Photodetachment and autodetachment of the Be^- ion

C. Y. Tang, J. R. Wood, and D. J. Pegg*
Department of Physics, University of Tennessee, Knoxville, Tennessee 37996

J. Dellwo and G. D. Alton
Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
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The metastable Be anion has been experimentally investigated using a crossed laser–negative-ion-beam apparatus. The Be($2\,^3P$) electron affinity of 261 ± 10 meV has been determined by photodetached-electron spectroscopy. It is also demonstrated that the Be($2\,^3P$) excitation energy of 2.723 ± 0.007 eV can be determined by means of a hybrid technique involving the use of both autodetached- and photodetached-electron spectroscopies.

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We present the results of an experimental investigation of the metastable Be anion using a crossed laser–negative-ion-beam apparatus. The electron affinity and excitation energy of the Be($2\,^3P$) state have been measured by the use of the techniques of photodetached-electron spectroscopy (PES) and autodetached- and photodetached-electron spectroscopy (APES), respectively.

The Be^- ion was first observed over two decades ago by Bethge, Heinicke, and Baumann [1] in mass spectra of ions extracted from a negative-ion source. Subsequently, a theoretical investigation of the structure of this ion was made by Weiss [2]. It was demonstrated that although the ion is not stable, an extra electron can be attached to the Be atom in the metastable $(2s2p)^3P$ state to form a long-lived Be^- ion in the spin-aligned $(2s2p^2)^4P$ state. Weiss predicted that the electron affinity of the parent Be($2\,^3P$) atom would be about 240 meV. The $2\,^4P$ state in Be^- is relatively long lived as a result of being metastable against Coulomb autodetachment. Eventually the ion autodetaches via the weaker magnetic interactions. A partial energy-level diagram of the Be and Be^- systems and the relevant transitions is shown in Fig. 1. There exists a differential metastability among the three fine-structure levels of the $2\,^4P$ state since each couples with a different strength to the continuum. Calculations of these level lifetimes [3–5] and the fine-structure intervals [6] were subsequently made. The first experimental investigation of the lifetimes of levels associated with the $2\,^4P$ state was made by Bae and Peterson [7] via autodetachment measurements. Accurate lifetimes of these levels have been recently reported by Balling *et al.* [8]. The $J=\frac{3}{2}$ level was found to be 180 times longer lived than the $J=\frac{1}{2},\frac{5}{2}$ levels. Since the early work of Weiss, there have been several other theoretical estimates [6,9,10] of the electron affinity of Be($2\,^3P$). Currently the most accurate calculation, that of Bunge [10], yields a value of 276.1 ± 6.5 meV. There has only been one previous measurement of this quantity. Kvale *et al.* [11] used autodetached-electron spectroscopy (AES) to obtain a value of 195 ± 90 meV. The large uncertainty on this result is primarily associated with the measurement of the ion-beam energy. In the present work this uncertainty has been significantly reduced by the use of PES. The measured value is now sufficiently accurate to meaningfully test the calculation of Bunge [10].

A crossed-beam apparatus [12] has been used to study the spectra of photoelectrons detached from beams of negative ions. Be^+ and other ions (He^+, Li^+, B^+, etc.) were first produced in a hot cathode ion source. After being extracted, accelerated, and mass selected by a 90° bending magnet, the Be^+ beam was passed through a Li vapor charge-exchange cell situated approximately 1 m upstream of the interaction region. Sequential electron-capture collisions in the cell produced a secondary beam

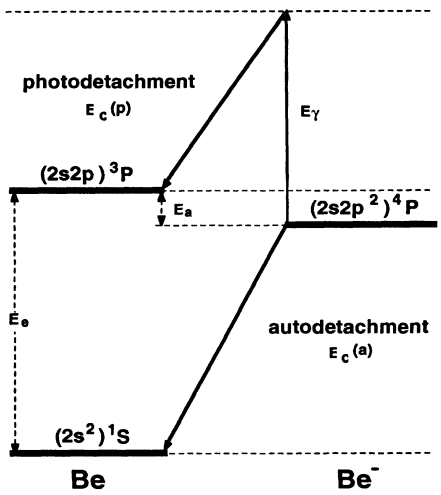

FIG. 1. Partial energy-level diagram for the Be and Be^- systems showing photodetachment via the $2\,^3P\varepsilon s,d$ channels and autodetachment via the $2\,^1S\varepsilon s,d$ channels. The ion-frame energies of the photodetached and autodetached electrons are represented by $E_c(p)$ and $E_c(a)$, respectively.

of negative ions following charge-state analysis. The ion beam is defined by two apertures of diameters 1.5 and 2.0 mm separated by 85 mm. Between the apertures the ion beam was crossed perpendicularly by a beam of linearly polarized photons from a flashlamp-pumped dye laser. The interaction region was situated approximately 15 mm upstream of the entrance aperture of a spherical-sector electrostatic electron-energy analyzer equipped with a channel electron-multiplier detector. Photoelectrons ejected from the interaction region in the direction of motion of the ion beam were collected and energy analyzed to produce the spectra. Backward-ejected photoelectrons (in the ion's frame) were not measured because of much lower signal-collection efficiency and much higher background rate in the low-energy region. The centroids of the spectral peaks were determined by fitting to symmetric Gaussian functions. The photoelectron signal was normalized to the ion-beam intensity and laser output power in order to correct for beam fluctuations. The signal-to-background ratio was enhanced by employing a gated detection scheme synchronized to the laser pulses.

The photodetachment of Be^- was performed via the $2\,^3P\varepsilon s,d$ channels. If the ion-frame energy of the detached electrons, E_c, can be measured for a known value of the photon energy E_γ, the electron affinity E_a, can then be determined from the energy-balance equation, in this case, $E_a = E_\gamma - E_c$ (see Fig. 1). The photon energy was determined by the use of a wavelength-calibrated spectrometer. In the present experiment a fixed photon energy of $E_\gamma = 2.075 \pm 0.002$ eV was used. The measurement of the electron energy E_c is complicated by the fact that, in the present experiment, the electrons are detached from a beam of ions that move with large and essentially unidirectional velocities. Kinematic corrections, that depend on the ion-beam energy E_i, must be applied to the measured laboratory-frame electron energy E_L to determine the energy E_c of the electron in the rest frame of the ion. The two electron energies are related, in the case of forward-directed electron spectroscopy, via the kinematic-transformation equation: $\sqrt{E_L} = \sqrt{E_c} + \sqrt{\varepsilon}$. Here ε represents the ion-beam energy reduced by the electron-to-ion mass ratio. In the present work we were able to determine the Be^- ion-beam energy (44.6 keV) to about 1% using an *in situ* analysis of a reference spectrum obtained by photodetaching a beam of He^- ions at the same beam energy and under the same experimental conditions. This spectrum, shown in Fig. 2(a), consists of two peaks that correspond to photodetachment via the $2\,^3S\varepsilon s,d$ and the $2\,^3P\varepsilon p$ channels. In the analysis we have assumed the measured $2\,^3S - 2\,^3P$ energy separation (1.1445 eV) from photon spectroscopy [13] and the calculated [14] electron affinity (77.51 ± 0.04 meV) of $He(2\,^3S)$. The latter value has also been experimentally confirmed [15]. A knowledge of the ion-beam energy allows one to calibrate the electron-energy scale for the Be^- spectrum shown in Fig. 2(b) and perform the transformation from the laboratory to the ion reference frame. As a check of the calibration procedures, we also measured the separations of the peaks in the spectra of Li^- and B^- relative to those in the He^- spectrum taken under identical conditions. The electron affinities of Li (618 ± 16 meV) and B (283 ± 26 meV) that were determined from this measurement are in good agreement with more accurately measured values [16,17]. Environmental effects such as contact and surface potentials can shift the energy of individual peaks in an electron spectrum. However, as indicated by the Li and B electron-affinity results such offsets tend to cancel in measuring peak separations.

From ten independent PES measurements, it is determined that $Be(2\,^3P)$ has an electron affinity of 261 ± 10 meV. Although the standard deviation of the mean of these results is only 2 meV, the quoted error reflects a conservative estimate based on the range of results shown in Fig. 3. The present result, obtained by PES, is compared in Table I to the previous AES measurement and theoretical estimates. The fine-structure transitions were unresolved in this measurement, but most of the ions passing through the interaction region were in the $J = \frac{3}{2}$ level. Autodetachment occurring in the ≈ 2 μs delay between the production and interaction regions substantially depleted the populations of the $J = \frac{1}{2}$ and $\frac{5}{2}$ levels relative to that of the $J = \frac{3}{2}$ level [8]. The present electron-

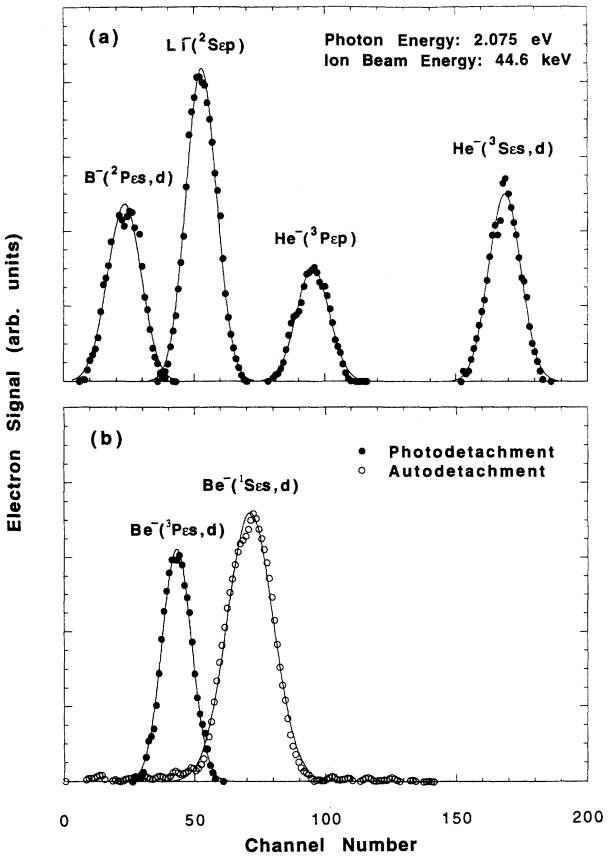

FIG. 2. Electron spectra arising from the detachment of various negative ions. Reference spectra are shown in (a) and the PES and AES of Be^- are shown in (b). The energy per channel is 48.84 ± 0.01 meV.

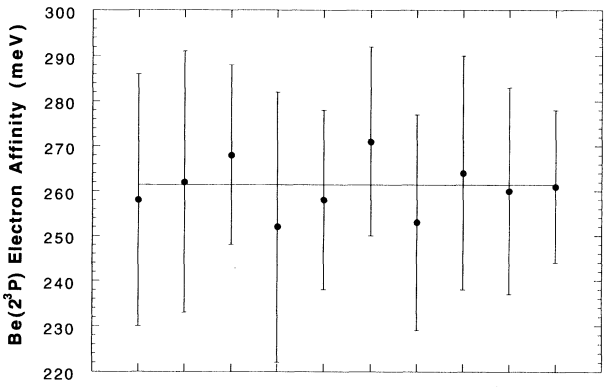

FIG. 3. Scatter plot of Be($2\,^3P$) electron-affinity measurements by PES. The horizontal line represents the weighted least-squares fit to the data.

affinity result for Be is somewhat lower than the currently accepted theoretical value [10] although there is agreement within the overlapping error limits. Gaardsted and Anderson [18] have observed a radiative transition between the $(2p^3)^4S$ and $(2s2p^2)^4P$ states of Be^-. From this measurement they were able to predict that the difference in the electron affinities of Be in the $(2p^2)^3P$ and $(2s2p)^3P$ states is 4.2 meV. Combining this result with the present measurement of the electron affinity of the $(2s2p)^3P$ state yields a value of 265 meV for the electron affinity of the $(2p^2)^3P$ state. This result is in agreement, within the uncertainty limit, with the theoretical value [9] of 262 meV. In the same paper, however, the authors quote a value of 285 meV for the electron affinity of Be($2s2p\,^3P$). This value was subsequently reduced to 276 meV in the calculation of Bunge [10] but the calculation still implies that the electron affinity of Be($2s2p\,^3P$) is larger than that of Be ($2p^2\,^3P$), a result that is inconsistent with the photon spectroscopic measurement [18]. Although this discrepancy has been eliminated [19], the corrected theoretical value has not yet been published.

Since the $Be^-(2\,^4P)$ state may autodetach via the $2\,^1S\varepsilon s,d$ channels, one can also perform an additional consistency check by measuring the energy of the autodetached electrons. This was achieved by the use of a hybrid method in which the spectrum of autodetached electrons was accumulated using AES and the ion-beam energy and electron-energy scale calibration were determined from a PES experiment using, in the manner previously described, a reference beam of He^- ions. Figure 2(b) shows the peaks associated with both the autodetachment and photodetachment of electrons from Be^- ions while Fig. 2(a) shows the He^- peaks used for calibration. By use of this APES technique we were able to determine the ion-frame energy of the autodetached electrons to be $E_c(a)=2.463\pm0.021$ eV. If one accepts the measured photon spectroscopic value of $E_e=2.7252$ eV [18] and subtracts $E_c(a)$ from the accepted value of the excitation energy E_e of the $2\,^3P$ state of Be (see Fig. 1), one obtains a Be($2\,^3P$) electron affinity of $E_a=262\pm21$ meV. Alternatively, combining the measured autodetached electron energy with the electron affinity of $E_a=0.261\pm0.017$ eV obtained from the PES peaks of Fig. 2 (the last data point in Fig. 3) allows us to determine the $2\,^1S-2\,^3P$ energy separation in the Be atom. The present result of $E_e=2.723\pm0.007$ eV is in excellent agreement with the accepted value of 2.7252 eV obtained from a difficult spectroscopic measurement using the rather weak intercombination line [20]. Although less accurate, the measurement does represent an independent check of the excitation energy of the Be($2\,^3P$) state. Interestingly, the uncertainty limit on the sum of the two measured energies is considerably less than on each individual energy because of cancellations in the error propagation.

TABLE I. The electron affinity (EA) of BE($1s^2 2s2p)^3P$.

EA (meV)	Method	Reference
240±100	Theoretical	[2]
285	Theoretical	[9]
217.7±57.1	Theoretical	[6]
195±90	AES	[11]
276.1±6.5	Theoretical	[10]
261±10	PES	This work

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*Also at Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

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