PHYSICAL REVIEW VOLUME 188, NUMBER 1 5 DECEMBER 1969

Mean-Life Measurements of Excited Electronic States in Neutral and Ionic Species of Beryllium and Boron

T. Andersen
Institute of Chemistry, University of Aarhus, Aarhus, Denmark
and
K. A. Jessen and G. Sørensen
Institute of Physics, University of Aarhus, Aarhus, Denmark
(Received 16 June 1969)

Lifetimes of excited states in neutral and ionic species of beryllium and boron have been measured by using the foil-excitation technique. Ion beams from 60 to 400 keV produced with an electromagnetic isotope separator or a heavy-ion accelerator were used. The 1600–7000 Å wavelength region was investigated. For low-lying states in Be, the beam-foil excitation mechanism was studied. Mean lives of 11 states in Be I, nine in Be II, and one in Be III have been measured. Three lines belonging to beryllium could not be identified. In the boron case, seven mean lives were determined for excited neutral and ionic states. Transition probabilities and oscillator strengths have been evaluated and compared with theoretical predictions.

I. INTRODUCTION

The scope of the present investigation was to determine the mean lives of excited electronic states of neutral and ionic states of beryllium and boron by using the foil-excitation technique[1] with singly charged ion beams ranging from 60 to 400 keV. The measured mean lives are directly related to transition probabilities and oscillator strengths, which are the quantities of atomic and astrophysical interest.

In recent years, the foil-excitation technique has been extensively used since it has the advantage of giving rise to a temporally well-defined excitation yielding a decay of the excited states without disturbing phenomena such as collision deexcitations, recombinations, etc. Cascading effects may sometimes limit the advantages of the beam-foil technique. The energy of the ion beam, corrected for energy loss in the foil, yields the velocity of the excited atom or ion beam which is of importance for the population of excited states. For instance, low-ion velocities have been found to favor excited neutrals in nitrogen[2] and aluminum[3] because of charge-exchange processes. The energy interval investigated, i.e., 60–400 keV, makes it possible to study excited levels in neutral, singly, and doubly charged beryllium and boron.

Experimental investigations of mean lives in Be and B are few and not systematic. Lawrence and Savage[4] have studied some uv multiplets in B by means of the phase-shift method, and Hese and Weise[5] used the level-crossing technique to measure the mean life of the $2p^2\ ^2D$ level in B I. Andersen *et al.*[6,7] used the foil-excitation technique to measure the $2p^2\ ^1D$ level in B II and the $2p^2P$ levels in Be II and B III. Bergström *et al.*[8] have measured 11 mean lives in Be I and Be II and four mean lives in B I and B II using the foil-excitation technique.

II. EXPERIMENTAL METHOD

The experimental method has been previously described in detail.[3] Singly charged ions of beryllium and boron with energies ranging from 60 to 400 keV were obtained by using an electromagnetic isotope separator and a 600-keV heavy-ion accelerator, both equipped with universal ion sources. Ion beams of beryllium were obtained by oxidizing beryllium metal in a quartz tube. The beryllium oxide was converted into the volatile chloride in the ion source by means of carbon tetrachloride. Ion currents up to 1 μA with a diameter of 2 mm were passed through the carbon foil. Boron ion beams were obtained by direct synthesis in a furnace inserted into the ion source. Finely grained boron trioxide and potassium fluoborate (KBF_4) were mixed in the furnace and heated to about 400 °C. The synthesized boron trifluoride then evaporated into the ion source. Currents of 0.1 μA with a diameter of 2 mm were passed through the carbon foil. The thickness of the carbon foils (Yissum Research Company) varied from 2 to 20 $\mu g/cm^2$. Uncertainty in the thickness determination was within 10%, relatively. The emission spectra were observed with a McPherson model 218 grating spectrometer with either a 1200 mm^{-1} or a 2400 mm^{-1} grating. Photoelectric detection with EMI 6256S or 9558B photomultiplier tubes was applied.

Corrections for energy loss in the carbon foil were calculated from the Lindhard-Scharff-

Schiøtt theoretical treatment[9] which gives the following equation:

$$\left(\frac{\partial\epsilon}{\partial\rho}\right)_{\text{total}} = \left(\frac{\partial\epsilon}{\partial\rho}\right)_n + k\epsilon^{1/2} ,$$

where ϵ and ρ are energy and range in dimensionless units, $(\partial\epsilon/\partial\rho)_n$ is the nuclear stopping power, and $k\epsilon^{1/2}$ represents the electronic stopping where k is of the order of 0.1 – 0.2 for $Z_1 \gtrsim Z_2$. Only for $Z_1 \ll Z_2$ can k become larger than unity. Schiøtt[10] has recently tabulated nuclear stopping power in reduced units and k values.

III. RESULTS

A. Beryllium

In the emission spectra observed, 20 spectral lines have been assigned as belonging to either Be I or Be II. A spectral line at 3722 Å was assigned as belonging to $2s\,^3S - 2p\,^3P^0$ in Be III since it only appeared for high ion energies (> 200 keV). Shown in Figs. 1 and 2 are partial-term diagrams for Be I and Be II, constructed on the basis of the measurements by Johansson.[11,12] The transitions investigated in the present study are shown as fully drawn lines. Further, three unidentified lines in the uv region were observed at 1910, 2080, and 2328 Å. Of these, the 2080 Å line was observed only at ion energies above 200 keV, just as the 3722 Å line was observed in the case of the presumed Be III. Since the population of doubly excited states in Li I has been found to increase considerably with increasing ion energy,[13] the 2080 Å line might originate from such a level in beryllium. Holöien and Geltman[14] have classified doubly excited levels in Be II, but the possible transitions in their report do not fit in the present case. No quantitative measurements of the population of the different excited levels have been performed so far. However, it seems that S terms in general are populated to a much less degree than other terms.

Attempts have been made to elucidate the beam-foil mechanism. There has been some dispute over the existence of charge equilibrium in the passage of the beam through the foil.[15,16] A beam of 200-keV Be^+ ions was passed through carbon foils of thicknesses 2, 4, 8, 13, and 20 $\mu g/cm^2$. For intensity reasons, only a detailed investigation of the 3131 Å line from the $2s\,^2S - 2p\,^2P$ transition in Be II was possible. No variations in the strength of the 3131 Å line could be observed when the foil thickness was changed. This indicates that excitation equilibrium for a low-lying state, such as the $2p\,^2P$ state in Be II, is already present for a 2-$\mu g/cm^2$ foil.

Beam-foil excitation of lithium between 0.5–2 MeV[13] showed a decrease in intensity for transitions in Li II with increasing energy, while the maximum intensity for the 4500 Å transition in Li III was reached at 1.7 MeV. Shown in Table I is the energy variation between 300 and 500 keV for the 2650 Å line from the $2s2p\,^3P - 2p^2\,^3P$ transition in Be I; for the 3131 Å line from the $2s\,^2S - 2p\,^2P$ transition in Be II; and for the 2328 Å unidentified line, these three lines being the strongest lines in the beryllium spectra.

As shown, the Be I and Be II lines decrease with approximately the same slope with increasing energy, while the unidentified line exhibits a different energy dependence. In the present as well as in other cases,[3] different ion energies have been used to identify spectral lines belonging to different charge states, and to facilitate a mean-life determination in the case where the line in question is blended with a spectral line from a different charge state. In the case of beryllium, the strongest transition, even at an ion energy of 60 keV, is the 3131 Å line in Be II, and therefore the energy dependence is less significant than in other cases.[3]

The present observations indicate that the number of collisions for a fixed initial energy plays no important role for the intensity of spectral lines originating from low-lying states as in Be II. A more detailed study is needed to clear up the beam-foil-excitation mechanism. An interesting approach would be the application of electrostatic deflection plates together with a position-sensitive ion detector, sucessfully used by Hvelplund *et al.*[17] for the study of charge states populated in ion-gas collisions.

Table II shows the mean lives of excited terms in beryllium, excited by means of the technique described above. The mean lives listed are average values of several determinations for a variety of foil thicknesses and ion energies. In the cases where cascade corrections have been performed, the mean life is marked with an asterisk superscript. No attempts have been made to determine mean lives of cascading parts with a mean life superior to 20 nsec. For the sake of comparison, the results recently published by Bergström *et al.*[8] are shown.

It should be noted that the 2898 and the 3110 Å lines which, according to Fig. 1 have the same upper level, yield widely different mean lives for the $2p3d\,^3D$ level. This inconsistency may be due to an

TABLE I. Energy variation of intense spectral lines of beryllium.

	Arbitrary intensities		
Spectrum	300 keV	400 keV	500 keV
Be I (2650 Å)	1	0.4	0.2
Be II (3131 Å)	1	0.4	0.3
Unidentified (2328 Å)	1	0.6	0.5

TABLE II. Mean lives of excited neutral and ionic states of beryllium. (The asterisk indicates cases where cascade corrections have been performed.)

	Measured wavelength (Å)	Lower state	Upper state	τ (Upper state) 10^{-9} sec	τ (Upper state) 10^{-9} sec (Ref. 8)
	2125*	$2s2p\,^3P$	$2s5s\,^3S$	10.5 ± 0.5	
	2175	$2s2p\,^3P$	$2s4d\,^3D$	11.5 ± 0.5	
	2348	$2s^2\,^1S$	$2s2p\,^1P$	2.3 ± 0.1	2.05 ± 0.06
	2494	$2s2p\,^3P$	$2s3d\,^3D$	4.9 ± 0.2	5.00 ± 0.14
	2650	$2s2p\,^3P$	$2p^2\,^3P$	2.3 ± 0.2	2.42 ± 0.06
Be I	2898*	$2p^2\,^3P$	$2p3d\,^3D$	2.6 ± 0.2	
	3110	$2s3d\,^3D$	$2p3d\,^3D$	6.8 ± 0.2	
	3321*	$2s2p\,^3P$	$2s3s\,^3S$	7.3 ± 0.2	5.95 ± 0.16
	3455	$2s2p\,^1P$	$2p^2\,^1S$	5.0 ± 0.2	5.35 ± 0.14
	3813	$2s2p\,^1P$	$2s4d\,^1D$	13.6 ± 0.2	18.8 ± 0.5
	4572	$2s2p\,^1P$	$2s3d\,^1D$	10.0 ± 0.2	12.0 ± 0.3
	1776	$2p\,^2P$	$3s\,^2S$	3.3 ± 0.3	
	3046	$3p\,^2P$	$5d\,^2D$	5.1 ± 0.3	
	3131*	$2s\,^2S$	$2p\,^2P$	8.1 ± 0.4	9.29 ± 0.20
	3197	$3d\,^2D$	$5f\,^2F$	9.7 ± 0.7	
Be II	3274	$3s\,^2S$	$4p\,^2P$	8.1 ± 0.8	
	4360*	$3p\,^2P$	$4d\,^2D$	2.3 ± 0.2	2.22 ± 0.06
	4673*	$3d\,^2D$	$4f\,^2F$	7.0 ± 0.4	5.02 ± 0.14
	5270	$3p\,^2P$	$4s\,^2S$	4.4 ± 0.3	3.77 ± 0.10
	6279	$3p\,^2P$	$6d\,^2D$	8.0 ± 0.8	
Be III	3722	$1s2s\,^3S$	$1s2p\,^3P$	22.3 ± 1.0	
	1910			2.1 ± 0.2	
Other	2080*			2.0 ± 0.2	
lines	2328			3.2 ± 0.2	
	2125			1.5 ± 0.2	

erratic term diagram for Be I or an erratic assignment of the spectral lines produced by the beam-foil excitation. In the 2125 Å line, a fast-decaying component is observed (1.5 ± 0.2 nsec), but it has not been possible to assign this fast-decaying component. The lifetimes of the $2p^2\,^3P$ state and its precursor, the $2p3d\,^3D$ state, have nearly the same value. Since the intensity ratio I_{2650}/I_{2898} is of the order of 5 at the energies investigated, the influence of cascading on the determination of the $2p^2\,^3P$ state will be small.

In Be II, for the $6d\,^2D$ level feeding the $4p\,^2P$

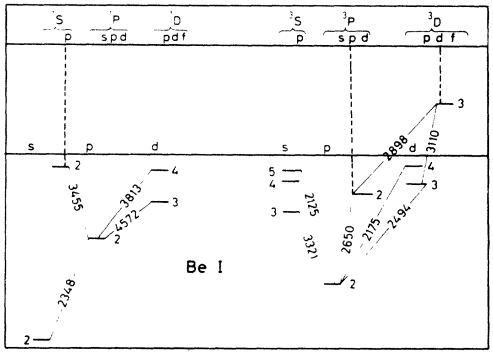

FIG. 1. Partial-term diagram for Be I. Transitions, which have been measured, are indicated.

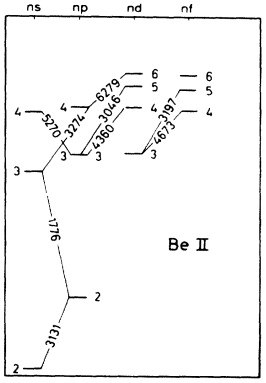

FIG. 2. Partial-term diagram for Be II. Transitions, which have been measured, are indicated.

level, identical mean lives were also obtained. In this case, the intensity ratio I_{3274}/I_{6279} is more difficult to evaluate since two widely different photomultiplier tubes were used. In any case, the 3274 Å line is stronger than the 6279 Å line, which excludes an overwhelming influence of cascading.

Table III shows mean lives of the $2p\,^2P$ level in Be II at various energies for varying thicknesses. Systematic errors such as uncertainties in the foil thickness and energy evaluations have been included. The reproducibility of the method is excellent.

B. Boron

In the emission spectra, seven spectral lines sufficiently intense for mean-life determinations were observed. Figure 3 shows a detail of the emission spectra obtained at various energies. As shown in Fig. 3, the present technique allows a separation of the 2089 Å line in B I from the 2067 Å line in B III. Even at 60 keV, the B III line is comparable to the B I line as regards intensity. Thus, an insufficient spectrometer resolution would result in a too-short mean life for the $2p^2\,^2D$ state in B I, as reported in Ref. 8.

Our results were obtained with a spectrometer slit of 200 μ, a scanning rate of 500 Å/min, and a reasonable resolution was obtainable. Table IV lists mean lives of excited neutral and ionic species of boron. Other experimental values are included for the sake of comparison.

IV. DATA EVALUATION

In general, the measured mean lives are the average values of several determinations at different energies and foil thicknesses. The quoted errors include the uncertainties in the foil thickness, the energy loss of the beam passing the foil, and in the cascading effects.

The measured mean lives can easily be converted into transition probabilities A_{if} and oscillator

TABLE III. Mean life of the $2p\,^2P$ level in Be II.

Ion energy (keV)	Foil thickness ($\mu g/cm^2$)	$\tau\,10^{-9}$ sec
60	2	8.0 ± 0.2
60	2	7.5 ± 0.4
60	5	7.5 ± 0.4
60	8	7.4 ± 0.4
100	10	8.3 ± 0.4
200	13	8.2 ± 0.2
300	4	8.1 ± 0.2
300	8	8.4 ± 0.3

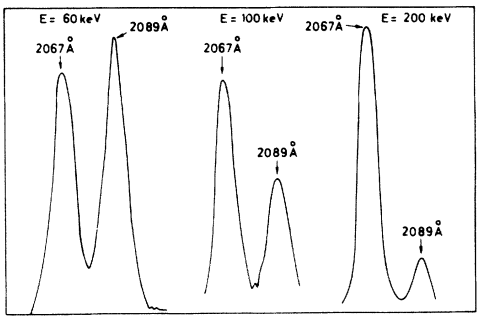

FIG. 3. Partial-emission spectra observed when 60–200-keV ion beams of boron are passed through a 5-$\mu g/cm^2$ carbon foil.

strengths f_{fi} by means of the following relation

$$\tau^{-1} = \sum_f A_{if} \ ,$$

where the sum should be taken over all levels to which the upper level can decay. The corresponding oscillator strength is calculated as

$$f_{fi} = 1.499\lambda^2 (g_f/g_i) A_{if} \ ,$$

where the wavelength λ is measured in cm, and g_i and g_f are the statistical weights of initial and final states. The calculated transition probabilities and oscillator strengths for Be I, Be II, and Be III are shown in Table V. Only in the case of the $2s - 2p$ transition arrays in the Be I triplet and Be II is excellent agreement found between experimental values and theoretical estimates. It should be mentioned that the *N. B. S* theoretical values[18] are taken from Weiss's unpublished self-consistent field calculations for Be I, and for Be II from Weiss's calculations.[19]

An evaluation of transition probabilities and oscillator strengths was not performed where non-observable far uv transitions were known to depopulate an excited level, the mean life of which was determined by an observed transition.

Table VI gives transition probabilities and oscillator strengths for B I, B II, and B III. The theoretical f values included are taken from the *N. B. S* compilation,[18] Gruzdev and Prokofev,[20] and Linderberg.[21]

Excellent agreement exists between experiment[7] and theory[19] for the $2s\,^2S - 2p\,^2P^0$ transition in B III as well as for other members of the Li I isoelectronic sequence. The $2s2p\,^1P^0 - 2p^2\,^1D$ transition in the Be I isoelectronic sequence has earlier been investigated.[6] A number of lifetime measurements exists for the members of this sequence.[6,22] However, so far experiment and theory have disagreed by a factor of 3.[6] A new calculation by Linderberg[21] has shown much better agreement between

TABLE IV. Mean lives of neutral and ionic states of boron.

	Measured wavelength (Å)	Lower state	Upper state	τ Upper state 10^{-9} sec	τ Upper state 10^{-9} sec Other data
B I					23.1 ± 2.5[a] 23.0 ± 2.0[b]
	2089	$2p\,^2P^\circ$	$2p^2\,^2D$	26.4 ± 1.0	18.4 ± 0.8[c]
	2497	$2p\,^2P^\circ$	$3s\,^2S$	3.8 ± 0.2	5.7 ± 0.2[c]
B II	2394	$2p^2\,^1D$	$3p\,^1P^\circ$	3.6 ± 0.3	
	3319	$3p\,^3P$	$4d\,^3D$	2.1 ± 0.3	
	3452*	$2p\,^1P^\circ$	$2p^2\,^1D$	13.8 ± 0.7	12.9 ± 1.0[d] 15.5 ± 0.7[c]
	4122	$3d\,^3D$	$4f\,^3F$	3.6 ± 0.3	4.8 ± 0.2[c]
B III	2067*	$2s\,^2S$	$2p\,^2P^\circ$	5.6 ± 0.3	5.6 ± 0.3[e]

[a]Reference 5.
[b]Reference 4.
[c]Reference 8.
[d]Reference 6.
[e]Reference 7.

TABLE V. Transition probabilities and oscillator strengths for beryllium.

	Transition	A_{expt} (10^8/sec)	f_{expt}	f_{theor}[a]	f_{theor}[b]	f_{theor}[c, d]
Be I	$2s^2\,^1S$-$2s2p\,^1P$	4.00	0.99	1.36	1.7	1.59
	$2s2p\,^3P$-$2s3d\,^3D$	2.04	0.32	0.16	0.21	
	$2s2p\,^3P$-$2p^2\,^3P$	4.35	0.46	0.466	0.4	
	$2s2p\,^3P$-$2s3s\,^3S$	1.37	0.08	0.034	0.038	0.08
	$2s2p\,^1P$-$2p^2\,^1S$	1.8	1.02			
	$2s2p\,^1P$-$2s4d\,^1D$	0.74	0.27	0.084		
	$2s2p\,^1P$-$2s3d\,^1D$	1.00	0.52	0.19	1.3	
Be II	$2p\,^2P$-$3s\,^2S$	3.03	0.05	0.0665		
	$2s\,^2S$-$2p\,^2P$	1.24	0.54	0.505		0.50
	$3d\,^2D$-$4f\,^2F$	1.43	0.66	1.01		

[a]Reference 18.
[b]H. Pfennig, R. Steele, and E. Trefftz, J. Quant. Spectr. Radiative Transfer 5, 335 (1965).
[c]P. F. Gruzdev, Opt. Spectrosc. 22, 89 (1967).
[d]Reference 20.

TABLE VI. Transition probabilities and oscillator strengths for boron.

	Transition	A_{expt} (10^8/sec)	f_{expt}	f_{theor}[a]	f_{theor}
B I	$2p\,^2P^0$-$2p^2\,^2D$	0,38	0,04	0,24	
	$2p\,^2P^0$-$3s\,^2S$	2,64	0,08	0,11	0,07[b, c]
B II	$2p\,^1P^0$-$2p^2\,^1D$	0,73	0,22	0,65	0,42[d]
	$3d\,^3D$ -$4f\,^3F$	2,78	1,00	0,91	
B III	$2s\,^2S$-$2p\,^2P^0$	1,78	0,343	0,366	0,36[b, c]

[a]Reference 18.
[b]See Ref. c, Table V.
[c]Reference 20.
[d]Reference 21.

experimental and theoretical values for the Be sequence.

V. CONCLUSION

The tabulated experimental and theoretical values of oscillator strengths clearly demonstrate discrepancies far beyond the uncertainties quoted in the theoretical treatments. The theoretical determination of oscillator strengths in a single configuration approximation is based on an estimate of the relative line strength and the transition integral. In both cases, large uncertainties can be introduced, especially for higher terms. The beam-foil excitation technique is, therefore, considered an important tool for the study of atomic transitions where theoretical estimates have been shown to fail. The present study has shown that a systematic investigation of a large number of levels in excited neutral and ionic species of beryllium and boron has become possible by applying beam-foil spectroscopy to ion beams in the keV region.

---

[1]Beam-Foil Spectroscopy, edited by S. Bashkin (Gordon and Breach, Science Publishers, Inc., New York 1968), Vol. I and II; Proceeding of the Tucson Conference on Beam-Foil Spectroscopy, 1967 (unpublished).

[2]S. Bashkin, H. G. Berry, W. S. Bickel, and J. Desesquelles, Compt. Rend. 268, 234 (1969).

[3]T. Andersen, K. A. Jessen, and G. Sørensen, J. Opt. Soc. Am. 59, 1197 (1969).

[4]G. M. Lawrence and B. D. Savage, Phys. Rev. 141, 67 (1966).

[5]A. Hese and H.-P. Weise, Z. Physik, 215, 95 (1968).

[6]T. Andersen, K. A. Jessen, and G. Sørensen, Phys. Letters 28A, 459 (1968).

[7]T. Andersen, K. A. Jessen, and G. Sørensen, Phys. Letters 29A, 384 (1969).

[8]I. Bergström, J. Bromander, R. Buchta, L. Lundin, and I. Martinsson, Phys. Letters 28A, 721 (1969).

[9]J. Lindhard, M. Scharff, and H. E. Schiøtt, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 33 (1963) No. 14.

[10]H. E. Schiøtt, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 35, No. 9 (1966).

[11]L. Johansson, Arkiv Fysik 23, 119 (1962).

[12]L. Johansson, Arkiv Fysik 20, 489 (1961).

[13]J. P. Buchet, A. Denis, J. Desesquelles, M. Dufay, F. Gaillard, and M. Gaillard (to be published).

[14]E. Holöien and S. Geltman, Phys. Rev. 153, 81 (1967).

[15]S. Bashkin and P. R. Malmberg, Proc. Phys. Soc. (London) 87, 589 (1966).

[16]W. S. Bickel, J. Opt. Soc. Am. 58, 213 (1968).

[17]P. Hvelplund, E. Laegsgaard, and E. Horsdal Petersen (to be published).

[18]W. L. Wiese, M. W. Smith, and B. M. Glennon, NSRDA-NBS 4, (1966).

[19]A. W. Weiss, Astrophys. J. 138, 1262 (1963).

[20]P. F. Gruzdev and V. K. Prokofev, Opt. Spectrosc. 22, 151 (1967).

[21]J. Linderberg, Phys. Letters 29A, 467 (1969).

[22]W. S. Bickel, H. G. Berry, I. Martinsson, R. M. Schechtmann, and S. Bashkin, Phys. Letters 29A, 4 (1969).