Experimental Evidence that the $6s6p\ ^3P_J$ States of Cs^- Are Shape Resonances

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An experimental study of the previously unobserved and controversial $Cs^-(6s6p\ ^3P_J^o)$ states has been conducted using a combination of infrared laser and storage ring experiments. This first application of photodetachment spectroscopy to the study of low-lying resonances in atomic negative ions has resulted in the observation of a narrow resonance structure, lying only 8.0(3) meV above the first detachment threshold of Cs^-. The storage ring experiments suggest that all fine structure levels of the $6s6p$ configuration are unbound, thereby eliminating possibly the only serious candidate for a stable atomic negative ion with opposite parity bound states. [S0031-9007(97)05108-9]

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Atomic negative ions are a topic of considerable current interest [1], in part motivated by a number of practical implications. Negative ions play an important role in a variety of atomic and plasma phenomena, and in a more specialized context, they provide the basis of ultrasensitive atom and isotope detection through accelerator mass spectrometry (AMS) [2]. In a general context, the interest in negative ions stems from the fact that they are qualitatively different in their structure from neutral atoms and positive ions. To a large extent these differences are a result of the short range interactions between the extra electron and the atomic core; in a mean field treatment the electron is bound in the dipole potential that it induces in the atom. Negative ions therefore offer the unique opportunity to study short range potentials on an atomic scale, which are of fundamental importance to other fields such as nuclear physics. In contrast to a Coulomb potential, a short range potential cannot support an infinite number of bound states; in fact, most negative ions have only one. On the other hand, all negative ions possess many unstable excited states which are embedded as resonances in the energy continuum associated with an atom and a free electron. The extensive theoretical and experimental work on atomic negative ion resonances was recently reviewed by Buckman and Clark [3]. Resonances involving the atom in its ground state occur when the extra electron is trapped in a potential well resulting from the overlap of the attractive short range potential of the polarized atom and the repulsive centrifugal potential. Traditionally, these low-lying shape resonances have been investigated via electron-atom scattering or ion-atom collisions, but the study of very low-lying resonances has proven to be rather challenging with these techniques. Despite considerable efforts on various atomic ions the recently observed $Li^-(2s2p\ ^3P)$ resonance at 50(6) meV [4] is the lowest-lying feature previously reported. The present work therefore employs photodetachment spectroscopy which is new to the study of low-lying atomic shape resonances.

The cesium negative ion, which is the important example of a H^--like two-electron system with a polarizable core and strong relativistic effects, has been the subject of considerable investigation in the past, both experimental and theoretical. A diagram of the energy level structure of Cs^- and Cs, up to Cs($6p$), is given in Fig. 1. Two decades ago, laser-based experiments [5] of the Cs^- continuum just below the Cs($6p$) threshold

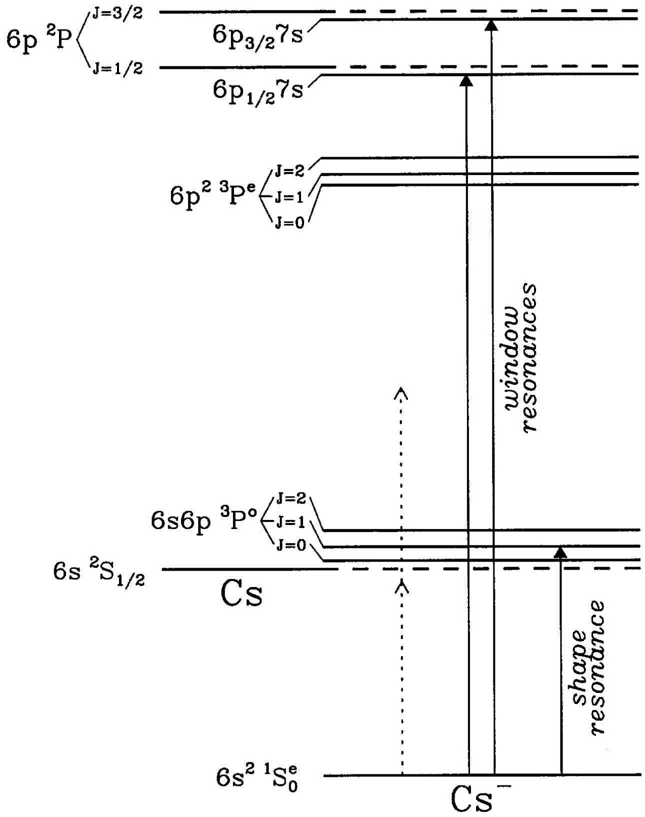

FIG. 1. Schematic energy level diagram of Cs^- and Cs. For clarity of presentation level splittings are not to scale.

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revealed a narrow window resonance. Recently, Greene [6] conducted an extensive theoretical study of Cs^-, in part reproducing the window feature. Also, multiphoton studies have incorporated the narrow window resonances in Cs^- and Rb^- [7]. The cesium negative ion has been much discussed in numerous theoretical studies as potentially the only known candidate for a stable atomic negative ion that possesses an *excited bound configuration of opposite parity to the ground state.* Initially, several calculations on $\mathrm{Cs}^-(6s6p\ ^3P_J^o)$ indicated that the $^3P_J^o$ state might be slightly bound, by a maximum of a few tens of meV [6,8–10], although Fabrikant [8], and Krause and Berry [9] expressed that this might not hold true if their calculations were refined. More recently, a relativistic scattering calculation based on the Dirac R-matrix method by Thumm and Norcross predicted the $J = 0, 1, 2$ levels to be narrow shape resonances just above the Cs($6s$) threshold [11]. This result contradicted earlier scattering calculations [12] which employed a semirelativistic Breit-Pauli R-matrix formalism, and which did not show any low energy resonance structure. This discrepancy was partially resolved in a subsequent theoretical study by Bartschat [13], in favor of the conclusions by Thumm and Norcross. This study compared the two different methods directly, but the earlier Breit-Pauli formalism was modified, in particular through the inclusion of a dielectronic core polarization term. The work reported in the present Letter is the first experimental investigation aimed at resolving this long-standing issue.

The experimental approach involved tunable infrared laser spectroscopy at McMaster University, and heavy ion storage ring experiments at Aarhus University using the ASTRID [14] storage ring. The experimental setup at McMaster is described in detail elsewhere [15,16]. A tunable laser source consisting of a Nd:YAG pumped dye laser and nonlinear optical conversion equipment provided nanosecond infrared pulses with energies of ≈ 0.5 mJ at 3 μm. In an ultrahigh vacuum chamber the infrared laser beam was crossed at 90° with a 10 keV Cs^- beam, which was extracted from a Cs sputter ion source. Photodetached neutral atoms were detected by a discrete dynode electron multiplier.

A series of careful experiments was conducted with tunable infrared laser light, either in a $1 + 1$ (two-photon) detachment scheme, in search of a possibly bound $6s6p\ ^3P_1^o$ level, or aimed at observation of a resonant feature above threshold in the one-photon detachment spectrum. A resonant enhancement of the two-photon detachment yield due to a spin-forbidden $^1S_0^e \rightarrow {}^3P_1^o$ electric dipole transition would be expected in the $1 + 1$ photon detachment regime. The laser-based experiment is only sensitive to the $J = 1$ level of $6s6p\ ^3P_J^o$. Greene [6] predicted binding energies of 32, 25 and 11 meV for the $J = 0, 1, 2$ levels, respectively, while Fabrikant [8], Krause and Berry [9], and Froese Fischer and Chen [10] determined the average binding energy for the $^3P_J^o$ term to be 27, 12, and 1 to 11 meV, respectively. In addition, Greene predicted an Einstein A coefficient for the $6s6p\ ^3P_1^o$ level of 77 s^{-1}, but other theoretical estimates indicate that the A coefficient would be substantially larger [17]. Since we have previously demonstrated [18] that we can readily observe signals for resonantly enhanced $1 + 1$ transitions via magnetic dipole transitions with A coefficients of $\sim 1\ \mathrm{s}^{-1}$, then a large signal, in the case of a bound excited level, would be expected in the present case.

We have performed a series of experiments in the near-threshold region of Cs^- without observing any indication of a bound $6s6p\ ^3P_1$ level. The experiments were carried out under a wide range of experimental conditions, utilizing a tightly focused laser beam or an unfocused beam in order to allow for a range of oscillator strengths and detachment cross sections. The expected experimental signals were modeled on a computer program. Both analog and digital data collection methods were utilized. In all, the first 100 meV below threshold were probed.

Subsequently, we conducted one-photon infrared laser detachment spectroscopy above the Cs($6s$) threshold. We obtained good signals for the Wigner p-wave threshold and also explored the relative single photon detachment cross section to an energy of 75 meV above the photodetachment threshold. The results are shown in Fig. 2. A feature which represents an enhancement of $\approx 25\%$ over the direct, p-wave photodetachment yield is seen centered at a photon energy of 479.6(3) meV, 8.0(3) meV above threshold, with a width of 5.0(5) meV (full width at half maximum) according to a Lorentzian fit. We attribute this relatively weak resonant feature to the $\mathrm{Cs}^-(6s6p\ ^3P_1^o)$ level embedded in the continuum. A blowup of the resonant feature, with the photodetachment "background" subtracted, is shown in Fig. 3. Numerous checks were done in an attempt to verify the validity of this feature. In order to remove the effects of atmospheric absorption of the

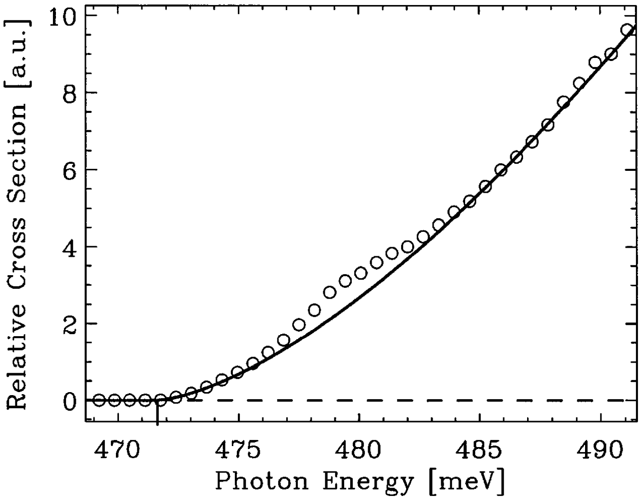

FIG. 2. Photodetachment yield versus laser wavelength. The solid line represents a fitted Wigner p-wave threshold.

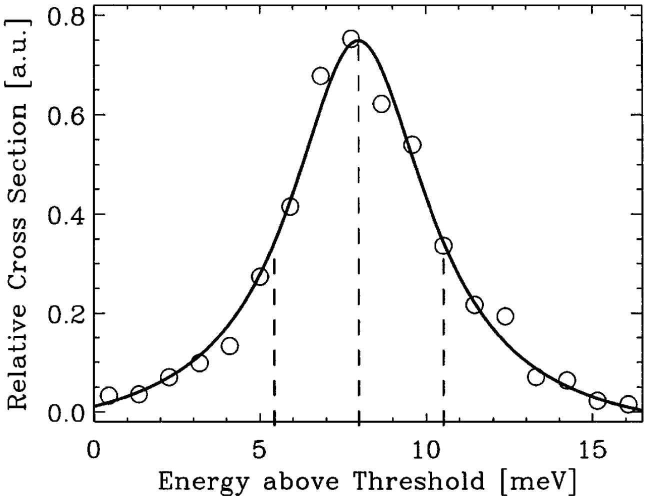

FIG. 3. Blowup of the one-photon detachment scan showing the resonant feature with the p-wave "background" subtracted. The result of a Lorentzian fit is indicated by the solid line.

infrared light the laser path was purged with dry nitrogen and the data normalized to the laser power in the interaction region. We do not believe that this results in any artifact in the final data for the following reasons: the absorption features are small and much narrower than the observed feature, they do not coincide with the proposed resonance, and variations in purge quality in different experiments have led to the same result. It is also possible that a molecular impurity ion, with a mass close to that of Cs^-, could lead to a false resonance, but the relative size of the feature was constant in measurements separated by a few months. Moreover, this is the only feature which we observe in the entire spectral region, including a 100 meV region below threshold where a (unstructured) very weak background was obtained. We consider it very unlikely that a single impurity-ion-based feature would manifest itself solely at this photon energy.

In addition, our infrared photodetachment data enable an accurate determination of the electron affinity (EA) of Cs. We obtain a final value of 471.64(6) meV. A somewhat more accurate value, 471.630(25) meV, which was determined by Lineberger and co-workers via photodetachment to Cs($6p$) using visible cw laser light, was only tabulated in the Hotop and Lineberger review [19] from 1985. Our tunable infrared laser work provides a second and entirely complementary measure of the EA of Cs with high accuracy.

The absence of a $1 + 1$ resonant signal in our laser based studies, combined with the observation of a resonant feature in the single-photon detachment yield, which we attribute to the $6s6p\ {}^3P_1^o$ level, is in excellent agreement with the theoretical work of Thumm and Norcross [11] and Bartschat [13]. These advanced theoretical works predict the resonant structure in the case of electron scattering on Cs, and seem to have achieved a high level of accuracy. Thumm and Norcross calculated the $J = 0, 1, 2$ levels to lie 1.78, 5.56, and 12.76 meV above threshold with widths of 0.42, 2.42, and 9.32 meV, respectively (Bartschat obtained very similar results), compared to our values for the $J = 1$ photodetachment resonance, 8 and 5 meV for position and width, respectively. Our increased width would appear to be qualitatively consistent with the increased energy above the Cs($6s$) threshold. The excellent agreement of theory [11,13] and the present experiment on the $J = 1$ resonance energy is even more convincing when presented with respect to the energy of the Cs^- ground state: 477.2 meV versus 479.6 meV, respectively. We do not yet have theoretical input on the expected magnitude of the feature due to an unbound ${}^3P_1^o$ level in the optical case, since the existing theoretical results apply to electron scattering. Crude extrapolations from the isoelectronic neutral Ba atom might suggest an order of magnitude of a few percent enhancement in the photodetachment yield.

Although we cannot probe $J = 0, 2$ in the laser-based experiments, the theoretical predictions on fine structure splittings would suggest that $J = 0$ is also unbound, based on our position for $J = 1$. Greene [6], Thumm and Norcross [11], and Bartschat [13] predict the $J = 0 - 1$ splitting to be 7, 3.78, and 3.33 meV (Breit-Pauli approach), respectively. In order to make an entirely separate check on the possibility of bound excited levels in Cs^- (especially $J = 0$), we conducted a series of storage ring experiments at the ASTRID facility in Aarhus. The Cs^- ions were produced in either of two different ways, which enhanced the probability of effectively populating a weakly bound Cs^- level. In one run, the ions were extracted directly from a cesium sputter (negative) ion source. Subsequently, in a separate run, Cs^+ ions were extracted from a positive ion source at a kinetic energy of 100 keV, and were charge exchanged in a K metal vapor cell to produce Cs^- ions, which were then injected into the storage ring. The Cs^- beam currents were a few nA. Neutral atoms stemming from either collisional or blackbody-radiation-induced detachment were detected at one corner of the storage ring. The measured 1.1 s lifetime of the Cs^- ground state was consistent with the expected collisional detachment rate. Blackbody-radiation-induced photodetachment on a short ms time scale would provide a sensitive measure of a weakly bound level, up to a binding $\approx$150 meV. A description of the blackbody-radiation effects on weakly bound negative ions can be found in Ref. [20]. We observed no signal associated with a weakly bound level, despite a sensitivity of $\approx 5{:}10^4$ or better [20]. The storage ring experiment has limitations, but offers a very useful double check. The most notable limitation in the present context is that the experiment is insensitive for binding energies less than $\approx$3 meV. Our calculations, based on Ref. [21] indicate that the Lorentz force generated during passage of the 90° bending magnets would destroy more weakly bound ions before they could be observed [14,20]. Hence our final conclusion that $J = 0$ is likely unbound depends on the validity of the earlier fine structure calculations [11,13]. In contrast to the magnetic field stripping effect, our simulations predict no serious limitation due to an excessive blackbody detachment rate for very weak bindings since the Planck radiation flux drops off rapidly at long photon wavelengths—corresponding to an ionic binding of a few meV.

In summary, we have reported the first experimental evidence that the $J = 1$ level of the $\mathrm{Cs}^-(6s6p\ ^3P_J^o)$ state is a shape resonance, rather than a bound state of opposite parity to the $\mathrm{Cs}^-(6s^2\ ^1S_0^e)$ ground state. We have further obtained substantial evidence that the $J = 0$ and $J = 2$ levels are also unbound, although the conclusion for $J = 0$ hinges on earlier calculations of the $^3P_J^o$ fine structure. To this extent, Cs^- can be eliminated as possibly the only known good candidate for a stable atomic negative ion with a second bound state of opposite parity to the ground state [22], thereby resolving a long-standing controversy. With regards to future experimental work, the successful application of photodetachment spectroscopy to the study of low-lying shape resonances in the present work strongly suggests similar investigations in other atomic negative ion systems. For Cs^-, Thumm and Norcross [11] and Bartschat [13,23] have also predicted the existence of a $6p^2\ ^3P_J^e$ state embedded in the continuum, below $\mathrm{Cs}(6p)$. A multiphoton experiment aimed at the first optical observation of these levels might proceed using Raman coupling via the window resonance, ideally using picosecond-duration optical pulses. We finally note that the cesium negative ion is forming the basis of a relatively new tracer in AMS [24], and that knowledge of its excited states is of practical importance.

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