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Effect of a virtual state near an s-wave threshold: Absolute Li^- photodetachment cross sections near the $Li(2\,^2P)$ threshold

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Absolute cross sections for Li^- photodetachment have been measured near the $Li(2\,^2P)+\epsilon s$ channel threshold. The energy dependence deviates rapidly from normal Wigner-cusp behavior on each side of threshold. From an analysis of the total cross sections in terms of a two-channel scattering theory that includes the effects of a virtual state, a parametric expression has been derived which accurately describes the energy dependence. A least-squares fit of the data yields the position of the virtual state (55 ± 10 meV below $2\,^2P$), the phase shift at the $Li(2\,^2P)+\epsilon s$ threshold (1.4 ± 0.1 rad), and the electron affinity of Li (617.3 ± 0.7 meV).

The threshold behavior of scattering and excitation cross sections has been a subject of extensive theoretical and experimental studies for more than three decades in the fields of atomic, nuclear, and elementary-particle physics. However, only with the recent development of high-resolution laser-photodetachment methods have experimental studies begun to disclose the strong effects that neighboring resonances can have on the threshold behavior. It is therefore of experimental usefulness as well as theoretical importance to understand, describe, and predict these effects.

Similar to the resonance phenomena in other short-range potential scattering systems (atom-atom, neutron-nucleus, etc.),[1] electron scattering and photodetachment resonances are of three types. In the electron-atom (molecule) systems they are caused by the short-range attractive (correlation energy) forces that commonly exist in the collision complex at energies near the thresholds of excited-state channels. If the correlation potential is sufficiently strong that the compound state is "bound" below the continuum of the excited state channel, it is a "bound," "closed-channel," or "Feshbach" resonance. If the attractive potential is not quite strong enough to form a bound resonance, a "virtual state" can exist for an s-wave channel,[2] or a "shape" resonance can exist if $l\geq 1$. The scattering phase shift changes rapidly and passes through $(n+\frac{1}{2})\pi$ as the total energy passes through the levels of bound and shape resonances, but it does not quite reach $(n+\frac{1}{2})\pi$ in the case of a virtual state.

In his treatment Wigner[3] showed that in the neighborhood of a threshold the cross section is, apart from a constant, the same function of energy regardless of the excitation mechanism so long as the long-range interaction of the product particles is the same. Thus, photodetachment threshold behavior is the same as that of electron scattering for the same final state, and studies by photodetachment have the advantages of high-energy resolution and the definition of the final-state spin and angular momentum.

Dramatic interference effects due to Feshbach resonances were first observed by Patterson *et al.*[4] in the photodetachment of K^-, Cs^-, and Rb^- just below the thresholds of the first excited neutral product channels. Lee[5] applied multichannel reaction-matrix theory to develop a ten-parameter expression which was capable of fitting the Cs^- results. Later, Watanabe and Greene[6] treated the K^- problem using multichannel quantum-defect theory (MQDT) including the effects of polarizability. In later experiments, departures from the Wigner threshold law for the production of these excited s-wave channels were found to exist within about 120 μeV for K and Cs (Ref. 7) and subsequently, within 25 μeV for Cs.[8] While the use of the MQDT permits the inclusion of resonance effects on the thresholds, they do not appear in an explicit form. We have recently examined the effects of a shape resonance on the behavior of He^- photodetachment near the $He(2^3P)$ threshold.[9] The presence of the $^4P^e$ shape resonance causes the cross section to deviate rapidly from the Wigner[3] threshold law, and we found that its behavior can be quite accurately described by a modified formula.[9] Now, in this paper we disclose and discuss the effects of a virtual-state resonance near a photodetachment threshold.

The negative alkali-metal ions have the valence electronic configuration ns^2, so the first excited state in Li^- photodetachment occurs as $h\nu+Li^-(2s^2\,^1S)\rightarrow Li(2p\,^2P)+\epsilon s$. Moores and Norcross[10] performed an *ab initio* calculation of the total photodetachment cross section for Li^-. They also used effective-range theory to generalize the Wigner threshold law for the many-channel case and compared it to their calculations near the "Wigner cusp" that occurs at the opening of the s-wave channel at the $2\,^2P$ threshold. They found that their partial cross sections could not be adequately described by the Wigner law even 0.07 meV away from the threshold and attributed this deviance to "resonant behavior," taking note of the rapid variation in the phase shift of their final-state wave functions. In rearranged form, the Wigner law for the photodetachment cusp derived by Moores and Norcross can be expressed as

$$\sigma\sim\sigma_0(1-A\sqrt{E_0-E}) \tag{1a}$$

below the threshold, and by

$$\sigma\sim\sigma_0(1-B\sqrt{E-E_0}) \tag{1b}$$

above the threshold. Here, σ_0 is the total cross section at the threshold energy, $E=E_0$, and A and B are constants.

We have recently measured the cross sections for Li^- photodetachment in the region of the $Li(2\,^2P)$ threshold. An examination of the results showed that the cross section rapidly deviates from Eq. (1), in agreement with the findings of Moores and Norcross.[10] Noting that the phase shift calculated by Moores and Norcross, although changing rapidly just below the $2\,^2P$ threshold, did not quite reach $\pi/2$, we sought to interpret the deviations from the Wigner law

as resulting from the near presence of a virtual state. In this case we were able to use the theoretical work of Nesbet[11] on multichannel threshold structure in electron scattering. We derived an appropriate parametric formulation of the cross-section behavior that contains corrective terms of Eq. (1) accounting for these effects. It not only describes the threshold behavior very well, but fits our data over their full range of 40 meV on each side of threshold, and yields information on the location of the virtual state and on the phase shift of the ground-state p wave at threshold.

We consider a two-channel scattering system, in which channel 1, with an $l=1$ outgoing wave [here the $\mathrm{Li}(2s\,^2S)+\epsilon p$ continuum], is continually open, and the $\mathrm{Li}(2p\,^2P)+\epsilon s$ channel 2, with an $l=0$ outgoing wave, is open above a threshold energy E_0. By applying Eqs. (1), (2), (13), and (16) of Nesbet[11] to this two-channel scattering system and neglecting second-order terms, the total cross section for energies $E<E_0$ can be shown to be approximated by

$$\sigma \sim \sigma_0\left[1-(2\tan\eta_0)|\gamma|^2\beta\left(\frac{\kappa}{\kappa+\beta}\right)\right] , \tag{2a}$$

and for energies $E \geq E_0$ becomes

$$\sigma \sim \sigma_0\left[1-(1-\cot^2\eta_0)|\gamma|^2\beta^2\left(\frac{k}{k^2+\beta^2}\right)\right] . \tag{2b}$$

Here, σ_0 and η_0 are the total cross section and the phase shift of channel 1 at E_0, k and κ are defined by $k^2=-\kappa^2=2(E-E_0)$, and $E_0-\beta^2/2$ is the energy level of the virtual state, for which $\beta>0$. The above equations can be transformed so that for $E<E_0$,

$$\sigma \sim \sigma_0\left(1-\frac{A\sqrt{E_0-E}}{\sqrt{E_0-E}+\sqrt{E_0-E_v}}\right) , \tag{3a}$$

and for $E \geq E_0$,

$$\sigma \sim \sigma_0\left(1-\frac{B\sqrt{E-E_0}}{(E-E_0)+(E_0-E_v)}\right) . \tag{3b}$$

A and B are constants, and $E_v=E_0-\beta^2/2$. Note that Eqs. (3) are in fact the normal Wigner threshold laws, Eqs. (1), modified in the denominator of the second terms to include the resonance effects, and when $|E-E_v| >> |E-E_0|$, i.e., when the virtual state is far removed from E_0, they become the same.

The phase shift η_0 of channel 1 at $E=E_0$ can be obtained from the relation

$$B/A=[\beta(1-\cot^2\eta_0)\cot\eta_0]/2\sqrt{2} . \tag{4}$$

For a bound (Feshbach) state, $\beta<0$; thus we have a singularity in (2a) at $\kappa=-\beta$ and this approximate formula is invalid.

The details of the experimental arrangement are given elsewhere;[12] only a brief description is given here. The laser beam and a 3-keV Li^- beam were directed coaxially over a 10-cm field-free interaction region between two electrostatic quadrupoles that are used to deflect the ion beam. Two 1.4-mm (horizontal) × 2.2-mm (vertical) apertures at the exit of the first quadrupole and the entrance of the second quadrupole served to define the interaction region as both laser and ion beams were initially larger than the apertures and essentially uniform over this area. Fast Li neutrals that were formed by photodetachment or collisonal detachment along the interaction region eventually struck the conducting surface (indium oxide) of a glass plate, creating secondary electrons that were counted using a channel electron multiplier. To separate neutral signals from photodetachment and collisional detachment, the laser beam was mechanically chopped and counts with the laser on and off were stored and subtracted by a Princeton Applied Research Model No. 1112 processor. Using a Coherent CR 3000 K laser with 3-W output in the violet lines to pump a Coherent 590 dye laser with Coumarine 515 dye and green optics, the photon wavelength region between 495 and 520 nm was accessible.

As both the laser and ion beams filled the beam-defining apertures nearly uniformly, the photodetachment cross section σ is well approximated by

$$\sigma = Sav/i^- i_p lD , \tag{5}$$

where D is the detection efficiency of the $2\,^2S$ and $2\,^2P$ Li neutrals, S the photodetachment signal per second, a the area of the defining apertures, v the velocity of the Li^- ion, i^- the Li^- current, i_p the effective photon current, and l the length of the interaction region. The efficiency of counting the neutral atoms D, can depend on the secondary electron coefficient of the 3.0-keV Li neutrals that hit the indium oxide coating of the glass plate. To determine D, relative cross sections at a fixed photon energy were measured at several ion-beam energies in the range 2–5 keV. The results are plotted in Fig. 1. The data increase steadily at the lower energies, reaching a plateau at 3.5 keV, which should occur when $D=1$. Above this energy the data are constant. By assuming that $D=1$ at the plateau, this curve was used to obtain the value of D at 3.0 keV, the energy used for the cross sections reported here.

The results of the absolute cross sections obtained in this experiment along with the calculations by Moores and Norcross[10] are shown in Fig. 2. Since the electron affinity of Li used to fix their absolute energy scale is different from that of the present results, their calculated results were shifted in energy by +1.3 meV to make the peak position coincide with our data. The total absolute uncertainty in our results

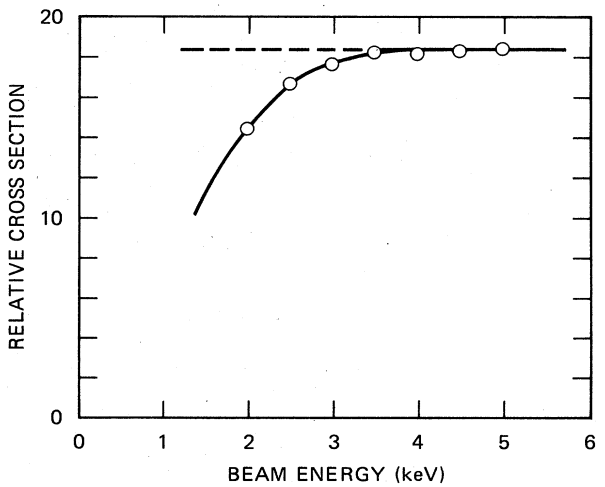

FIG. 1. Relative cross section at the photon energy of 2.461 eV vs Li^- beam energy. The plateau is associated with a detection efficiency of 1.0.

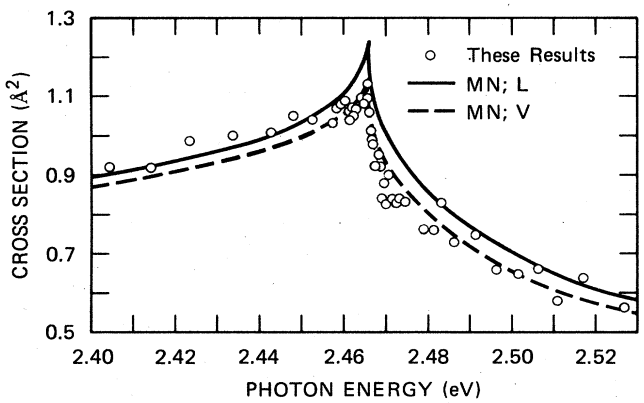

FIG. 2. Photodetachment cross section vs photon energy. MN represents the calculated results of Moores and Norcross. L and V denote the dipole length and velocity forms.

TABLE I. Values of the electron affinity E_{EA} as determined by calculations and by experiments.

Authors	E_{EA} (eV)
Calculations	
Weiss (Ref. 14)	0.62
Fung and Matese (Ref. 15)	0.613
Grün (Ref. 16)	0.614
Victor and Laughlin (Ref. 17)	0.591
Kancerevicius (Ref. 18)	0.602
Moores and Norcross (Ref. 10)	0.615
Cooper and Gerratt (Ref. 19)	0.611
Experiments	
Kaiser, Heinecke, Rackwitz, and Feldmann (Ref. 20)	0.611 ± 0.020
Patterson *et al.* (Ref. 4)	0.620 ± 0.007
Feldmann (Ref. 13)	$0.6182^{+0.0004}_{-0.0006}$
This work	0.6173 ± 0.007

has been estimated to be 15% by combining various uncertainties. Even though there is a small systematic difference in general shape, the absolute values of the present results are in agreement with the calculated results, considering the experimental uncertainties and the difference in the velocity and length forms of the calculations.

It can be seen in Fig. 3 that, while the Wigner-law [Eqs. (1a) and (1b)] fit deviates rapidly from the data, a very good fit is given by Eqs. (3a) and (3b). These equations not only give an accurate value of E_0, but also provide information on the resonance state. The fitting yielded $E_0 = 2.4652 \pm 0.0006$ eV and $\beta^2/2 = 55 \pm 10$ meV with $\beta > 0$ (a virtual state). The electron affinity of Li was determined (by subtracting the 1.8479-eV ^2S-^2P energy difference from E_0), to be 617.3 ± 0.7 meV, in agreement with the value $618.2^{+0.4}_{-0.6}$-meV result obtained by Feldmann[13] from an analysis of the $\mathrm{Li}(2^2S) + \epsilon p$ ground-state threshold photodetachment data. Comparisons of the results of various experiments and calculations are given in Table I. The phase shift at threshold obtained from Eq. (4), using the results of the data fit to Eqs. (3), is 1.4 ± 0.1 rad, which is in good agreement with that of Moores and Norcross (~ 1.3 rad). Although random fluctuations in the present data do not allow more accurate and detailed analysis near the threshold, the general shape of the cross section still reveals a Wigner cusp in good detail and shows that it can be strongly affected by a virtual-state resonance. Because most inelastic electron scattering and opening photodetachment channels are accompanied by neighboring negative-ion resonances, these effects would seem to be quite common, and virtual-state

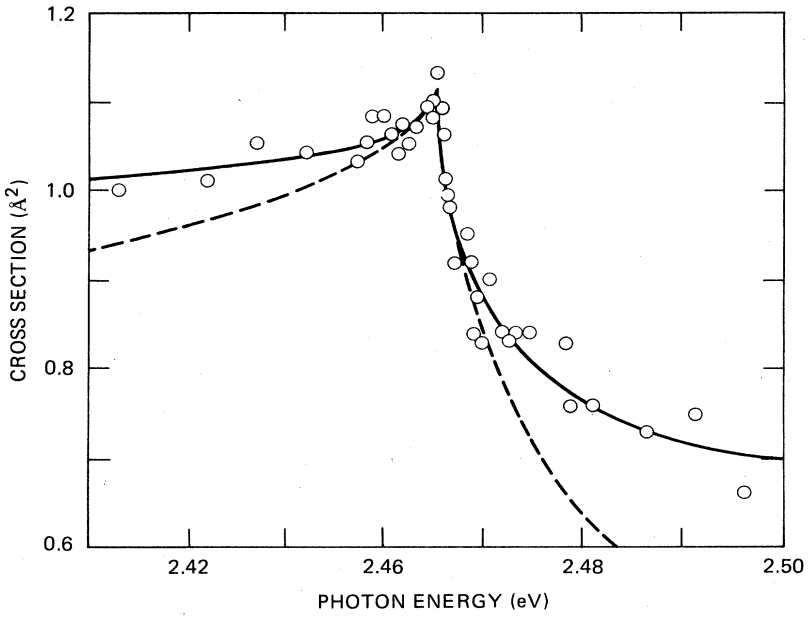

FIG. 3. Results of a least-squares fit of the data to the modified threshold law (solid curve) and the normal Wigner law (dashed curve).

resonance effects can be generally expected near excited s-wave channel thresholds, where Feshbach interferences are not observed below the thresholds.

In summary, we have measured absolute cross sections of Li^- photodetachment near the threshold of the $Li(2^2P)+\epsilon s$ channel. Nesbet's[11] multichannel scattering theory has been applied to develop a parametric formula for analyzing total cross sections near s-wave excitation thresholds that are energetically close to a virtual state. The behavior of the cross sections can be accurately fitted using the formula, which can be used to determine the location of the threshold and characteristics of the virtual state resonance as well.

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