Photodetachment study of B^- ions: The influence of the first excited boron state

P. Kristensen, H. H. Andersen, P. Balling, L. D. Steele,* and T. Andersen
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark
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Measurements of the photodetachment cross section of $B^-(2s^22p^2\ ^3P)$ have been performed in the vicinity of the $B(2s2p^2\ ^4P)$ threshold with photon energies ranging from 3.37 to 4.83 eV. The experimental technique is based on a crossed-ion-laser-beam setup using a dye laser combined with standard nonlinear techniques. The behavior of the cross section above the threshold indicates the presence of the theoretically predicted quasibound $B^-(2s2p^3\ ^3P,^3D)$ states.

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INTRODUCTION

The investigation of photodetachment processes can provide important contributions toward an understanding of the structure of negative ions (see, e.g., Hotop and Lineberger [1] and Bates [2]). As already suggested by Wildt [3], the production and destruction of negative ions in systems such as the cold, dilute plasmas appearing in the outer atmosphere of stars are strongly affected by the properties of these ions. The ability to model, e.g., the opacity of stellar atmospheres is based on detailed information about the structure of the components. However, negative ions also constitute excellent model systems for testing the ability of theoretical calculations to incorporate electron-correlation effects [4,5]. The reduction of the total energy of these weakly bound systems, due to the correlated motion of the electrons, is in some cases as large as the binding energy itself. Although negative ions usually exist only in a single bound configuration, it is known that numerous resonances exist in the detachment cross section originating from short-lived excited states above the first detachment limit (for review article, see the work of Esaulov [6]). These resonances are normally divided into classes according to the process responsible for their decay.

A shape resonance can appear when the one-electron potential produced by the short-range attraction to the neutral core and the centrifugal repulsion together form a barrier sufficiently large to trap an electron behind it. The lifetimes of shape resonances are determined by the probability for the electron to tunnel through the barrier, and thus the shape and strength of the resonances are influenced by the particular form of the potentials. The Feshbach resonance corresponds to a state formed much in the same manner as the ground state of the negative ion, however with the attachment of an electron moving in the field produced by the atom in an excited state. These doubly excited states of the negative ion decay by autodetachment since they are energy degenerate, with continuum states corresponding to a free electron and a lower-excited state of the atom. The strength of the interaction leading to autodetachment, either via the interelectronic Coulomb repulsion or via relativistic terms, determines the lifetime of the state. The analogy between autodetaching and autoionizing states makes it possible to apply the analytical expression derived by Fano [7], describing the shape of the interference structure in the ionization cross section originating from the presence of an autoionizing state.

Experimental studies of Feshbach and shape resonances have been performed for a number of negative ions. A prominent example is the study of resonances in H^- [8–10], in which a series of resonances was revealed by angle tuning a fixed-frequency laser beam to a relativistic H^- beam. Patterson *et al.* [11] have shown that the presence of a resonance, close to the threshold for detachment to an excited state of the neutral atom, will strongly affect the usual Wigner dependence [12] of the photodetachment cross section. This inspired a subsequent study of the energy dependence of the photodetachment cross section by Peterson, Bae, and Huestis [13] and Bae and Peterson [14], resulting in simple analytical expressions for the cross section when a resonance occurs in the vicinity of a threshold. The new analytical expression could account for shape resonances in He^- [13] and Ca^- [14] as well as for resonances in the alkali-metal negative ions located close to the threshold for detachment to the first-excited states of the corresponding neutral systems.

More recently, theoretical investigations by Amusia *et al.* [15] have demonstrated that intershell correlation, which is known to strongly influence the photoionization cross section in some neutral systems (see, e.g., [16]), creates dramatic deviations from the independent-electron picture in the photodetachment cross section of negative ions such as $Si^-(3s^23p^3\ ^4S)$. The calculated photodetachment cross section for Si^- exhibits an interference pattern below the $3s3p^3\ ^5S$ threshold as a consequence of the interaction between the "$3s3p^4$" shape resonance in the unperturbed $3s3p^3\ ^5S+\varepsilon p$ continuum and the $3s^23p^2\ ^3P+\varepsilon s,\varepsilon d$ continua. The interaction between the two continua implies significant correlation between the outer $3s$ and $3p$ electrons. The interference resonance is of autodetaching character since it is located below the corresponding $3s3p^3\ ^5S$ threshold, thus prohibiting decay by tunneling. A thorough theoretical investigation of the reported interference structure and analogous structures in C^- and Ge^- was later performed by Gribakin *et al.* [17] and Ivanov and Krukovskaya [18]. Experimental studies by Balling *et al.* [19] have confirmed the existence of the interference structure in Si^-. The measured cross section, in a photon-energy region covering the pre-

*Also at McMaster University, Hamilton, Ontario, Canada L8S 4M1.

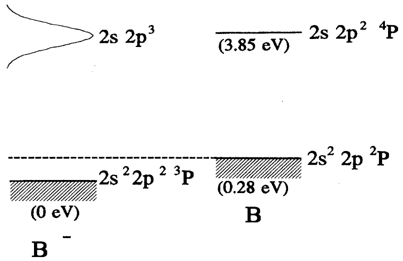

FIG. 1. Simplified energy-level diagram of B^- and the relevant energy levels of B.

dicted interference pattern, displayed a deep window resonance, in accordance with the calculation. The actual position of the resonance was, however, ~0.5 eV above the predicted position.

The aim of the present experimental study is to investigate whether the photodetachment cross section of other negative ions with an open outer p shell, specifically B^-, exhibits interference structures similar to those identified in Si^-, thus signifying the importance of intershell correlation. A schematic energy-level diagram of B^- is shown in Fig. 1. The electron affinity of B was measured by Feigerle, Herman, and Lineberger [20], whereas the energy difference between ground state of B and $B(2s2p^2\ {}^4P)$ is based on an isoelectronic extrapolation by Edlén *et al.* [21]. A theoretical investigation of the photodetachment cross section for B^- has recently been made by Ivanov, Andersen, and Ipatov [22], who performed many-body calculations in the framework of the spin-polarized random-phase approximation with exchange (SPRPAE). In that work, the spin-polarized version of the Hartree-Fock approximation was used as a first approximation to construct the initial wave function of the $B^-(2s^22p^2\ {}^3P)$ ground state and by additionally applying the frozen-core approximation also to construct the final states of the detachment processes. Photodetachment of $B^-(2s^22p^2\ {}^3P)$ proceeds from the outer $2p$ shell via the three channels

$$B^-(2s^22p^2\ {}^3P)+\hbar\omega\rightarrow B(2s^22p\ {}^2P) + \varepsilon s[{}^3P] \quad \text{or} \quad \varepsilon d[{}^3P,{}^3D]$$

when the photon energy exceeds the electron affinity (0.28 eV). Excitation of the $2s$ electron, leading to quasidiscrete $2s2p^3({}^3S,{}^3P,{}^3D)$ shape resonances in the unperturbed $2s2p^2\ {}^4P+\varepsilon p$ continuum, becomes possible at higher photon energies (greater than 3.85 eV). The transitions to the ${}^3P$ and ${}^3D$ resonances may interfere with the corresponding transitions of the $2p$ electrons into continuum. According to the theoretical predictions [22], this interference may manifest itself as a window resonance, similar to the window resonance predicted and observed in Si^-. The window resonance should appear just below the calculated $B(2s2p^2\ {}^4P)$ threshold.

The validity of the theoretical calculations can be estimated since experimental cross sections have very recently been reported at $\hbar\omega=1.871$ and 2.77 eV by Lee *et al.* [23]. The experimental and predicted total cross sections [22] were in agreement within the experimental error of 15%. However, it should be noted that the performed calculations overestimate the electron affinity of the B^- ground state by 0.5 eV and the energy of the $B(2s2p^2\ {}^4P)$ state by 0.7 eV. In spite of this deficiency in the calculations, it was assumed that the applied spin-polarized random-phase approximation with the exchange method would give a qualitatively good description of the B^- photodetachment cross sections, such as the existence of the window interference structure in the vicinity of the excited $B(2s2p^2\ {}^4P)$ state. The SPRPAE method, however, was developed to deal with atoms and ions with filled or half-filled subshells. Thus the B^- ion represents a system that is inherently much more difficult to describe with this method, and it is complicated by the large number of decay channels.

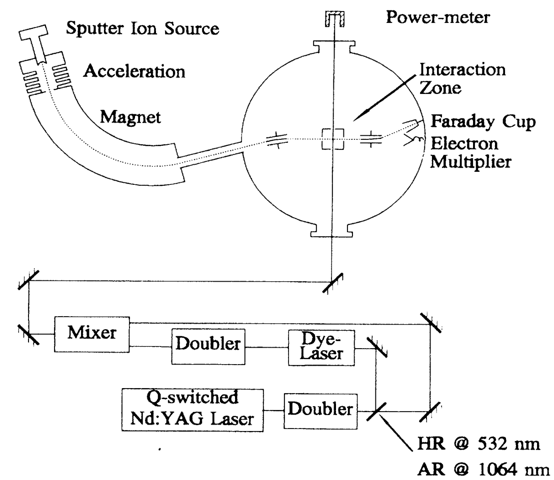

FIG. 2. Schematic diagram of the experimental setup. After acceleration and mass selection the ions are crossed at 90° with the laser beam. The uv wavelength is created using standard nonlinear techniques. The detached neutral atoms are separated from the ion beam by electrostatic deflection and are detected using an electron multiplier.

EXPERIMENTAL APPROACH

The experiment was based on a perpendicularly crossed ion- and laser-beam setup (see Fig. 2). An ion beam of $B^-(2s^22p^2\ {}^3P)$ was created by extracting ions produced in an Aarhus negative ion source [24], using a cathode containing a mixture of 50% Al and 50% B and accelerating the ions through 10 kV. Following a mass- and charge-state separation achieved by magnetic analysis, the beam was electrostatically deflected through 15° just prior to the interaction region. This deflection removed the B atoms formed from B^- ions as a result of collisions with the residual gas. A second set of deflection plates, positioned after the interaction with the pulsed-laser beam, facilitated detection of the different charge-state components of the beam. A discrete dynode electron multiplier with a large dynamic range was used for detection of the detached neutrals. Thus the analog signal from this detector, integrated in a fixed time window after the laser pulse, was proportional to the number of the neutral atoms created by the interaction with the laser light. The collisionally induced background was reduced by operating at a pressure of typically 10^{-8} Torr and by making use of the time-gated detection scheme. The typical ion currents of 1–2 nA for $^{10}B^-$ and 3–6 nA for $^{11}B^-$ were measured by a Faraday cup. Although the ratio between the ion current of $^{10}B^-$ and $^{11}B^-$ was in accordance with the natural abundance ratio, we performed the measurements with the weaker $^{10}B^-$ isotope to avoid possible contamination of the ion beam from the molecular $^{10}BH^-$ ion.

The laser system consisted of a dye laser pumped by the second harmonic of a 10-ns Q-switched Nd:YAG laser (where YAG denotes yttrium aluminum garnet) with a repetition rate of 10 Hz. The desired photon-energy range (3.37–4.83 eV) was obtained by using seven different dyes (Rhodamine 560, 590, 610, and 640, DCM, LDS 698, and 750) combined with frequency doubling of the output from the dye laser in a potassium dihydrogen phosphate (KDP) crystal. To create the highest photon energies, the uv laser beam was sum frequency mixed with the fundamental infrared laser beam in a second KDP crystal (the residual ir light from the initial second-harmonic generation). Accurate intensity control of the laser beam was established without disturbing the spatial profile by employing a combination of a Soleil Babinet compensator (to rotate the polarization continuously) and a Glan-Thompson polarizer. The average pulse energy of the laser beam was determined with a power meter immediately after the UHV chamber. The size of the ion beam (less than 3 mm in diameter) and the laser beam (approximately 5 mm in diameter) was defined by apertures that also ensured that the two beams were overlapping.

The photodetachment cross section was obtained by measuring the neutral-atom production in the photon-energy range from 3.37 to 4.83 eV. The ability to reproduce the data was checked by recording several scans for each of the different dyes. Each data point, which corresponds to the average neutral-atom production during several hundred laser pulses, was normalized to the average laser-pulse power and ion-beam current. The assumption that the neutral-atom production is proportional to the cross section is only correct assuming that the laser intensity is low enough and the interaction short enough to avoid depletion saturation of the ion beam [25]. The occurrence of depletion saturation was avoided by recording the laser-pulse-energy dependence of the neutral-atom yield at several different photon energies and only recording data for the cross-section measurements within the linear regime. The dyes were chosen so that the photon-energy intervals covered by the individual dyes were overlapping each other in a few data points. The neutral-atom signal obtained with different dyes was then scaled in order to minimize the root-mean-square deviation of data points at coinciding photon energies, thus eliminating any effect of the changing laser-beam intensity profile when changing dye. Within each photon-energy region, corresponding to a specific dye, additional changes in the direction of the laser beam, and hence changes in the ion-beam laser overlap, could appear when the photon energy was varied. This originates from the dispersing Pellin-Broca prism used for separation of the different harmonics. The prism was rotated to compensate for the change in direction, so that the laser beam was positioned at a specific point, within 1 mm on a screen placed 3 m after the interaction region.

Measurements of absolute cross sections are normally associated with difficulties since they involve accurate determination of the detection efficiency, the spatial and temporal profile of both laser and ion beam, and, in addition, the extension of the interaction volume. Hotop and Lineberger [25] and later Balling *et al.* [26] circumvented the problem of determining the detection efficiencies. This was achieved by studying the intensity dependence of the yield of neutral atoms, since the transition from a linear dependence to the saturated regime depends critically on the size of the cross section. A different approach has been explored by Pegg *et al.* [27]. The concept of this method is to extract the absolute cross section by measuring the yield of one of the detachment products, either photoelectrons or neutral atoms, relative to the yield from a reference species, for which the photodetachment cross section is known. Although the method avoids the problems associated with a determination of the intensity of the interacting beam and the interaction volume, it relies on the assumption that well collimated ion beams of two different species can be passed through the laser beam in an identical manner. By using this ratio method, the yield of neutral B atoms was measured relative to that of neutral O atoms in order to calibrate the absolute scale of the cross section.

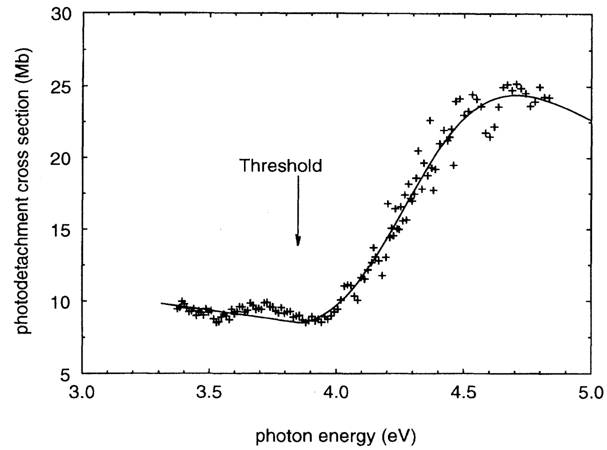

FIG. 3. Data points show the measured photodetachment cross section of B^-. The scale of the cross section is made absolute by measuring the cross section relative to that of O^- at a photon energy of 3.402 eV. The solid line represents a fit to a modified Wigner law (see the text).

RESULTS AND DISCUSSION

The present experiment comprises measurements of the neutral-atom production in the energy range from 3.37 to 4.83 eV, as presented in Fig. 3. The scale of the cross section was made absolute at a photon energy of 3.402 eV by measuring the neutral-atom production from a B^- ion beam relative to that from an O^- ion beam. Measurements of the cross section of O^- have previously been reported by Branscomb, Smith, and Tisone [28] in the energy region from 1.47 to 4 eV. Although the O^- measurements extend up to 4 eV, it seems reasonable to perform the calibration at a somewhat lower photon energy since it was pointed out [28] that difficulties appeared above 3.7 eV in connection with the calibration of the apparatus. The ratio $\sigma(B^-)/\sigma(O^-)$ was determined to be 1.51 ± 0.03 when correcting for the different beam velocities. The uncertainty represents one standard deviation from the mean value, obtained by measuring the ratio several times, and it is primarily caused by the difficulties associated with the overlap between the ion and the laser beam. Multiplication of this ratio with the previously measured cross section $\sigma(O^-) = 6.3$ Mb gives a cross section of $\sigma(B^-) = 9.6 \pm 0.2$ Mb at a photon energy of 3.402 eV. Including the uncertainty on the $\sigma(O^-)$ value, our absolute data are estimated to have an accuracy better than 10%.

The main features of the measured cross section in Fig. 3 are a decrease in the cross section just below the B $(2s2p^2\ {}^4P)$ threshold followed by a large increase above the threshold. There are some small deviations from the linear slope below the threshold most pronounced near approximately 3.7 eV. Considering the cross section above threshold, the data can only be represented by the Wigner threshold law $\sigma \propto (\hbar\omega - \hbar\omega_{\text{th}})^{l+1/2}$ in a limited region (less than 0.25 eV). In this context σ is the cross section, $\hbar\omega$ the photon energy, $\hbar\omega_{\text{th}}$ the threshold energy, and l the angular momentum of the photoelectron. The deviation from Wigner's threshold law is not surprising since the law was derived under the assumption of low photoelectron energy. Previous experiments [29,30] have shown that the Wigner law is a valid description of the cross section in a small energy region typically less than 0.1 eV above the threshold. However, it has also been reported for He^- [13] and Ca^- [14] that the presence of shape resonances was responsible for the deviation from the Wigner threshold law. In both cases, it was found that the measured cross sections were well represented by the analytical expression

$$\sigma \propto \frac{(\hbar\omega - \hbar\omega_{\text{th}})^{l+1/2}}{(\hbar\omega - \hbar\omega_{\text{res}})^2 + (\Gamma/2)^2},$$

which is just the Wigner law multiplied by a Lorentzian profile. $\hbar\omega_{\text{res}}$ and Γ are the resonance position and width. The present data above the threshold are well represented by this modified threshold law, as seen from Fig. 3, in spite of the fact that the modified Wigner law is used over a rather large energy region (3.85–4.83 eV). The position and full width at half maximum of the resonance were determined to be 4.31 and 1.16 eV, with the maximum cross section of 24 Mb appearing at a photon energy of 4.7 eV.

According to the theoretical prediction [22] the behavior of the cross section in the vicinity of the threshold is primarily determined by the presence of the two quasidiscrete $B^-(2s2p^3[{}^3P, {}^3D)$ states. In the independent-electron model these resonances correspond to shape resonances in the two continua, but taking correlations into account, the $B^-(2s2p^3\ {}^3D)$ state would manifest itself as a window interference structure located below the calculated threshold, whereas the $B^-(2s2p^3\ {}^3P)$ state would appear as a shape resonance above the calculated threshold. The measured cross sections, however, do not display the predicted interference pattern. During the process of preparing this paper we were informed about elaborate R-matrix calculations presented by Bell and Ramsbottom [31]. These R-matrix calculations appear to be in very good agreement with the measured cross sections.

SUMMARY AND FUTURE PERSPECTIVES

The experiment comprises absolute measurements of the B^- photodetachment cross section in the photon energy interval from 3.37 to 4.83 eV. The measured cross sections are not in accordance with the original theoretical predictions based on the SPRPAE method, whereas very recent R-matrix calculations appear to reproduce the data very satisfactory.

A very accurate R-matrix calculation utilizing a large basis set has also been reported by Ramsbottom, Bell, and Berrington [32] for the photodetachment cross section of C^-. This calculation confirms previous calculations by Gribakin *et al.* [17] concerning the existence of a strong resonance behavior in the vicinity of the $C(2s2p^3\ {}^5S)$ threshold. However, the position and width of the resonance as calculated in the framework of R-matrix theory [32] differ markedly from the values obtained with the calculation based on SPRPAE [17]. Experimental studies of the photodetachment cross section of C^- are needed to guide the theoretical calculations and may also lead to a better understanding of the discrepancies observed in the present work between the experimental data and theoretical predictions.

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