Experimental Determination of the Energy Level of $Be^-(1s^22s2p^2)^4P$

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We report the first experimental measurements for the energy level of a metastable state of Be^-. The ions were produced in sequential charge-exchange collisions between 50- to 60-keV Be^+ ions and lithium vapor. The center-of-mass energy of autodetaching electrons was found to be 2.53 ± 0.09 eV. This result is in good agreement with previously calculated values for the $Be^-(1s^22s2p^2)^4P$-state energy.

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In this paper, we report the observation of a peak in the Be^- autodetachment electron-energy spectrum which is a signature of the decay of a metastable beryllium negative-ion state. These measurements represent the first time that the energy level of a long-lived metastable state has been experimentally determined for negative ions of the group II*A* (alkaline-earth) elements. In fact, limited experimental information is available on the structure of any metastably bound atomic negative ion. Notable exceptions to this include He^-, which is a classic example of a spin-aligned metastable negative ion (see, e.g., Alton, Compton, and Pegg[1]); resonance studies from electron-atom scattering experiments (see, e.g., Burrow, Michejda, and Comer[2]); and Li^-, in which photon emission was observed between high-lying metastable states of the negative ion (see, e.g., Brooks *et al.*[3]). The fundamental nature of Be^- makes it of considerable experimental and theoretical interest. As early as 1966, the ion was reported[4,5] to be present in mass spectra of ions emitted from direct-extraction negative-ion sources. Since the first observation of Be^-, experimental values for production efficiencies[6] and autodetachment lifetimes[7] have been reported. In recent measurements on the autodetaching decay of Be^-, Bae and Peterson[7] have shown that the ion has at least two distinct lifetime components of $\sim 10^{-4}$ and $\sim 10^{-5}$ s.

Most theoretical studies indicate that Be^- is metastable,[8-13] although early theoretical calculations[14-16] suggest that $Be^-(1s^22s^23s)^2S$ is bound with respect to the ground state, $(1s^22s^2)^1S$, of beryllium. Recent theoretical calculations do not predict the existence of a stable Be^- state but predict the existence of two states, both metastable against autodetachment, which lie below the first ionization threshold of neutral beryllium—$Be^-(1s^22s2p^2)^4P$ which is bound with respect to $Be(1s^22s2p)^3P^\circ$, and $Be^-(1s^22p^3)^4S^\circ$ which is bound with respect to $Be(1s^22p^2)^3P$. The radiatively allowed $^4S^\circ \rightarrow {}^4P$ transition is predicted to occur at either 263.8 nm (Ref. 9), 267.1 nm (Ref. 12), or 265.4 nm (Ref. 10). Radiation from this transition was searched for by Andersen[17] without success. A third metastable state, $Be^-(1s2s2p^3)^6S^\circ$, has also been predicted.[9,12] This state, however, lies energetically outside the present experimental range [> 100 eV from $Be(1s^22s^2)^1S$]. Other Be^- ion states have also been theoretically studied. For instance, the $Be^-(1s^22s^22p)^2P$ configuration is predicted[18] to be a shape resonance; however, the lifetime of this state is too short to be studied with the present apparatus.

Theoretical calculations of the structure of negative ions are particularly difficult since the electron affinities are typically of the same magnitude as the difference in correlation energies between the atom and ion. Even so, most of the present information concerning metastable negative ions, other than He^-, has been provided by theoretical studies of open-shell excited-state negative-ion configurations. The first theoretical investigations of the structure and binding energies (electron affinities) for the group I*A* elements Li^-, Na^-, and K^- and the group II*A* elements Be^- and Mg^- were made by Weiss[8] who employed variational-superposition techniques. The Be^- ion was predicted to be bound relative to the neutral atomic $(1s^22s2p)^3P^\circ$ state by 240 meV with the most likely configuration postulated to be $Be^-(1s^22s2p^2)^4P$. This configuration is metastable against autodetachment by spin-forbidden transitions—analogous to the $(1s2s2p)^4P^\circ$ state of He^-.

Configuration-interaction calculations have been employed by Bunge *et al.*[9] in a search for possible bound excited negative-ion state configurations for the elements hydrogen through calcium. The results of these investigations indicate the existence of two metastable states of Be^-—the $Be^-(1s^22s2p^2)^4P$ which is bound relative to $Be(1s^22s2p)^3P$ by 285 meV, and $Be^-(1s^22p^3)^4S^\circ$ which is bound relative to the $(1s^22p^2)^3P$ atomic state by 262 meV.

The fine and hyperfine energy separations, as well as

electron affinities of the lowest two bound states of Be^-, have been calculated by Beck and Nicolaides[10] through the use of a nonrelativistic many-body calculation. These studies indicate that $Be^-(1s^22s2p^2)^4P$ is bound by 218 meV relative to $Be(1s^22s2p)^3P°$, while $Be^-(1s^22p^3)^4S°$ is bound by 244 meV relative to $Be^-(1s^22p^2)^3P$. The lifetimes of the $Be^-(^4P_J)$ levels were also predicted[13] in a recent calculation.

The experimental techniques utilized for determining the energy levels of metastable Be^- are very similar to those used for the measurement[1] of the energy level of $He^-(1s2s2p)^4P°$. For the present investigation, a Be^+ ion beam was post-accelerated to the chosen kinetic energy, momentum analyzed, and focused through a lithium vapor cell situated 1 m away from the electron spectrometer as shown in Fig. 1. This resulted in a time delay of ~ 1 μs between the Be^- production and detection of electrons ejected from the decay of Be^-. Thus only ions produced in states metastable against both autodetachment and radiation survive long enough to be experimentally studied. The positive, neutral, and negative components of particles emergent from the lithium vapor cell were separated upon entrance into the experimental chamber by an electrostatic deflector. Ions passing through the device were deflected by $\pm 10°$ into a 1.5-cm-long gas cell. The purpose of the gas cell was to produce a high-pressure region for collisional stripping of electrons from the Be^- ion beam. A small aperature located in front of the gas cell served to collimate the Be^- beam prior to its passage through the gas cell and through the 160° spherical-sector electron-energy analyzer. The ion beam, after straight-line transit through the analyzer, was monitored in a shielded Faraday cup located at the rear of the spectrometer. Mutually perpendicular sets of Helmholtz coils were used to nullify the Earth's and stray magnetic fields in the vicinity of the electron spectrometer.

Electrons ejected in the forward direction following autodetachment or collisional stripping were energy analyzed by the electron spectrometer which was operated in the fixed-pass-energy mode. The collisionally detached peak served as the absolute reference for the determination of the energy of the autodetached electron peak in each spectrum. The ion beam energies were chosen sufficiently high (50, 55, and 60 keV) so that the collisionally detached electron peak could be resolved from the low-energy electron background peak centered at zero laboratory energy. Autodetached electrons ejected in the backward direction could not be resolved from this low-electron-energy "noise" peak. The electron signal from the analyzer was input to a CAMAC-based multichannel-analyzer data-acquistion system. Each channel of the multichannel analyzer corresponded to a unique electron energy, and the typical voltage increment used during these measurements was 24.24 meV.

The center-of-mass (or state) energy $E_{c.m.}$ of autodetached electrons ejected in the forward direction from a moving ion beam can be determined relative to the electrons which move at the projectile velocity (collisionally detached) by use of the small-angle kinematic expression (see Ref. 1). The resulting relation for $E_{c.m.}$ is given by

$$E_{c.m.} = [\sqrt{E_a} - \sqrt{E_c}]^2, \quad (1)$$

where E_a is the laboratory energy of the autodetaching peak and E_c is the laboratory energy of the collisional detachment peak. E_c is determined from the kinetic energy of the ion beam. By use of this procedure to determine $E_{c.m.}$ which is based on two peaks corresponding to physical events occurring in the same spectrum, errors due to contact and surface potentials are minimized and the need for precise knowledge of the spectrometer constant is avoided.

Electron energy spectra were acquired for Be^- ion

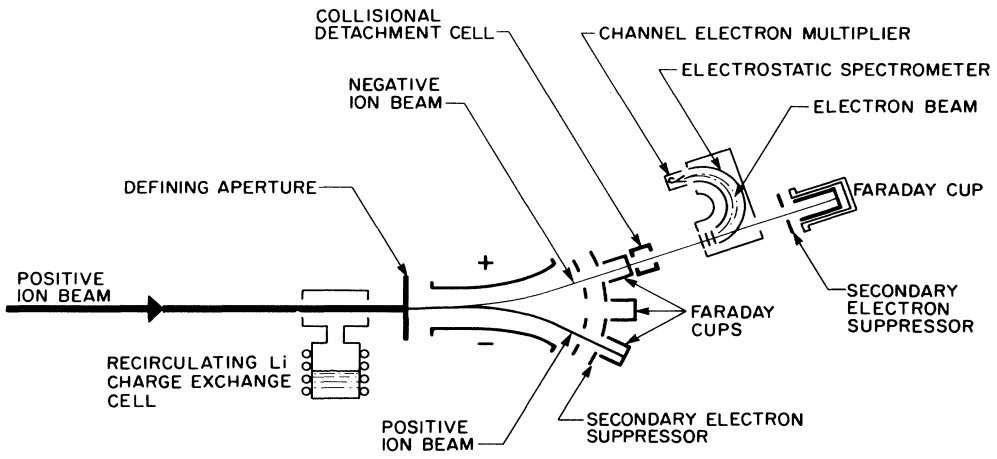

FIG. 1. The experimental arrangement used to measure the energy level of the metastable $Be^-(^4P)$ state.

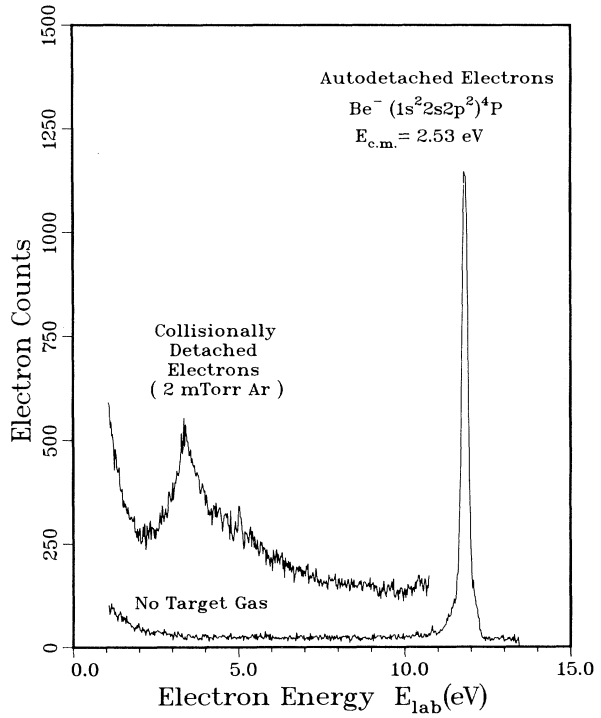

FIG. 2. Electron energy spectra from 55-keV Be^- ions with and without a thin argon target.

energies of 50, 55, and 60 keV. Figure 2 displays a high-resolution autodetachment spectrum taken without target gas and a spectrum taken with ~ 2 mTorr argon in the gas cell to enhance the collisional-detachment peak. The spectra were taken sequentially and at an ion energy of 55 keV. The very low-energy–electron background peak is attributable to low-energy electrons generated by ion impact with apertures, etc. The collisional-detachment peak was only detectable whenever a target gas (e.g., argon) was introduced into the gas cell, while the autodetachment peak was present in all of spectra. The addition of gas in the cell does not change the shape or the energy position of the autodetachment peak. This peak, which occurs at the laboratory energy of 11.71 eV for 55-keV Be^- ions, is attributable to autodetaching electrons from the decay of the $Be^-(^4P)$ state. This signal (typically several kilohertz) was well resolved from the electron background (typically < 100 Hz), while the signal-to-noise (S/N) ratio of the collisional-detachment peak was typically less than that of the autodetachment peak. The lower S/N of the collisional-detachment peak was due primarily to the higher electron background at lower electron energies. The present measurements gave an average value for the center-of-mass energy of this state measured with respect to the ground state of neutral beryllium of 2.53 eV with a standard deviation of ± 0.09 eV. The FWHM in the laboratory frame of the peak shown in Fig. 2 is ~ 0.2 eV, which corresponds to a FWHM of ~ 0.04 eV in the center-of-mass frame. From these results, we estimate an electron affinity of 195 ± 90 meV using the value from Bashkin and Stoner[19] for the energy of $Be(1s^2 2s 2p)^3P°$. A search for the electron autodetachment peak from $Be^-(1s^2 2p^3)^4S°$ was made without success. This is not unexpected since this state is permitted to decay radiatively to the lower-lying $Be^-(1s^2 2s 2p^2)^4P$ state.

Table I compares the present results with previous theoretical calculations. The electron affinity is defined as the energy difference between $Be(^3P°)$ and $Be^-(^4P)$, whereas the energy separation between $Be(^1S)$ and $Be^-(^4P)$ is the state energy of $Be^-(^4P)$. In cases where the total energy of the ground state $Be(^1S)$ was not reported, the latest reported value by Bunge[20] was used in order to arrive at the $Be^-(^4P)$ state energy. In both cases, the resulting energy is a small difference between rather large numbers; and er-

TABLE I. Summary of experimental and theoretical values for the energy levels of the $Be^-(1s^2 2s 2p^2)^4P$ state.

Electron affinity $E(Be(^3P))$-$E(Be^-(^4P))$ (meV)	State energy $E(Be^-(4P))$ (eV)	Type	Reference
240 ± 100	2.49[a]	Theoretical	8
> 122	2.66[b]	Theoretical	12
285		Theoretical	9
217.7 ± 57.1	2.56[c]	Theoretical	10
195 ± 90[d]	2.53 ± 0.09	Experimental	Present work

[a]Used -14.6189 a.u. for the ground state of beryllium.
[b]Used -14.6684 a.u. for the ground state of beryllium, as quoted from Bunge (Ref. 20).
[c]Used -14.667328 a.u. for the ground-state energy of beryllium, as quoted from Ref. 20.
[d]Used 2.272 48 eV as the state energy of $Be(1s^2 2s 2p)^3P°$ taken from Ref. 19.

rors, uncertainties, or omissions are extremely important. For example, calculations (see, e.g., Ref. 8) which do not take electron correlation effects into account predict $Be^-(^4P)$ to be unbound (electron affinity $= -68$ meV). The present electron-energy measurements covered the whole region below the first ionization threshold of neutral beryllium, and only one autodetaching peak was observed in the spectrum. However, this does not conclusively rule out the existence of other metastably bound states for Be^- since our apparatus is insensitive to ions having lifetimes much less than 1 μs or much greater than a few tens of microseconds. This includes, of course, ion states that are not metastable against radiative decay.

In conclusion, the present results support the theoretical predictions that there is only one state of the negative beryllium ion lying below the $Be(1s^22s2p)^3P^\circ$ threshold which is metastable against both autodetachment and radiative decay. The agreement between the theoretically predicted electron-affinity and state-energy values and our experimentally determined values permits us to identify the observed autodetaching state as $Be^-(1s^22s2p^2)^4P$. Additional support for this identification comes from lifetime predictions[13] and measurements[7] which indicate that $Be^-(^4P_J)$ will have a lifetime component matched to the time window of our apparatus.

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