

Observation of resonance structure in the Na^- photodetachment cross section

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We have used a collinear laser-ion beam apparatus to investigate the partial cross section for the photodetachment of Na^- via the $\text{Na}(4s) + e^-(\epsilon p)$ channel. The measured cross-section spectrum is compared to a recent R -matrix calculation [C.-N. Liu and A. F. Starace, preceding paper, *Phys. Rev. A* **59**, 3643 (1999)]. The photodetachment cross section was measured in the energy range 4.657–4.880 eV. In this spectrum, we have identified four resonances that converge on the $\text{Na}(4d)$ threshold. The energies and widths of the resonances were determined from the measured cross section. A semiempirical formula has also been used to predict the positions of the four resonances and to show that, in a semiclassical model, the resonances belong to the same $^1P^o$ series. [S1050-2947(99)10805-9]

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I. INTRODUCTION

Independent electron models have been successful in describing the grosser features of many-electron atomic systems, but experiments continue to reveal a rich array of phenomena that cannot be explained by these simple models. Electron-electron interactions, which give rise to correlated motion, must be taken into account. In a doubly excited atomic system, for example, a pair of electrons move in the field of a positively charged core. Under certain conditions it is possible for the interaction between the two excited electrons to be comparable to or greater in strength than the interaction of each electron with the core. The motion of the two electrons then becomes highly correlated and the independent particle model breaks down. This condition is easiest to attain for a loosely bound system such as an atomic negative ion. Here the core field is weaker than that of the isoelectronic atom or positive ion. The correlated motion of a pair of highly excited electrons is thus enhanced due to the suppression of the core field.

The simplest three-body Coulomb system is the H^- ion. As such, it has been extensively investigated both theoretically [1] and experimentally [2]. This prototypical ion consists of two electrons moving in the pure Coulomb field of a point nuclear core. Double excitation of H^- corresponds to an outer electron moving in the field of an excited H atom. In the asymptotic limit this field has a potential of a permanent dipole, $V(r) = -d/r^2$, associated with the degeneracy of excited states of the H atom. When the dipole moment d is sufficiently large, this potential can support an infinite series of bound excited states [3]. The members of a given series then converge exponentially on the corresponding excited state threshold [4].

An alkali-metal negative ion can be considered as an effective two-electron atomic system. Here the two valence electrons move in a field of a closed shell core which is inert. However, the force which binds the outer electron to the excited atom is fundamentally different. The presence of the finite core breaks the degeneracy of excited states of the atom and, thus, the existence of a permanent dipole moment. In this case the outer electron moves in the shorter range field of an induced dipole, which has an asymptotic potential $V(r) = -\alpha/2r^4$, where α is the static dipole polarizability of the parent atomic state. This potential can support only a finite number of bound states. The energy of such states relative to the parent atomic state was recently described by Kiyani *et al.* [5]. Here it was shown that the convergence of members of a given series on the corresponding excited state threshold has a polynomial character.

Up to now experimental investigations of doubly excited states in alkali-metal anions have focused on Li^- [6–8]. In the present work we extend our studies of doubly excited states in alkali-metal anions to Na^- in order to further understand the effect of a finite core on the energies and widths of the resonances. An important difference in this case is that the higher principal quantum number, n , of the atomic states allows states of higher orbital angular momenta l . The energy separation of opposite parity states of the same n and large, but different, l becomes small. As a consequence, the dipole polarizability of an atomic state can be rather large, even at relatively low levels of atomic excitation. In this work we have studied doubly excited states of Na^- in the vicinity of the $\text{Na}(4d)$ parent state threshold. The dipole polarizability of the $4d$ state is large due to the presence of the close lying $4f$ state.

We have used photodetachment as a method of investigating doubly excited states in high resolution. Here, the two valence electrons are simultaneously excited by the absorption of a single photon. The highly excited states are embedded in continua and can therefore decay by autodetachment. The decay of these transient states is manifested as resonance structure in the photodetachment cross section near excited

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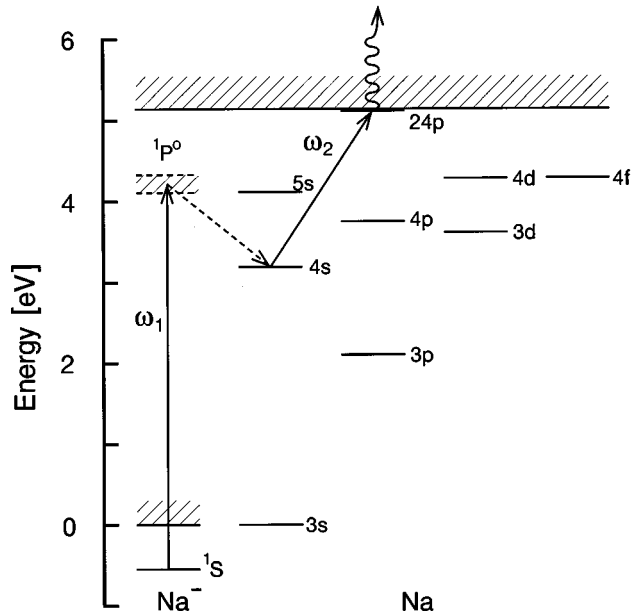


FIG. 1. Excitation and detection scheme showing selected states of Na/Na⁻. The solid lines indicate the transitions induced by the lasers of frequency ω_1 and ω_2 , respectively. The dashed arrow represents the autodetachment process into the channel studied in the present work. The field ionization process is indicated by the wavy arrow.

state thresholds. An analysis of the resonances yields information on the energies and widths of the corresponding doubly excited states. These parameters can be used to assess the ability of theory to incorporate electron correlations into the wave functions describing the initial and final states of the photodetachment process. In the present case we compare our measurements with the recent *R*-matrix calculation by Liu and Starace [9].

II. EXPERIMENT

A. Procedure

The relative cross section for photodetachment of the Na⁻ via the Na(4s) + e⁻(ϵp) partial channel has been investigated in this experiment. The measurement has been performed in the 4.657–4.880 eV photon energy range, which encompasses the Na(4d) threshold. The experimental procedure is based on an excitation-detection scheme that employs resonance ionization spectroscopy in the state selective detection of Na atoms left in the 4s excited state. Essentially the same method has previously been used in measurements of partial photodetachment cross sections in He⁻ and Li⁻ [7,10,11].

The excitation-detection scheme is shown in Fig. 1. One laser of frequency ω_1 induces the photodetachment process, for which Na(4s) is one of the possible final states of the residual atom:



A second laser of frequency ω_2 is used to resonantly excite atoms in the 4s state to the 24p Rydberg state, which is subsequently field ionized in a static electric field of approxi-

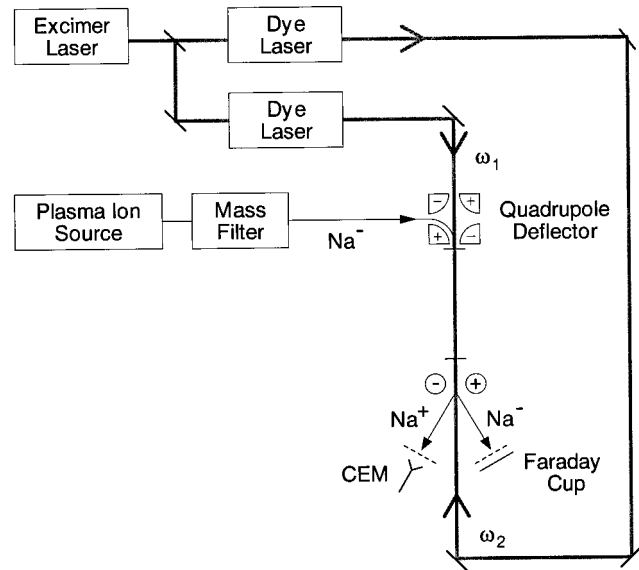
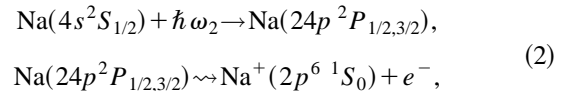


FIG. 2. Schematic drawing of the collinear laser and ion beam apparatus used in the experiment. The figure shows the two counterpropagating laser beams overlapping the Na⁻ beam in the interaction region.

mately 2 kV/cm. This two-step process of state selective ionization can be described by the following equations:



where the wavy arrow represents field ionization. The intensity of ω_2 was sufficient to saturate the 4s-24p transition and the field ionization was estimated to have an efficiency of essentially unity. The yield of Na⁺ ions as a function of ω_1 was proportional to the Na(4s) + e⁻(ϵp) partial cross section since only Na⁺ created by field ionization of the 24p state were detected. The positive ion signal was recorded as a function of ω_1 and the relative photodetachment cross section was determined by subtracting a small background from the signal and normalizing the data to the ion current and the ω_1 photon flux [12].

B. Experimental arrangement

The apparatus was essentially the same as the one we used to study partial photodetachment cross sections in previous measurements [7,10–12], although the detection system has been improved and the interaction region has been extended for the present experiment. A schematic of the setup is shown in Fig. 2. Na⁻ 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. The pressure in the interaction region was approximately 1×10^{-8} mbar. A typical ion current was 1 nA, as measured by a Faraday cup at the end of the interaction region.

Highly excited Na atoms were field ionized in an inhomogeneous electric field created by two cylindrical electrodes.

The ionizer voltage was adjusted to deflect into the channel electron multiplier (CEM) detector only those positive ions originating from the ionization of $\text{Na}(24p)$. This type of field ionizer was originally developed for isotope separation that employed a collinear beams geometry [13]. It has more recently been used in photodetachment studies by Petrunin *et al.* [14].

Radiation of the two frequencies ω_1 and ω_2 was generated by two dye lasers pumped by a common excimer laser that delivered pulses of approximately 15 ns duration. Radiation of frequency ω_1 was obtained by frequency doubling laser light generated by a Coumarin 307 dye. A typical pulse energy in the interaction region was $100 \mu\text{J}$. This energy was sufficiently low to avoid saturation of the photodetachment process or any higher-order processes. Radiation of frequency ω_2 was generated by a Rhodamine 101 dye. The pulse energy was typically $200 \mu\text{J}$. The two laser beams counterpropagated in the interaction region. An optical delay line was used to delay the pulse ω_2 slightly with respect to the pulse ω_1 in order to optimize the signal.

The frequency scale of laser ω_1 was calibrated by measuring spectral lines of Ar generated in a hollow-cathode lamp. The scale between these absolute frequency markers was calibrated by interpolation using the internal wavelength scale of the dye laser, which is sufficiently accurate in comparison to the resolution of the present experiment. The energy resolution of the apparatus has been measured to be approximately 0.2 cm^{-1} [10], limited only by the laser bandwidth. The Doppler shift was calculated from the known ion beam energy and was taken into account in the calibration.

The signal pulses from the detector were counted by a gated counter. The counter was also used to monitor the background by counting the detector pulses in a time window where no photodetachment events occurred. The ion current and intensity of laser ω_1 were recorded during data collection for normalization purposes.

III. RESULTS AND DISCUSSION

The measured relative cross section for photodetachment of Na^- via the $\text{Na}(4s) + e^-(\epsilon p)$ channel is shown in Fig. 3. The scattering of the data corresponds to the shot noise in the counting of positive ions. The signal-to-background ratio at the peak of the cross section was better than 35. The background was independent of the pressure in the interaction chamber under the condition of the present experiment, which indicates a negligible contribution from collisions with the residual gas. The state selective detection also suppressed any significant potential contributions from positive ions created in the possible two-step photodetachment/photoionization process induced by radiation ω_1 alone. Therefore, the main source of background, which scaled linearly with the ion current, was interpreted as being due to particles created by the Na^- beam impinging on apertures or other objects in the interaction chamber.

The thin solid line in Fig. 3 shows the result of a recent calculation by Liu and Starace using the R -matrix method [9]. The experimental cross section has been normalized to the theoretical result by multiplying by a factor which is the ratio of the areas below the experimental and theoretical cross-section curves in the energy region shown in the figure.

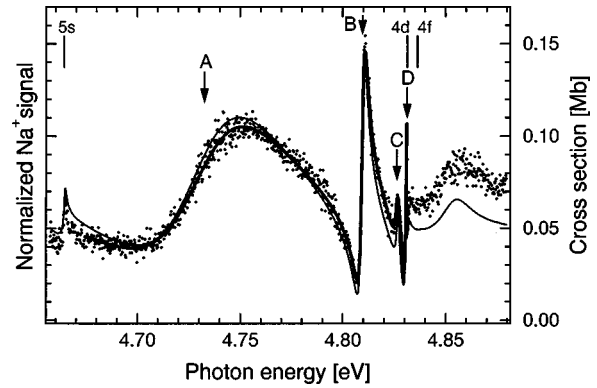


FIG. 3. $\text{Na}(4s) + e^-(\epsilon p)$ partial photodetachment cross section. The experimental result (dots) is a relative cross-section spectrum and the thick solid curve is a fit to the function described by Eq. (4) to the experimental data. The thin solid line is a calculation of Liu and Starace of the absolute cross section (right vertical scale). The experimental curve is normalized to the theoretical spectrum as described in the text.

There is, in general, a good agreement between the experiment and theory. The only disagreement is in the region above the $4f$ threshold. We cannot, however, exclude that this is caused by a small but unavoidable change in the overlap of the laser and ion beams as the laser frequency ω_1 was scanned over the large range in this experiment.

Kiyan *et al.* [5] have recently derived a semiempirical expression which characterizes the energies of members of a series of doubly excited states of negative ions converging on an excited atomic state threshold. This formula applies to the case where the outermost electron is bound to an excited atom via a short range induced dipole potential. The energies of resonances in such a series $E(m)$, relative to the parent atomic state, are given by

$$E(m) = -\frac{2C^4}{\alpha}(m_{\max} - m)^4, \quad (3)$$

where m denotes the principal quantum number of the outer electron, α is the static dipole polarizability of the parent atomic state, $C \approx 1.848$ is a constant, and m_{\max} is a noninteger parameter. The integer part of m_{\max} corresponds to the maximum quantum number of the outer electron in the series. The expression in Eq. (3) has recently been successfully applied to two series of 4P resonances in the photodetachment spectrum in He^- [5]. The fits of Eq. (3) to the spectra in each case predicted the observed number of resonances in the series and a value of the dipole polarizability that was in reasonable agreement with estimates based on tabulated oscillator strengths.

We interpret the resonance structure in the cross section below the $\text{Na}(4d)$ threshold as being due to a series of doubly excited Na^- states of $^1P^o$ symmetry since photoexcitation of states of a different symmetry is forbidden by the selection rules in the dipole approximation. The number of resonances in the Na^- spectrum shown in Fig. 3 is not immediately obvious from mere inspection, since higher energy and narrower resonances are in the close vicinity of the $\text{Na}(4d)$ threshold. In order to determine the number of members that should be expected in a series of resonances below

TABLE I. Energies and widths of the resonances in eV determined from the fit of the function described by Eq. (4). The resonances are labeled according to the notation in Fig. 3.

Resonance	E_r	Γ
<i>A</i>	4.73268(56)	0.066(2)
<i>B</i>	4.80969(4)	0.00363(7)
<i>C</i>	4.82647(18)	0.00293(35)
<i>D</i>	4.83132(16)	0.00226(12) ^a

^aSee text.

the Na(4*d*) state, we used Eq. (3). The energies of the two most prominent and statistically significant resonances *A* and *B* were first obtained from a fit of the sum of two Shore profiles with a linear background:

$$\sigma_{\text{fit}}(E) = a + bE + \sum_i \frac{c_i \epsilon_i + d_i}{1 + \epsilon_i^2},$$

$$\epsilon_i = \frac{E - E_i}{(\Gamma_i/2)}, \quad (4)$$

where *i* is the index of a single resonance, E_i is the resonance energy, Γ_i is the resonance width, E is the photon energy, a and b are the coefficients describing a linear background cross section, and c_i , and d_i are the Shore parameters [15]. This fit was performed in the energy range 4.6748–4.8214 eV. The energies of resonances *A* and *B* obtained from the fit were then used in Eq. (3) to determine the values $m_{\text{max}} = 4.17$ and $\alpha = 6.53 \times 10^5$ a.u. The value of m_{max} implies that four doubly excited states should be bound. By use of these parameters in Eq. (3), we were able to predict the energies of resonances *C* and *D*. The energy of resonance *C* was predicted to be 4.829 58 eV. The energy of resonance *D* was predicted less than 1 μeV below the Na(4*d*) threshold. The Na(4*d*) state has an energy of 4.831 43 eV with respect to the ground state of Na[−] [16]. The value of α obtained from the fit agrees quite well with the previously measured value of static dipole polarizability of the Na(4*d*) state, $\alpha(4d) = 6.2 \times 10^5$ a.u. [17].

As a second step of data evaluation, the experimental data have been fitted to a sum of four Shore profiles with a linear background [Eq. (4)]. The range of this fit was 4.6768–4.8313 eV and it included the whole of the resonance structure below the 4*d* threshold. This fit curve is represented in Fig. 3 by a thick solid line. The energies and widths of the four resonances derived from this fit are presented in Table I. The quoted errors are the statistical uncertainties from the fit. It should be noted that the width of resonance *D*, as derived from the Shore parametrization, is larger than the energy separation of this resonance from the Na(4*d*) threshold. It is essentially impossible to obtain a meaningful width for a resonance when it is so close to a threshold. Resonance *D*, however, is clearly present in the spectrum and its energy, as derived from the Shore parametrization, is in reasonable agreement with the value predicted by Eq. (3). As expected, the energies of the resonances *A* and *B* are not affected by the extension of the fit range and by including two more Shore profiles into the function. Also the energy of resonance *C*

obtained from the fit is in reasonable agreement with the values predicted above from the semiempirical formula, Eq. (3). This implies that all four resonances belong to the same series of doubly excited $^1P^o$ states that converge on the Na(4*d*) threshold.

It should be noted that the four resonances observed can be described as a series within a semiclassical model. The applicability of such a model is based on the assumption that the outer electron moves basically in an asymptotic potential created by the core. The criterion for such an assumption is that the radius r_0 , which separates the inner and the asymptotic regions, is much smaller than the classical turning point of the outer electron in the asymptotic region. In the present case, the classical turning point is estimated to be approximately 100 a.u. for resonance *A* and is gradually increasing up to 500 a.u. for resonance *D*. For the value of r_0 , we take the radius of the maximum in the electron density distribution of the Na(4*d*) state, which is of the order of 20 a.u. [18]. Thus, one can conclude that the criterion of the applicability of the semiclassical model is satisfied for all of the resonant states.

In the asymptotic region the electron potential represents polarization potential $-\alpha/2r^4$, where α is dipole polarizability of the residual excited atom. According to this picture, only atomic states of positive value of polarizability can support bound doubly excited states. It provides an argument why the series of states, observed in this experiment and described by the semiclassical formula, should be assigned to the Na(4*d*) parent state. An estimate of the value of α for the nearby state Na(4*f*), based on tabulated oscillator strengths, indicates that it is negative and, as such, will be unable, in the asymptotic limit, to support bound states. We therefore conclude that we have observed a series of four $^1P^o$ resonant states that converge on the Na(4*d*) threshold.

The semiclassical model does not take into account the motion of the inner electrons and, thus, does not describe the two-electron symmetry. One can expect that the two-electron symmetry can be different for different members of the same ‘‘semiclassical’’ series of states. The parent atom is polarized in a field created by the outermost electron and, therefore, the parent atomic state is represented by a mixture of different configurations. In the present case, the major contributions to the Na(4*d*) parent state wave function are expected to be configurations involving the 4*d* and 4*f* orbitals.

The mixture depends on the strength of the field created by the outermost electron and, thus, on the state of this electron. The outermost electron is bound most strongly to the core in the resonant state *A*. In this case, the admixture of the 4*d* and the 4*f* orbitals in the parent atom is largest. In the case of resonance *D*, the parent state 4*d* is expected to have only a small admixture of configurations involving the 4*f* orbital. The resonances *B* and *C* represent an intermediate case. As a result, the two-electron density distributions might be expected to have different angular symmetries for the four resonances, as was found in the calculation of Liu and Starace [9].

It is difficult to identify the dominant configurations of the members of the $^1P^o$ series without recourse to theory. Due to the dipole selection rules we expect, however, that the configurations 4*d**m**f* and, perhaps, 4*d**m**p* make a significant contribution to the multiconfigurational states. Since the *d*

and f electrons only minimally penetrate the core, one might expect the doubly excited state of Na^- with a configuration $4dmf$, for example, to approximate a two-electron system reasonably well. In fact, the series of the resonances in the Na^- spectrum below the $\text{Na}(4d)$ threshold agree quite well with resonances in the H^- spectrum below the $\text{H}(n=4)$ threshold. In both cases, the energies are calculated relative to the double detachment limit. One might expect agreement in the case of the intrashell resonances where the excitation of two electrons is symmetric. In the case of the asymmetrically excited intershell resonances, however, the outermost electron in Na^- is bound in a fundamentally different potential than is the corresponding electron in H^- . As expected, the widths of the resonances in the Na^- spectrum are considerably larger than the widths of the corresponding resonances in the H^- spectrum.

IV. SUMMARY

In summary, we have studied the $\text{Na}(4s) + e^-(\epsilon p)$ partial photodetachment cross section in the energy range 4.657–

4.880 eV. The general behavior of the cross section agrees well with the recent calculation of Liu and Starace [9]. We interpret the structure in the cross section below the $\text{Na}(4d)$ threshold as being due to four resonances of $^1P^o$ symmetry all belonging to a series of doubly excited states of Na^- described within a semiclassical model.

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