Spectrum of Doubly Excited States in the K^- Ion

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The energies and widths of doubly excited states of the K^- ion in the vicinity of the $K(5\,^2D, 7\,^2S, 5\,^2F)$ thresholds have been measured in high resolution using a sensitive collinear laser-ion beam apparatus. These transient states appeared as resonances in the partial cross section for photodetachment via the $K(5\,^2S) + e^-(\epsilon p)$ channel. Series of two states below the $5\,^2D$ threshold and four states below the $5\,^2F$ threshold have been found. The relative widths of members of the series below the $5\,^2F$ threshold exhibit anomalous behavior, as predicted by a semiclassical model.

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The structure of a negative ion differs fundamentally from that of an isoelectronic atom or positive ion. This is the result of the nature of the force that binds the outer electron in each system. In atoms and positive ions the valence electron moves in a long range Coulomb potential arising from the positively charged core. This produces an infinite spectrum of bound states associated with the excitation of a single valence electron. In the case of a negative ion, however, the outer electron moves in a much shorter range potential arising from the polarization of the neutral atomic core. Typically, this potential can support only a single bound state below the first detachment threshold. In general, singly excited states are not bound in negative ions. However, a rich spectrum of states exists in a negative ion above the first detachment threshold. Here the outer electron is bound to the parent atom in an excited state. The corresponding bound states are therefore doubly excited. These highly excited states are transient since they are embedded in continua and thus rapidly decay by the process of autodetachment.

The prototypical negative ion is H^-. The outer electron in a doubly excited state of this ion moves in the field of an excited H atom. This field is essentially that of a permanent dipole since excited states of the H atom are degenerate in the nonrelativistic approximation. It has been shown that in this special case the members of a series of doubly excited states converge exponentially on the series limit, which is defined by the excited H atom threshold [1]. The relative widths of these states are also known to decrease exponentially as they approach the threshold. In contrast, the outer electron in all other negative ions moves in a shorter range field of a nondegenerate excited atom. This field is that of an induced dipole arising from the polarization of the atom by the outer electron. Recently, Kiyan *et al.* [2] derived a formula, based on a semiclassical model, that predicts the relative energies of members of a series of states bound by this type of potential. In this case the convergence of states on the nondegenerate thresholds has a polynomial character. The relative energies predicted by this formula have been verified in the cases of He^- [2] and Na^- [3]. In the preceding Letter [4], the semiclassical model is extended to investigate the relative widths of states in a series converging on a nondegenerate limit. This model demonstrates that the widths of states within a series do not always narrow monotonically as they converge on the limit. It predicts that a series of states for which the orbital angular momentum of the outer electron exceeds $l = 2$ can exhibit an anomalous behavior.

Series of doubly excited states have been observed in Li^- [5] and Na^- [3]. Calculations of the resonance structure in these negative ions have also been made [6,7]. In the present experiment we extend the study of doubly excited states in alkali-metal negative ions to K^-. In this case, thresholds associated with atomic states of higher angular momentum can be reached at the same level of excitation as in the previous experiments. It will be shown below that an observed series of four states converging on the $K(5\,^2F)$ threshold exhibit anomalous behavior as predicted by the semiclassical model.

The energies and widths of doubly excited states of $^{39}K^-$ were determined from the resonance structure in the partial cross section for photodetachment of K^- via the $K(5\,^2S) + e^-(\epsilon p)$ channel. The photon energy has been scanned in the range 4.193–4.298 eV, which includes the $K(5\,^2D, 7\,^2S, 5\,^2F, 5\,^2G)$ thresholds. The experimental method is based on a selective excitation-detection scheme that involves resonance ionization spectroscopy. In the first step, a laser of frequency ω_1 populates a doubly excited state of ^1P symmetry in a transition from the ^1S ground state of the K^- ion. This state rapidly autodetaches leaving the K residual atom in the $5\,^2S$ state. In the second step, the K atoms produced in the $5\,^2S$ state by autodetachment are resonantly excited into a Rydberg state by the use of a laser of frequency ω_2. In the present case the $23\,^2P$ Rydberg state was chosen. The Rydberg atoms thus produced are subsequently efficiently ionized in a relatively weak electrostatic field. The resulting K^+ ions, which were detected in the presence of only a small background,

constituted the signal in the present experiment. The signal was recorded as a function of frequency ω_1, while the frequency ω_2 was held constant on the transition to the Rydberg state. Since the intensity of laser ω_2 is also held constant during a scan, the K^+ signal, normalized to the ion current and the intensity of laser ω_1, is proportional to the partial cross section for photodetachment of K^- via the $K(5\,^2S) + e^-(\epsilon p)$ channel.

The experimental investigation of high lying doubly excited states of negative ions necessitates the use of an apparatus that possesses both a high sensitivity and a high energy resolution. In the present work we have used a collinear laser-negative ion beam apparatus. With this arrangement the sensitivity is enhanced by a combination of several factors: a large interaction volume defined by the overlap of the superimposed beams, an efficient collection in the forward direction of the residual atoms that are the product of the photodetachment process, and the state selective detection of these residual atoms. The energy resolution is enhanced by the large reduction in kinematic broadening brought about by the use of a collinear beam arrangement. With this geometry one can exploit the kinematic compression of the longitudinal velocity distribution that is inherent in the acceleration process. In the present apparatus the energy resolution is determined solely by the finite bandwidth of the laser used to excite the states. The resolution has been determined to be approximately 0.2 cm^{-1}.

The apparatus was essentially the same as used in previous studies of partial photodetachment cross sections for other negative ions [3,5]. K^- ions were extracted directly from a plasma ion source and accelerated to 4 keV. After mass selection, the beam was deflected into the interaction region by means of an electrostatic quadrupole. In the interaction region, the ion beam was coaxially superimposed with the laser beams over a 70-cm-long path that was defined by 3-mm-diameter apertures placed at both ends of the interaction region. A typical ion current was 1–2 nA, as measured by a Faraday cup at the end of the interaction region. Highly excited K atoms were field ionized in an inhomogeneous electric field created by two cylindrical electrodes. The ionizer voltage was adjusted to deflect into the detector only those positive ions originating from the ionization of K atoms in the $23\,^2P$ state. Radiation at the two frequencies ω_1 and ω_2 was produced by two dye lasers pumped by a common XeCl excimer laser. The frequency scale of laser ω_1 was calibrated by means of reference lines generated via optogalvanic spectroscopy. The Doppler shift, associated with the fast moving ions in the beam, was calculated from a knowledge of the ion beam energy and taken into account in the calibration procedure. The ion current and intensity of laser ω_1 were both recorded during data collection for normalization purposes.

In order to establish the threshold limits in the present measurement, we found it necessary to remeasure the electron affinity (EA) of K to higher accuracy. The measurement is described in a forthcoming publication [8]. The new result is EA(K) = 0.501 459(12) eV

Figure 1 shows the $K(5\,^2S) + e^-(\epsilon p)$ partial cross section over the photon energies 4.193–4.298 eV. Seven resonances labeled (*a–g*) were found in this region of the spectrum. Fits of the data to Shore profiles [9] with linear backgrounds were made in order to determine the energies and widths of the resonances. The cross section at the $K(7\,^2S)$ threshold is dominated by a cusp. The spectrum in the vicinity of this threshold was therefore excluded from the analysis of the resonance structure. Closely spaced resonances, such as (*a–b*) and (*d–g*), have been fitted together to a sum of Shore profiles. The solid lines in Fig. 1 represent the best fits to the spectral data. The extent of each line corresponds to the range of the individual fit. The resonance energies and widths obtained from the fits are presented in Table I. A preliminary scan

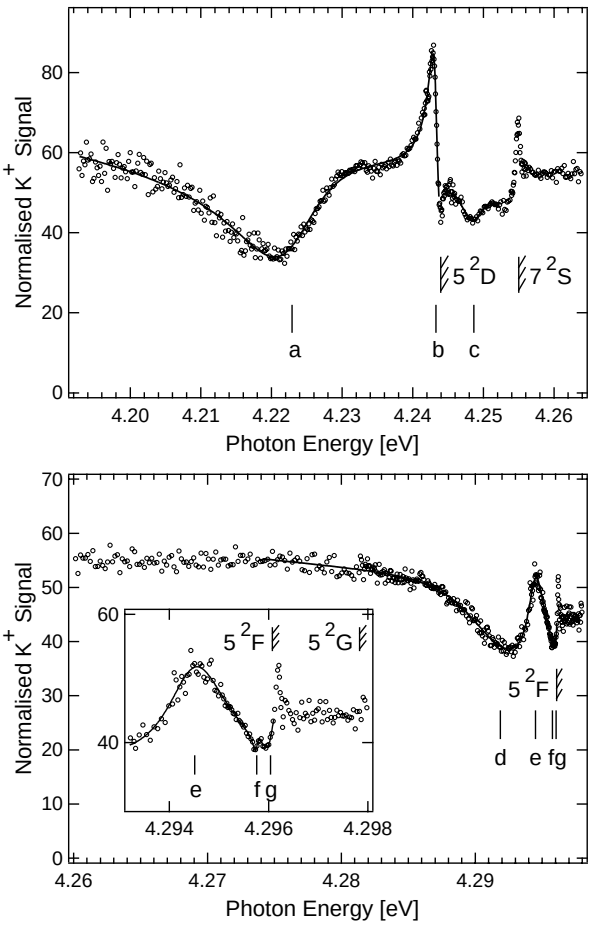

FIG. 1. Partial cross sections for photodetachment of K^- via the $K(5\,^2S) + e^-(\epsilon p)$ channel. The upper and lower spectra show the region below the $K(5\,^2D, 7\,^2S)$ and $K(5\,^2F, 5\,^2G)$ thresholds, respectively. Circles represent the experimental data. The fits of the data to sums of Shore profiles with linear backgrounds are shown by solid lines. The energies of the resonances (*a–g*) obtained from the fits are represented by short vertical lines. The inset shows the region near the $K(5\,^2F)$ and $K(5\,^2G)$ thresholds in greater detail.

TABLE I. Energies E_r (eV) and widths Γ (meV) of doubly excited states in K^-. Energies are relative to the ground state of the negative ion. Labels refer to the resonances shown in Fig. 1.

Label	E_r	Γ
a	4.2229(4)	14.5(6)
b	4.243 29(6)	1.41(8)
c	4.2486(4)	3.5(7)
d	4.292(2)	10(2)
e	4.2945(1)	1.5(2)
f	4.295 76(4)	0.10(8)
g	4.2960(2)	0.30(3)

was also made over the range 4.096–4.193 eV, which encompasses the $K(6\,^2P)$ threshold. A cusp was observed at this threshold but no prominent resonance structure was found in this region. The data from this region will therefore not be presented here.

The statistical scatter in the data points can be seen in Fig. 1. The statistical quality of the data varies over the spectrum. In order to resolve the weak resonances *f* and *g*, for example, required a long aquisition time to obtain data of high statistical quality. The scatter in the data in this region can be seen in the inset to be considerably less than in other parts of the spectrum.

First, we consider resonances shown in the upper part of Fig. 1. Resonances *a* and *b* were found to be members of a series of states converging on the $K(5\,^2D)$ threshold. Their experimental energies can be described by the semiclassical formula [2]

$$E(n) = -\frac{2C_0^4}{\alpha}\,(n_{\max} - n)^4, \qquad (1)$$

with $\alpha = 2.85 \times 10^5$ a.u. and $n_{\max} = 2.75$. Here $E(n)$ is the resonance energy with respect to the threshold, n is the principal quantum number of the outer electron, $C_0 = 1.848$ is a numerical constant, α is the dipole polarizability of the parent atomic state, and the integer part of the parameter $n_{\max}$ represents the maximum number of states that can be bound to the given atomic state. It should be noted that n refers to the quantum number of the outer electron in the model polarization potential and, thus, one should assign $n = 1$ to the lowest state *a* of this series. The value of $n_{\max}$ then indicates that *b* is the closest state to the threshold, which is consistent with the analysis of the spectrum in this region. A lower limit of the dipole polarizability of the $K(5\,^2D)$ state can be estimated using available oscillator strength data. This estimate gives the value $\alpha = 1.9 \times 10^5$ a.u., which is in a reasonable agreement with the value obtained by use of the semiclassical formula.

An estimate of the lower limit of the dipole polarizability of the $K(7\,^2S)$ state yields the value $\alpha = 1.8 \times 10^5$ a.u., which is rather close to the estimated value for the $K(5\,^2D)$ state. Thus, one might expect to observe the same number of doubly excited states converging on both the $K(5\,^2D)$ and $K(7\,^2S)$ thresholds. However, the resonance *c* is the only doubly excited state attributed to the $K(7\,^2S)$ threshold. The semiclassical model developed in Ref. [2] assumes that the outer electron moves in the asymptotic region and the effect of electron correlations can be reduced to the polarization potential experienced by the outer electron. This assumption, however, is less rigorous for lower lying states where the outer electron spends more time closer to the core. In such cases, the inner region may also be important in the determination of the energy of the lowest state. The situation can be complicated by the closeness of another atomic state. In this case the potential in the inner region depends on the type of crossing of the potential curves which, respectively, approach different thresholds. For example, the crossing of potential curves is of avoided character in H^- [10] which, in this case, reflects weak channel interactions. As a consequence, it has been predicted that at a high level of excitation, the lowest doubly excited state of a given series can lie below the closest lower photodetachment threshold. Such a situation has also been observed in He^- [2]. Here the lowest members of the $4pnp\,^4P$ and $5pnp\,^4P$ series that converge on the $He(4\,^3P)$ and $He(5\,^3P)$ thresholds lie below the $He(4\,^3S)$ and $He(5\,^3S)$ states, respectively. In the present study, however, the series of states below the $K(7\,^2S)$ threshold is likely interrupted by the presence of the $K(5\,^2D)$ threshold. As a result only one doubly excited state is observed in this region. Theoretical input is clearly needed at this point to verify the type of crossing experienced by the potential curves that approach the $K(5\,^2D)$ and $K(7\,^2S)$ thresholds.

In the following we will focus our consideration on the spectrum below the $K(5\,^2F)$ threshold. The four resonances (*d*–*g*) observed in this region are members of a common series. The resonance *d* is the lowest lying in this series and, thus, one should assign the principal quantum number $n = 1$ to the outer electron in this state. Resonance energies are plotted in Fig. 2 vs the quantum number of the outer electron. The solid line represents the result of a fit of measured energies to Eq. (1) with α and $n_{\max}$ as the fit parameters. One can see that experimental energies are well described by the semiclassical formula.

Resonances *f* and *g* lie very close to the threshold. The binding energy of the state *g* with respect to the parent $K(5\,^2F)$ atomic state is, for example, only about 30 μeV. It was therefore important to determine the threshold position with high accuracy. One can also determine the threshold position by defining the energy to which the series of states converges. In the present case, the energies of resonances (*d*–*g*) were fitted to Eq. (1) with the threshold energy as an additional fit parameter. As a result, the fit produced the value 4.296 069 eV for the threshold energy associated with the $K(5\,^2F)$ state. Subtracting the energy of the $K(5\,^2F)$ state with respect to the ground state of the K atom, we obtain the value 0.501 457 eV for the electron affinity, which is in excellent agreement

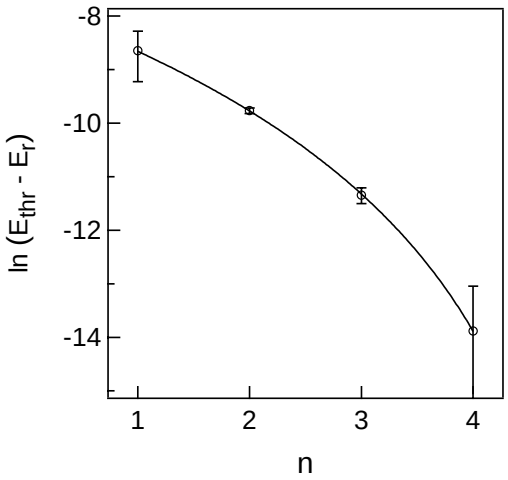

FIG. 2. Energies of resonances d–g of the series of states converging on the $K(5\,^2F)$ threshold vs the principal quantum number n of the outer electron. Energies are shown with respect to the threshold. The solid line represents the fit of the measured energies to Eq. (1).

with the newly measured value of 0.501 459(12) eV. This demonstrates that observation of a limit of a series of doubly excited states can be used to accurately determine electron affinities.

One can see from the table that the width of the resonance g is larger than the width of the resonance f, even though the state g lies closer to the threshold. This rather unusual effect is predicted in the preceding Letter [4]. It is shown that for small binding energies, the functional dependence of the width on the binding energy is determined by the normalizing coefficient of the semiclassical wave function representing the outer electron in the bound state. When the orbital angular momentum of the outer electron has $l \neq 0$, the normalizing coefficient has a minimum. This minimum arises from the presence of the repulsive orbital potential term which prevails over the attractive polarization term in the asymptotic region. The orbital term causes the classical turning point to be closer to the origin. Consequently, the outer electron is confined to a smaller region where it interacts with the inner electrons. Thus, the width of a doubly excited state becomes larger because of the presence of the orbital term. The orbital potential is important only in the far asymptotic region where $r > \sqrt{\alpha/l(l+1)}$. Therefore, it affects only states of small binding energies, i.e., resonances closest to a threshold. One can see from Fig. 2 of the preceding Letter that the region of the minimum, where the reduced coefficient C_r is smaller than its value on the threshold, $C_r(E = 0)$, is defined by the condition $\alpha|E|/[l(l+1)]^2 < 0.14$. Substituting the value of E from Eq. (1) and assuming that $n_{\max} - n \sim 1$ for states near the threshold, we find that the minimum in widths can exist only if the orbital momentum $l \geq 3$. In the present case, the outer electron can have such an orbital momentum when it couples with the $5f$ atomic electron to form a doubly excited state of ^1P symmetry.

In summary, we have measured the energies and widths of doubly excited states of the K^- ion. These highly correlated states were manifested as resonances in the partial cross section for photodetachment of K^- via the $K(5\,^2S)$ channel. Series of two states below the $5\,^2D$ threshold and four states below the $7\,^2S$ threshold have been found. The relative energies of the members of these series are in agreement with the predictions of the semiclassical model. This model also predicts that the widths of resonances within a series do not necessarily decrease monotonically as they approach the series limit as might be expected. Such anomalous behavior was observed in a series below the $K(5\,^2F)$ threshold.

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