited states must be

$^1P°$. The calculations of Moores and Norcross [1] and isoelectronic extrapolations by Simons [12] suggest that a $(2p3s,2p3d)$ $^1P°$ state could exist in the vicinity of the $^2P\epsilon s$ channel opening. An earlier calculation of $e^- + Li$ scattering by Burke and Taylor [13] also suggests the possible presence of a resonant $^1P°$ state just below the $2\,^2P$ threshold. The theoretical evidence is inconclusive, however, since in the calculations of both Burke and Taylor [13] and Moores and Norcross [1], the phase shifts rose sharply near threshold but just failed to reach the value of $\pi/2$ characteristic of resonance behavior. Calculations by Fung and Matese [14] and Lin [15] both indicate the presence of analogous resonances below the more hydrogenic states of Li with $n \geq 3$. Lin [15] failed, however, to detect a resonance below the $2\,^2P$ state. The lower part of Fig. 3 shows the opening of the $^2P\epsilon s$ channel. The results of a threshold energy measurement and electron affinity determination have been described in an earlier paper by Dellwo *et al.* [16]. The data here are relative and are scaled to the calculation of Moccia and Spizzo [3]. The overall shape of the cross section agrees well with the calculations of Moccia and Spizzo [3] and Burkov, Letyaev, and Strakhova [4].

The angular distributions of photoelectrons detached, via the $^2S\epsilon p$ channel, from both the ion of interest Li^- and the reference ion D^- are expected to be the same for all photon energies. During the course of the experiments, β for the $^2S\epsilon p$ channel in Li^- was measured in the pre- and post-$2\,^2P$ threshold regions. The classical dipolar value of $\beta=2$ was found in all cases, i.e., the value of β for the $^2S\epsilon p$ channel, in contrast to the cross section, was not affected by the strong interaction with the $^2P\epsilon s$ channel. This result is, or course, to be expected since the value of β is sensitive to phase changes resulting from the interference of two or more degenerate channels. The $^2S\epsilon p$ and $^2P\epsilon s$ final-state channels, although interacting configurationally, are not energetically degenerate and so will not interfere in the usual sense of the word.

The determination of a photodetachment cross section involves a measurement of the yield of one of the reaction products (photoelectron or residual atom) at a laser power sufficiently low that the yield is unsaturated, i.e.,

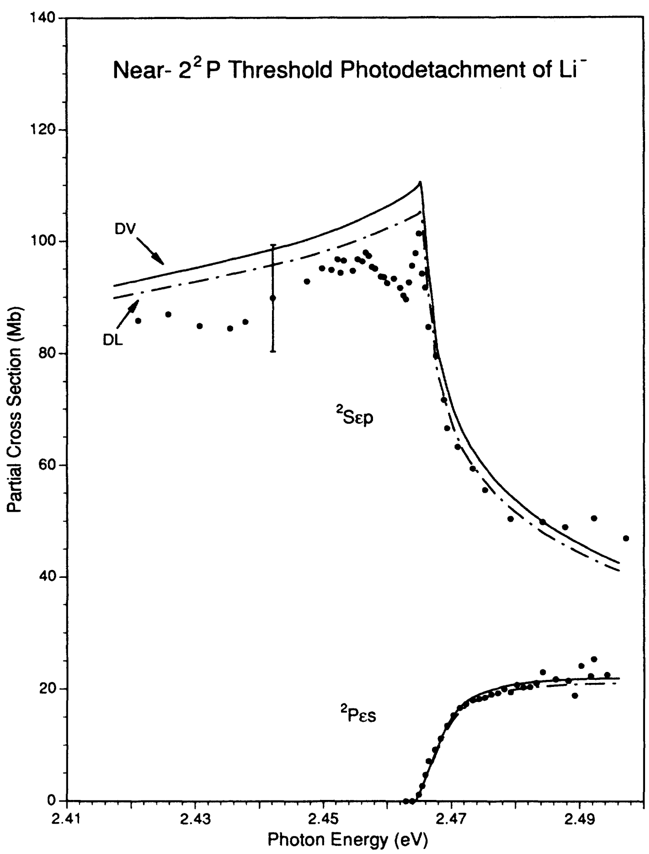

FIG. 3. Investigation of the shapes of the partial cross sections for the $^2S\epsilon p$ channel (upper) and the $^2P\epsilon s$ channel (lower) in the vicinity of the opening of the latter channel. The black dots represent the data and the lines represent the calculations of Ref. [3] (the solid line is the dipole velocity form and the dashed line is the dipole length form). The measurements in each channel are relative. In the case of the $^2S\epsilon p$ channel, an absolute cross-section scale was established by measuring the $\sigma(Li^-)/\sigma(D^-)$ ratio at 2.442 eV. The relative measurements for the $^2P\epsilon s$ channel are scaled to the calculation of Ref. [3].

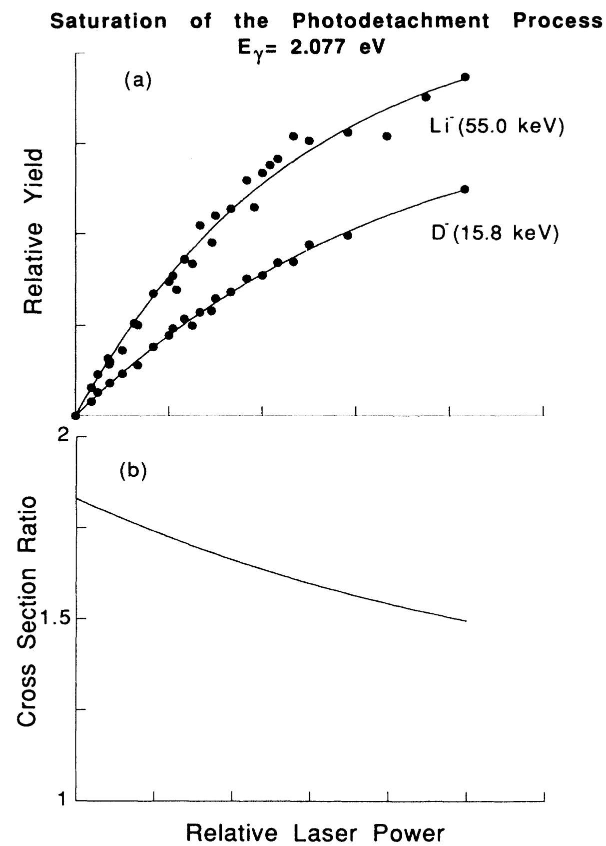

FIG. 4. Saturation characteristics (photoelectron yield vs laser power) for the photodetachment of Li^- and D^- ions are shown in (a). The black dots represent the experimental data and the solid line is a best fit to the function $y=1-e^{-p}$, where p is proportional to the laser power. The yield ratio at each laser power is corrected for kinematic differences and plotted as an effective cross-section ratio in (b). By extrapolating to zero laser power one obtains a cross-section ratio of 1.86.

where there exists, to a good approximation, a linear dependence on the photon flux. Unfortunately, associated with such low laser powers are correspondingly small signal rates which make the measurements rather time consuming. The problem is exacerbated if the ion beam intensity is also small. In the case of an ion with a relatively large photodetachment cross section, such as Li^-, saturation becomes significant even at rather low laser powers. Since our measured cross sections are observed to be consistently smaller than the theoretical predictions, it was decided to thoroughly investigate the saturation characteristics of the photodetachment process for both Li^- and D^- ions in order to determine where saturation effects become non-negligible. Saturation in the present case would tend to lower the cross section ratio $\sigma(Li^-)/\sigma(D^-)$ since Li^-, with a larger cross section than D^-, would tend to saturate more readily. It was found that only at very low laser powers are the processes linear. The saturation data, for a photon energy of 2.077 eV, are shown in Fig. 4(a). It was observed that the photoelectron yields fit rather well, over a wide range of laser powers, to the form $1-e^{-p}$ where p is proportional to the laser power. This form represents the probability that an electron will be photodetached from an ion as it passes through the laser field if the quantity p is identified with the product of the cross section, the photon flux experienced by the ion in the laser field, and the time of interaction of the ion with the field. In the present crossed-beam geometry, the interaction time is determined by the transit time of the fast moving ions through the laser beam and therefore should differ for the two beams only as a result of their different velocities. It is possible to use the fitted saturation curves for Li^- and D^- photodetachment to determine an effective cross section ratio that can be extrapolated to the unsaturated region. Figure 4(b) shows the ratio of effective cross sections $\sigma(Li^-)/\sigma(D^-)$ as a function of laser power. This ratio is determined, at each laser power, from the ratio of the fitted yield curves shown in Fig. 4(a), corrected for kinematics. The effect of saturation on the cross-section ratio is clearly demonstrated. The extrapolated zero laser power ratio is found to be 1.86. This result is consistent with the value of 1.84 ± 0.11 obtained by acquiring data solely in the linear (unsaturated) regime. The agreement between these two values is an indication that saturation did not play a significant role in the present measurements of the relative cross sections for photodetaching an electron from Li^- and D^- ions.

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