Negative Ion of Boron: An Experimental Study of the ^3P Ground State

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An investigation of the $B^-(2p^2\,^3P_J) \rightarrow B(2p\,^2P_{J'})$ photodetachment thresholds using a tunable infrared laser source has yielded a substantially improved value for the electron affinity of boron and the first experimental data on the fine structure of the ionic ground state. The $J = 0-1$ and $J = 1-2$ splittings are found to be 3.23(15) cm^{-1} and 5.18(15) cm^{-1}, respectively, and the electron affinity is determined to be 2256.12(20) cm^{-1} [(279.723(25) meV]. The present result for the electron affinity is the first to challenge the extensive and controversial theoretical studies of this system. [S0031-9007(98)05630-0]

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Present day high-performance computers enable sophisticated *ab initio* calculations of increasingly complex systems with unprecedented precision. Within the realm of atomic physics, negative ions are currently a subject of intensive studies (for recent reviews see Ref. [1]). In general, the fundamental interest in negative ions is motivated by a number of features which are qualitatively different from neutral or positively charged systems; short range interactions lead to a finite number of bound states, and strong electron correlations give rise to correlation energies which are often larger than or comparable to the binding energies in these systems. New experimental techniques now allow the determination of binding energies, fine structure, and excited states in a number of negative ion systems with very high accuracy [2]. The interplay of high-resolution experiments on negative ions and state-of-the-art theoretical calculations provides an important platform for advances in atomic physics. Finally, in terms of applications, negative ions play a role in a variety of atomic and plasma phenomena, as well as in some advanced experimental techniques (e.g., accelerator mass spectrometry).

The negative ions of the light elements, hydrogen through fluorine, have been studied extensively. The electron affinities (EA) of H, C, O, and F were measured via tunable laser threshold photodetachment leaving the neutral atom in its ground state [3–6], whereas the binding energies of Li^- [7,8] and the metastable He^- [9] and Be^- [10] ions have been determined through laser photodetachment involving an excited state of the atom and state-selective detection schemes. Accuracies of experimental EA's for these seven elements range from 0.3 meV (C^-) to 0.001 meV (O^-). In strong contrast, the EA of boron still relies on an early laser photodetached electron spectrum recorded by Feigerle *et al.* [11] which resulted in a value of 277(10) meV (after a subsequent recalibration [5]). Various approaches to the *ab initio* calculation of electron affinities of the light elements have been attempted in recent years [12,13], but even these small systems remain challenging as electron correlations play a dominant role. This is particularly true for boron which forms the most weakly bound stable ion among the light elements. Of the numerous theoretical studies of the EA of boron [12–16], three recent works were aiming at accuracies better than 10 meV. Noro *et al.* [13] obtained an EA of 278 meV as the result of a large-basis-set multireference singly and doubly excited configuration-interaction calculation. Large-scale finite element multiconfiguration Hartree-Fock (MCHF) calculations, which do not suffer from basis set limitations, have been performed by two groups, Sundholm and Olsen [14], and Froese Fischer *et al.* [15]. They report EA's of 268.6(17) and 273.2(2) meV, respectively, as the result of an initial valence correlation MCHF calculation that neglects core polarization effects. Sundholm and Olsen estimate core-valence correlations to lower the EA to 267.8(20) meV, whereas Froese Fischer *et al.* predict the EA to increase to 279.5(20) meV through the inclusion of core-valence and core-core correlations (the latter via core rearrangement). However, the experimental EA of 277(10) meV [11] agrees with all of the above values within uncertainties; hence the fundamental question as to the effect and strength of core-valence and core-core correlations in B^- remains open and controversial. The work reported in this Letter is the first experimental investigation aimed at resolving this important issue, and furthermore provides the first experimental values for the fine structure splittings of the $B^-(2p^2\,^3P_J)$ ground state.

An energy level diagram of B^- in the vicinity of the ground and first excited states of boron is shown in Fig. 1. The $B^-(2p^2\,^3P_J)$ ground state is expected to have fine structure levels with splittings estimated from isoelectronic extrapolations of 4(1) cm^{-1} for $J = 0-1$ and 9(1) cm^{-1} for $J = 0-2$ [17]. The ^1D and ^1S terms of $B^-(2p^2)$ are likely unbound; a recent communication on resonance structures in collisionally detached electron spectra of B^- tentatively identified the ^1D term with a resonance located 104(8) meV above the ground state of boron [18]. The latter is a $2p\,^2P_J$ state with a fine structure $J = 1/2-3/2$ splitting of 15.254 cm^{-1}

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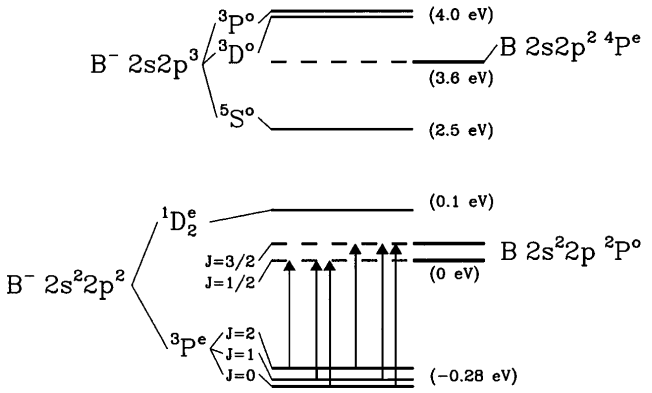

FIG. 1. Schematic energy level diagram of B^- and B. Arrows indicate photodetachment thresholds in order of increasing photon energy. For clarity of presentation, level spacings are not shown to scale. Parity labels on term symbols as shown here are omitted in the text.

[19]. The core excited $2s2p^2$ configuration gives rise to the first excited state of boron, a ^4P_J term which is located 3579(2) meV above the ^2P_J atomic ground state as derived on the basis of isoelectronic extrapolation [20]; as yet no intercombination lines between the doublet and quartet systems have been observed. The EA of the first excited state, i.e., the binding energy of the metastable $2s2p^3\,^5S_2$ negative ion level, was the subject of a recent theoretical study and predicted to be 1072(2) meV [21]. One experimental [22] and two theoretical [23,24] studies of the B^- photodetachment cross section in the vicinity of the ^4P threshold find the ^3P and ^3D terms of the $2s2p^3$ configuration quasibound and responsible for a resonance structure in that energy region. An accurate determination of the ^4P threshold would still be possible if state-selective detection (as in Li^- [7]) and tunable light around 320 nm were employed, and would, in fact, seem to be more convenient than the experimentally challenging infrared photodetachment around the ^2P threshold. Unfortunately, the uncertainty in the ^4P energy would prevent a determination of the EA of boron to a high accuracy. Therefore, our experimental approach involves tunable infrared laser spectroscopy in the 3.8 to 4.5 μm region.

The experimental setup is described in detail elsewhere [25]. Nanosecond laser pulses in the 920–950 nm range were produced with a dye laser, pumped by the second harmonic of a 10 Hz Q-switched Nd:YAG laser. Raman scattering in a high pressure hydrogen cell was employed to convert the dye laser output into tunable infrared radiation via second Stokes generation, with a measured Raman shift of 4155.20(2) cm^{-1}. The infrared pulse energies were $\approx$120 μJ, and the bandwidth was $\approx$0.1 cm^{-1}. Calibrations of the dye laser setup were routinely performed using an optogalvanic cell filled with argon. Second Stokes photon energies were also calibrated directly against well known transitions in N_2O using an absorption cell. A Cs sputter ion source with a cathode prepared from ^{10}B powder provided a 17 keV B^- beam. The ion beam and infrared laser beam were crossed at 90° within an ultrahigh vacuum chamber. At this stage the $^{10}B^-$ current was $\approx$60 nA. Neutral atoms resulting from photodetachment were detected with a discrete dynode electron multiplier.

Numerous infrared laser scans of the ^2P threshold region have been conducted. Figure 2 shows the sum of several scans over the region of 2240–2280 cm^{-1}. Approximately 5000 laser shots were utilized per wave number. Five nested thresholds are evident in Fig. 2, corresponding to the following transitions (from low to high energy): $^3P_2 \rightarrow {}^2P_{1/2}$, $^3P_1 \rightarrow {}^2P_{1/2}$, $^3P_0 \rightarrow {}^2P_{1/2}$, $^3P_2 \rightarrow {}^2P_{3/2}$, and $^3P_1 \rightarrow {}^2P_{3/2}$. It was possible to fit Wigner s-wave thresholds very accurately to the data, and the resulting threshold energies are summarized in Table I. The quoted uncertainties on the values are largely associated with the fits to the nested thresholds but also allow for systematic errors in the calibration and potential Doppler shifts. The sixth and last threshold ($^3P_0 \rightarrow {}^2P_{3/2}$) could not be resolved due to a weak transition strength and the noise in the other detachment signals. Thus, the fit was extrapolated beyond the sixth threshold using its calculated transition strength [26]. The $^3P_0 \rightarrow {}^2P_{1/2}$ threshold provides the EA of B and yields 2256.12(20) cm^{-1} or 279.723(25) meV (with 8.065 541 cm^{-1}/meV [27]). The well-known fine structure splitting of the atomic ground state can be obtained from the difference of the threshold values for the $^3P_2 \rightarrow {}^2P_{1/2,3/2}$ as well as $^3P_1 \rightarrow {}^2P_{1/2,3/2}$ transitions. This leads to values of 15.19(15) and 15.24(20) cm^{-1}, respectively, which are in excellent agreement with the accepted value of 15.254 cm^{-1} [19]. The fine structure splittings of the ion are obtained from the first three thresholds ($^3P_J \rightarrow {}^2P_{1/2}$): 3.23(15) cm^{-1} and 5.18(15) cm^{-1}, respectively, for $J = 0$–1 and $J = 1$–2 [and 8.41(20) cm^{-1} for $J = 0$–2]. A second determination of the $J = 1$–2 splitting of 5.23(20) cm^{-1} is provided by the next two thresholds ($^3P_{2,1} \rightarrow {}^2P_{3/2}$). The respective magnitudes of our threshold signals are in good agreement with theory [26], assuming a statistical population of the ionic levels. The calculated values for the relative strengths of the transitions are shown in Table I, together with the experimental values. The relative photodetachment cross section further above threshold was investigated by scanning the laser over the full tuning range of the dye used (LDS 925). The result of this scan, after correction for variations in the infrared pulse energy, is shown in the inset of Fig. 2. A single Wigner s wave has been fitted to the data (dashed line) as well as an s wave including the leading correction term to the Wigner law (solid line), as derived by Farley [28] on the basis of the zero-core-contribution (ZCC) model of photodetachment [29]. The latter curve fits the data well; hence, the ZCC model seems to be applicable here. In contrast, a limitation of the ZCC model was found in the case of Al^- photodetachment [30,31].

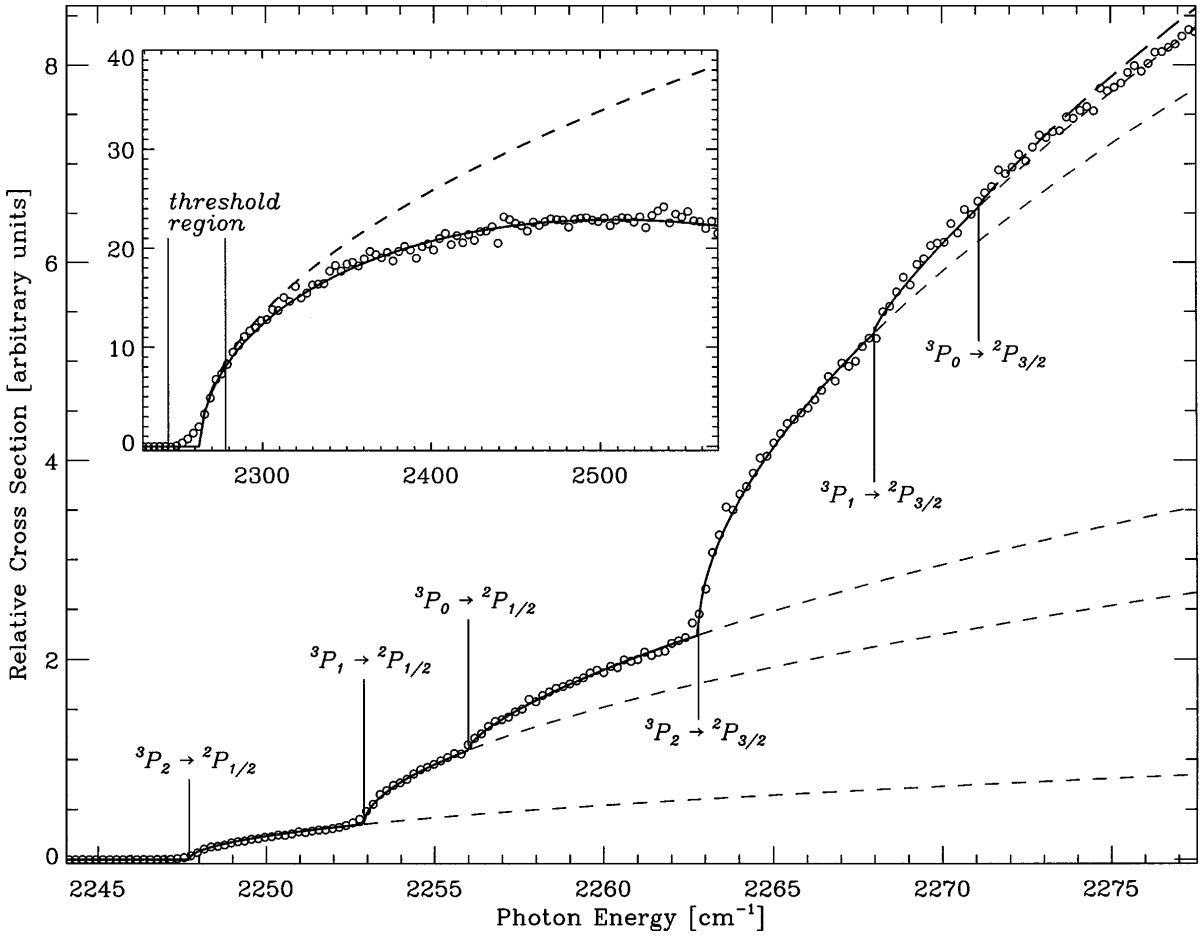

FIG. 2. Photodetachment yield versus laser wavelength. The overall result of a Wigner s-wave fit is indicated by the solid line (and extrapolated with long dashes). Individual thresholds are extrapolated with dashed lines. Inset: Relative photodetachment cross section up to 320 cm^{-1}(15%) above threshold. The dashed line represents a fitted Wigner s wave and the solid line an s wave with leading correction. These two lines define the upper and lower limits of s-wave thresholds within the ZCC model.

The present result for the electron affinity of boron [279.723(25) meV] is in agreement with the earlier measurement of Feigerle *et al.* [11,17] of 277(10) meV, in excellent agreement with the very recent theoretical result of Froese Fischer *et al.* [15] who obtained 279.5(20) meV, but in definite disagreement with the theoretical result of 267.8(20) meV obtained by Sundholm and Olsen [14]. Both theoretical works employ iterations of systematic MCHF calculations with orbital sets of increasing size. Thus, for a given model they are able to obtain the EA as the series limit with an uncertainty due to the necessary extrapolation. But even with an inactive $1s^2$ shell (i.e., valence correlation only) a complete active space calculation cannot be sustained to the limit, and some restrictions to the number of active orbitals need to be applied. This problem was handled differently by Sundholm and Olsen, and Froese Fischer *et al.* which seems to be responsible for their different results at this level, 268.6(17) and 273.2(2) meV, respectively. The choice of model restrictions becomes even more important if core polarizations are included through excitations of one of the $1s$ electrons. This was demonstrated by Froese Fischer *et al.* who treated core polarizations with two slightly different models, resulting in EA's of 273.1 and 279.5 meV, respectively (after a relativistic correction of -1.1 meV). Froese Fischer *et al.* consider the second core polarization model which increased the EA by 6.3 meV the more accurate one as it included core-valence correlation to a higher degree and even some core-core correlation via core rearrangement. Nevertheless, they estimated the uncertainty on their final EA value to be 2 meV, mainly due to the

TABLE I. Results of the s-wave fits to the data.

Threshold		Relative strength	
Transition	Energy [cm^{-1}]	Measured	Calculated
$^3P_2 \rightarrow {}^2P_{1/2}$	2247.71(15)	4.0(4)	5
$^3P_1 \rightarrow {}^2P_{1/2}$	2252.89(15)	8.6(6)	9
$^3P_0 \rightarrow {}^2P_{1/2}$	2256.12(20)	4.2(4)	4
$^3P_2 \rightarrow {}^2P_{3/2}$	2262.90(15)	27(3)	25
$^3P_1 \rightarrow {}^2P_{3/2}$	2268.13(25)	8(2)	9
$^3P_0 \rightarrow {}^2P_{3/2}$	...	...	2

uncertainty associated with the choice of a particular model. Sundholm and Olsen used yet another core polarization model which lowered the EA by 0.8 meV. It should be noted that the calculated EA's above represent weighted averages over the levels of each term and have to be reduced by 0.56 meV to give the EA of $^3P_0$ relative to $^2P_{1/2}$ (which would be the conventional defi-nition for the EA of B). The final EA of Froese Fischer *et al.* would then be 279(2) meV, a value that is only 0.7 meV lower than our experimental result. Earlier values for the fine structure splittings of B^-, 4(1) and 9(1) cm^{-1} for $J = 0-1$ and $J = 0-2$, respectively, which were based on isoelectronic extrapolations [17], are valid within quoted uncertainties if compared with our experimental values [3.23(15) and 8.41(20) cm^{-1}, respectively]. Unfortunately, Froese Fischer *et al.* perform a full Breit-Pauli calculation of the fine structure only in the context of their valence calculation. This calculation was later refined [32] yielding $B^-(^3P_J)$ splittings of 2.92 and 7.79 cm^{-1} for $J = 0-1$ and $J = 0-2$, respectively. These values are too small in comparison with experiment, but they are expected to increase in a Breit-Pauli calculation that includes core-valence correlations [32]. It is hoped that the present results will stimulate renewed theoretical interest in B^-.

In summary, we have obtained the first experimental values for the fine structure of the $B^-(^3P)$ ground state and have determined the electron affinity of boron with a 400-fold increase in accuracy over the previous experimental value. The new EA is in very good agreement with the most recent calculation [15] and thereby confirms the importance of core-valence and core-core correlation for the accurate treatment of this six-electron system.

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