RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 52, NUMBER 4 OCTOBER 1995

Laser spectroscopy of the Be^- ion: Binding energies of metastable states

P. Kristensen, V. V. Petrunin,* H. H. Andersen, and T. Andersen
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark
(Received 28 June 1995)

By using a combination of laser photodetachment and resonant ionization spectroscopy, the binding energy of the $1s^22s2p^2\ ^4P$ state in Be^- is determined with much improved accuracy to be 290.99±0.10 meV. This value is considerably larger than the recent measurement of 261±10 meV, but only slightly above the new theoretical value of 289.1±1.0 meV. The transition wavelength of $1s^22s2p^2\ ^4P_{3/2-1s^22p^3\ ^4S_{3/2}}$ is determined by laser excitation to be at 2653.18±0.08 Å, yielding the binding energy of the $1s^22p^3\ ^4S$ state in Be^- to be 295.49±0.25 meV, in good agreement with the newest theoretical result of 295.0±0.7 meV.

PACS number(s): 32.80.Ge, 31.15.Ar

We report here binding energies for metastable states in the five-electron Be^- ion. *Ab initio* calculations of electron affinities (EAs) even for small systems have been a challenge for many atomic and molecular codes, and accurate experimental data are urgently needed to test the various approximations used. Theoretical calculations of negative-ion structures are complicated since the electron-electron correlation energy contributions to the EAs are often as large as or even larger than the EAs themselves. Previously, many calculations only took the electron-correlation contributions from the valence shell into account, but the importance of including core-valence and core-core effects is now being accepted, leading to new theoretical results, in much better agreement with experiments than just a few years ago.

According to theoretical calculations [1–8], the Be^- ion possesses the metastable states $1s^22s2p^2\ ^4P$, $1s^22p^3\ ^4S$, and $1s2s2p^3\ ^6S$, but, so far, only the ^4P and ^4S states have been observed experimentally [9–12]. The $J=3/2$ component of the ^4P state has a lifetime [13] of 45±5 μs, which is two orders of magnitude longer than the $J=5/2$ and 1/2 components. The ^4S state decays preferentially by an optically allowed transition to the ^4P state, with a lifetime of 1.25±0.10 ns [11]. The binding energy of the ^4P state was first measured by Kvale *et al.* [10], using autodetached-electron spectroscopy, to be 190±90 meV, but recently Tang *et al.* [12] were able to improve the accuracy of this value by an order of magnitude to 261±10 meV by means of photodetached-electron spectroscopy. Since the $1s^22s2p^2\ ^4P-1s^22p^3\ ^4S$ optical transition had been observed by Gaardsted and Andersen [11] in a beam-foil study at 2653.01±0.09 Å, it was possible [12] to establish that the binding energy for the ^4S state was 4.2±0.2 meV larger for the ^4S state than for the ^4P state, i.e., 265±10 meV. When Tang *et al.* [12] reported their EA value for the Be $(2s2p\ ^3P)$ state, it was considered to be in agreement with the best available theoretical calculation, performed by Bunge [5], yielding the EA of 276.1±6.5 meV. However, very recently, Olsen, Pettersson, and Sundholm [7] and Hsu and Chung [8] have reported new theoretical values based on extensive calculations, with careful treatment of the core-core and core-valence effects, yielding the electron affinity of the Be$(2s2p\ ^3P)$ state to be 285±5 meV [7] and 289.1 ±1.0 meV [8], respectively. These predictions [7,8] clearly disagree with the experimental value of Tang *et al.* [12].

We have utilized the very sensitive collinear resonance ionization spectroscopy method [14] to obtain the EA $(2s2p\ ^3P)$ value with a high accuracy. The EA$(2s2p\ ^3P)$ measurement has been combined with a laser-photoabsorption measurement of the $Be^-(^4P\text{-}^4S)$ transition wavelength to obtain the EA value for the Be$(2p^2\ ^3P)$ state. The EA$(2s2p\ ^3P)$ value was determined using the same equipment as recently applied [15] to determine the EA values for the Ba$(6s^2\ ^1S)$ ground state. A fast 50-keV beam of mass- and charge-state-analyzed Be^+ ions was charge-exchanged in Na vapor, followed by a charge selection of the Be^- ion. After a flight distance of 60 cm, the $Be^-(^4P_{3/2})$ beam enters the field-free interaction zone where it is overlapped collinearly with two pulsed dye-laser beams. The first laser beam performs detachment of the negative Be^- ion, whereas the second laser beam, which is time-delayed with respect to the detaching beam, probes the produced Be atoms in the Be $(1s^22s3p\ ^3P)$ state, by photoexcitation to the $2s15d\ ^3D$ Rydberg state, followed by field ionization and detection as Be^+ ions. This detection technique is very sensitive and makes it possible to utilize even very weak reaction channels that could not be studied with the conventional detection technique, which relies on neutral-particle detection. In the present study, we have utilized the detachment channel to the $1s^22s3p\ ^3P$ state in neutral beryllium, which is associated with emission of an s electron. Due to Wigner's threshold law [16] for negative ions ($\sigma \propto E^{l+1/2}$, E being the excess electron energy), the opening of a new detachment channel is much more pronounced and easy to detect for $l=0$ electrons than for $l>0$ electrons.

The wavelength experiment was performed in a crossed laser–negative-ion-beam apparatus. The $Be^-(^4P_{3/2})$ ion beam, produced as described above, was crossed perpendicularly by a pulsed laser beam. The generated neutral beryllium atoms were monitored as a function of the laser wavelength by an electron multiplier. The laser system used for both experiments consisted of 10-ns dye lasers pumped by the second harmonic of the Q-switched Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, with a repetition rate

*Permanent address: Institute of Spectroscopy, Russian Academy of Sciences, 142092 Toitsk, Moscow Region, Russia.

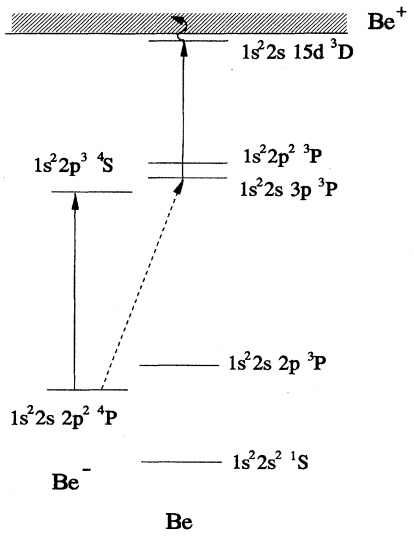

FIG. 1. Schematic energy diagram of Be^- and Be states with the studied detachment and excitation channels indicated; see text.

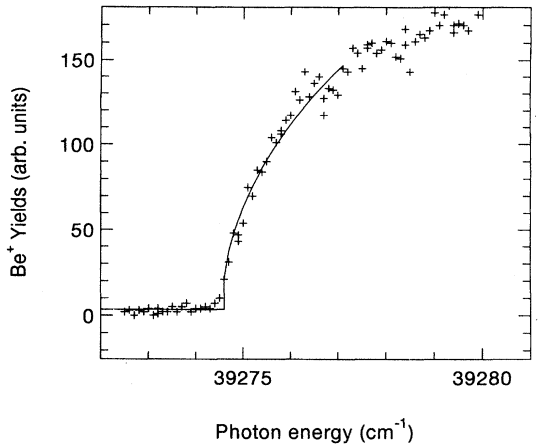

FIG. 2. Be^+ yield following the photodetachment of the $Be^-(1s^2 2s 2p^2\ ^4P_{3/2})$ component to the $Be(1s^2 2s 3p\ ^3P)$ state, which is subsequently monitored by resonance-ionization spectroscopy.

of 10 Hz. To produce the wavelengths in the 2653-Å region, a nonlinear optical technique, based on doubling of the dye-laser radiation followed by mixing with the fundamental ir pulse from the Nd:YAG laser, was applied. The linewidth of the uv light was less than 0.6 cm^{-1}, but the effective linewidth in the wavelength experiment was larger due to Doppler broadening resulting from imperfect perpendicular crossing of the laser and the ion beam. With a 1° divergence, the broadening is ~2 cm^{-1}, which is a representative value for the present experiment.

Figure 1 schematically illustrates the experiments performed, with the dotted line representing the photodetachment channel, while the solid lines represent the excitation processes: (i) the $^4P_{3/2}$-$^4S_{3/2}$ transition in the Be^- ion and (ii) the $1s^2 2s 3p\ ^3P$–$1s^2 2s 15d\ ^3D$ transition in the neutral beryllium atom, with the latter state subsequently being field-ionized, leading to Be^+.

Figure 2 shows the photodetachment cross section in the vicinity of the $Be(1s^2 2s 3p\ ^3P)$ threshold. The opening of a new reaction channel with the emission of an s electron can easily be identified. The observed threshold at 39 274.6 cm^{-1} can be attributed to the opening of the $Be^-(^4P_{3/2}) \rightarrow Be(1s^2 2s 3p\ ^3P)$ channel. The threshold value yields an EA value of 290.74±0.10 meV for the Be $(1s^2 2s 2p\ ^3P_0)$ level. The EA value for the ^3P state can be obtained taking the fine-structure splittings for the Be $(1s^2 2s 2p\ ^3P)$ state into account, together with the calculated fine-structure splitting for the $Be^-(^4P)$ state [8]. The final EA value for $Be(2s 2p\ ^3P)$ is then 290.99±0.10 meV. This value is considerably larger than the experimental value (261± 10 meV) reported by Tang *et al.* [12], and its accuracy is improved by two orders of magnitude. The obtained accuracy also allows a critical comparison with the newest theoretical values [5,7,8]. It is clearly outside the range given by Bunge (276.1± 6.5) [5], but also larger than values reported by Olsen, Pettersson, and Sundholm (285± 5 meV) [7] and Hsu and Chung (289.1± 1.0 meV) [8]. The latter may be considered the best theoretical value today, but small contributions of the order of ~2 meV are still missing from that calculation, which was performed using the method of full-core-plus-correlation (FCPC) and restricted variation. A comparison of the electron affinity for the Be $(1s^2 2s 2p\ ^3P)$ state is given in Table I for different approaches.

Figure 3 shows the production of neutral beryllium atoms as a function of the wavelength of the photons in the region around 2653 Å. The $1s^2 2s 2p^2\ ^4P_{3/2} \rightarrow 1s^2 2p^3\ ^4S_{3/2}$ transition appears as an enhancement in the neutral-atom production. This production is, away from the transition wavelength, due to direct photodetachment. The enhanced production of neutral atoms at the transition wavelength may appear somewhat surprising since similar "window resonances" in, e.g., Rb^- (Ref. [17]) lead to a near-complete cancellation in the neutral-atom production. However, there is a significant difference between the Be^- ion and the Rb^- ion at the window resonance. The excited $Rb^-(5p_{1/2} 6s)$ state mainly decays via autodetachment to the

TABLE I. Electron affinities for neutral-beryllium states and transition wavelengths for the Be^- ion.

EA($2s2p\ ^3P$) (meV)	EA($2p^2\ ^3P$) (meV)	Wavelength (Å) $2s2p^2\ ^4P$-$2p^3\ ^4S$	Reference
	Theory		
240±100			1
285	262	2638	3
217±57	220±41	2654	4
276.1±6.5			5
		2653.2	6
285±5	286±5	2650.4±2.8	7
289.1±1.0	295.0±0.7	2653.70±0.68	8
	Experiment		
195±90			10
		2653.01±0.09	11
261±10	265±10		12
290.99±0.10	295.49±0.25	2653.18±0.08	This work

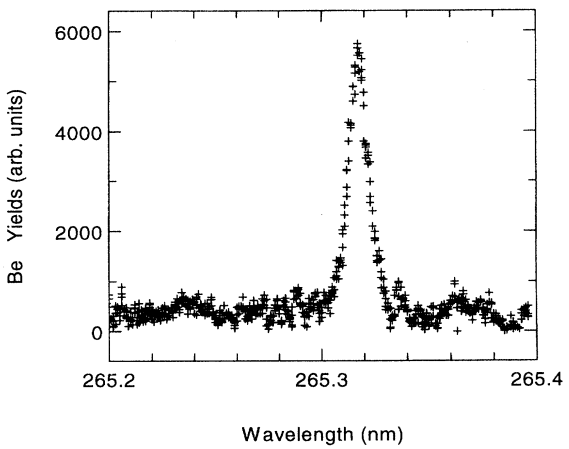

FIG. 3. Production of neutral Be atoms versus laser wavelength.

Rb $5s$ ground state, and thereby strongly interferes with the direct photodetachment channel responsible for the neutral-atom production. For Be^-, the excited $^4S_{3/2}$ level will decay via optical emission to all three J levels belonging to the ^4P state. The $J=5/2$ and 1/2 levels will subsequently autodetach to the neutral-beryllium ground state, with a lifetime of the order of 0.25 μs [13]. The transition wavelength was determined to be at 2653.18±0.08 Å (in air), with the main part of the uncertainty being due to uncertainty in the perpendicular overlap of the laser and the ion beam. This wavelength is in agreement with the previous beam-foil result (2653.01±0.09 Å) [11] within the quoted errors. The new transition wavelength can be combined with the known energies of the Be($1s^2 2s2p\ ^3P$) and Be($1s^2 2p^2\ ^3P$) states to yield the EA value for the latter to be 4.50±0.15 meV larger than the EA value for the former Be state. Combined with the directly determined EA value for the $1s^2 2s2p\ ^3P$ state, we obtain 295.70±0.25 meV for EA($1s^2 2p^2\ ^3P$). Hsu and Chung [8] have reported a theoretical value of 295.0±0.7 meV for this EA value. A comparison of the EA for Be ($1s^2 2p^2\ ^3P$) and for the transition wavelength is also included in Table I for different approaches.

In summary, resonance-ionization spectroscopy allows the determination of accurate binding energies for negative ions since the sensitivity of the method makes it possible to always rely on s-electron thresholds. By means of EA values obtained by this method, it will be possible to test and guide the present development of methods for calculating electron affinities. Very recently, multiconfiguration Hartree-Fock calculations of the EA of boron were performed [18], yielding 279.5±2.0 meV for the ground state, but the best available experimental value (277±10 meV) [19] is not capable of matching the theoretical accuracy for this six-electron system. The resonance-ionization method may also be able to shed new light on the Ca^- ion, which has attracted so much interest from experimentalists [20] and theorists [21], but which still may be considered a challenge to both groups due to the lack of precise EA values for the Ca ground state. Experiments are now in progress at this Institute to obtain such values.

This work is part of the research program of the Aarhus Center for Advanced Physics (ACAP), which is funded by the Danish National Research Foundation.

[1] A. W. Weiss, Phys. Rev. A **166**, 70 (1968).
[2] D. R. Beck, C. A. Nicolaides, and G. Aspromallis, Phys. Rev. A **24**, 3252 (1981).
[3] C. F. Bunge, M. Galán, R. Jáuregui, and A. V. Bunge, Nucl. Instrum. Methods **202**, 299 (1982).
[4] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. Symp. **18**, 467 (1984).
[5] A. V. Bunge, Phys. Rev. A **33**, 82 (1986).
[6] C. Froese Fischer, Phys. Rev. A **41**, 3481 (1990).
[7] J. Olsen, L. G. M. Pettersson, and D. Sundholm, J. Phys. B **27**, 5575 (1994).
[8] J-J. Hsu and K. T. Chung, Phys. Rev. A **52**, R898 (1995).
[9] Y. K. Bae and J. R. Peterson, Phys. Rev. A **30**, 2145 (1984).
[10] T. J. Kvale, G. D. Alton, R. N. Compton, D. J. Pegg, and J. S. Thompson, Phys. Rev. Lett. **55**, 484 (1985).
[11] J. O. Gaardsted and T. Andersen, J. Phys. B **22**, L51 (1989).
[12] C. Y. Tang, J. R. Wood, D. J. Pegg, J. Dellwo, and G. D. Alton, Phys. Rev. A **48**, 1983 (1993).
[13] P. Balling, L. H. Andersen, T. Andersen, H. K. Haugen, P. Hvelplund, and K. Taulbjerg, Phys. Rev. Lett. **69**, 1042 (1992).
[14] S. A. Aseyev, Yu.A. Kudryatsev, V. S. Letokhov, and V. V. Petrunin, Opt. Lett. **16**, 514 (1991), and references therein.
[15] V. V. Petrunin, J. D. Voldstad, P. Balling, P. Kristensen, T. Andersen, and H. K. Haugen, Phys. Rev. Lett. **75**, 1911 (1995).
[16] E.P. Wigner, Phys. Rev. **73**, 1002 (1948).
[17] See, e.g., H. Stapelfeldt, P. Kristensen, U. Ljungblad, T. Andersen, and H. K. Haugen, Phys. Rev. A **50**, 1618 (1994), and references therein.
[18] C. Froese Fischer, A. Ynnerman, and G. Gaigalas, Phys. Rev. A **51**, 4611 (1995).
[19] C. S. Feigerle, R. R. Cordermann, and W. C. Lineberger, J. Chem. Phys. **74**, 1513 (1981).
[20] C. W. Walter and J. R. Peterson, Phys. Rev. Lett. **68**, 2281 (1992); K. W. McLaughlin and D. W. Duquette, *ibid.* **72**, 1176 (1994), and references therein.
[21] See, e.g., H. van der Hart, C. Laughlin, and J. E. Hansen, Phys. Rev. Lett. **71**, 1506 (1993); D. Sundholm and J. Olsen, Chem. Phys. Lett. **217**, 451 (1994), and references therein.