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Absolute Cross Sections of Lithium and Other Alkali Metal Atoms for Ionization by Electrons*

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The absolute cross section for ionization by electron impact has been measured for lithium, sodium, potassium, rubidium, and cesium by a modulated-crossed-beam technique. The measurement for lithium is described in detail, inasmuch as it has never been previously measured. The cross sections for the other alkali metals are included and compared with prior measurements for reference.

INTRODUCTION

THE relative cross section for the ionization of lithium has been measured by the crossed-beam technique by Brink.[1] Other work[1–3] has been completed by different techniques toward the observation of the relative cross sections of the other alkali metals. More recently, Brink[4] successfully measured the absolute ionization cross section for all of the alkali metals with the exception of lithium. This paper discusses the experimental procedure used to improve the signal-to-noise ratio necessary for a successful measurement of the lithium ionization cross section.

The necessary equations for this measurement have been previously derived[4] and are only repeated here for completeness:

$$Q^+=C_1\frac{\bar{v}E}{I_e\sum n\alpha_n}\frac{I_i}{I_{sd}},\tag{1}$$

$$\log_{10}\bar{v}=\log_{10}\frac{C_2E}{MI_{sd}}+\frac{C_3A}{M\bar{v}^2}+B\,.\tag{2}$$

The symbol definitions are as follows:

Q^+= ionization cross section for singly ionized atoms.
C_1, C_2, and C_3= geometry factors dependent on oven slit area, defining slit width, relative distances from oven to electron gun and to surface detector wire, and size of wire. These were purposely changed during the experiment; but typical values were, respectively, 4.95×10^{-22}, 3.98, and 2.94×10^8.
$\bar{v}$= average atom velocity in beam.
E= ionization probability of beam atoms on hot wire.
I_e= electron beam current.
n= the number of electrons lost by the ion.
α_n= the ratio Q^{n+}/Q^+.
I_i= the ion current produced by the electron beam.
I_{sd}= the ion current produced by the surface detector.
M= the gram molecular weight of the beam material.
A,B= the constants giving the dependence of vapor pressure on temperature, $\log_{10}P=-(A/T)+B$.

Following the measurement of the lithium cross section, the improved cross-beam machine was utilized to remeasure the absolute cross section for ionization of the other alkali metals. These new values are presented and compared with earlier values.

APPARATUS AND PROCEDURE

The primary differences in this experimental system as compared to that previously used[4] involve improved vacuum pressures and beam chopping at 100 cps rather than at 2 cps. Using zeolyte forepumping and liquid nitrogen trapped mercury diffusion pumping, the base pressure of the vacuum system was held to less than 5×10^{-8} Torr. An additional feature involved utilization of heat shielding for improved oven heater efficiency.

A block diagram of the experimental system is shown in Fig. 1. The beam with a density of the order of 10^9 atoms/cc was chopped at a rate of 100 cps with a five-bladed wheel rotated by a synchronous motor at the rate of 1200 rpm. This allowed for phase detection with a reference 100-cps oscillator locked to the 60-cps ac line.

As indicated in the block diagram, the vacuum system consisted of three sections, differentially pumped. The major portion of the approximately 500-liter volume was that portion marked III. Its size and pumping

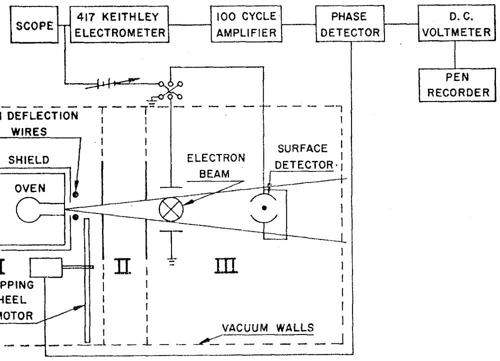

FIG. 1. A block diagram of the experimental system including the necessary electronics.

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[1] G. O. Brink, Phys. Rev. **127**, 1204 (1962).

[2] J. T. Tate and P. T. Smith, Phys. Rev. **46**, 773 (1934).

[3] Y. Kaneko, J. Phys. Soc. Japan **16**, 2288 (1961).

[4] G. O. Brink, Phys. Rev. **134**, A345 (1964).

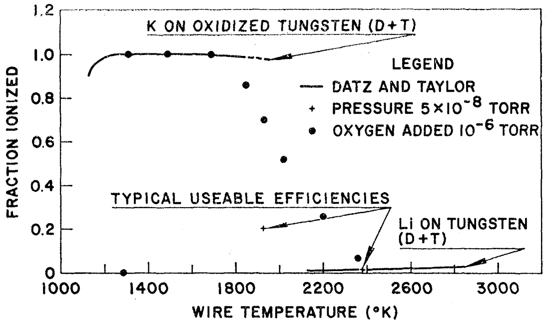

FIG. 2. The production of potassium and lithium ions on hot tungsten and oxidized tungsten wires.

speed were so planned that the chopped beam did not produce a 100-cps variation in the background gas. Also, the background pressure was capable of being maintained at less than 5×10^{-8} Torr, corresponding to a density of nearly an order of magnitude less than that of the beam.

The measurement of the lithium cross section presents interesting problems in terms of a relatively small cross section, a required oven temperature of the order of 1000°K, and the mode of action of lithium on the surface ionization detector.

Datz and Taylor[5] have discussed the surface ionization efficiency for the alkali metals on tungsten and oxidized tungsten. Figure 2 reproduces their results for potassium on oxidized tungsten and lithium on tungsten. They dispose of the other alkalies on oxidized tungsten by indicating that the results approximate those for potassium. In the present work the authors, working at a background pressure, lower by an order of magnitude, were unable to reproduce Datz and Taylor's inferred results for lithium on oxidized tungsten although a 5-cm, 0.002-in.-diam tungsten wire of high purity was used. Temperature measurements were duplicated by use of Jones-Langmuir tables.[6] On the other hand, upon adding oxygen to the system to a pressure of 10^{-6} Torr, the round data points of Fig. 2 were obtained, measuring the degree of ionization of lithium on oxidized tungsten. Following the reasoning of previous workers led by Langmuir, the authors have assumed 100% efficiency for that portion of the surface ionization efficiency versus temperature curve which is independent of hot-wire temperature and reasonable changes in oxygen pressure. It should be noted, however, that above 10^{-5} Torr oxygen pressure, tungsten-oxide ions evaporating from the wire must be avoided either through use of chopped-beam ac measurements or through subtraction of background obtained from interruption of the beam in dc measurements.

The somewhat higher threshold temperature for surface ionization of lithium than for potassium is understandable in terms of the lower vapor pressure of lithium and the resulting lithium surface that forms on the tungsten at prethreshold temperatures. The difference between the potassium and lithium measurements at the higher temperature is due to conflicting reaction rates. The oxidation of the tungsten is a function of the wire temperature and oxygen pressure. The loss of the effect of oxidation is a function of the temperature and the effective lithium pressure. Thus, the observations of ionization efficiency in the temperature range 1800–2400°K for a constant lithium beam depend on the oxygen pressure in the system. At the base pressure of 5×10^{-8} or less, 100% ionization efficiency was observable for only short time periods after oxidation of the wire at higher pressures and then only at temperatures in the 1300–1500°K range.

The residence time of a lithium atom on the tungsten wire was a second limiting characteristic in this experiment. Below 1800°K, the residence time was observed to markedly distort the surface ionization 100-cps current and thus affect the response of the surface detector output.

The developed procedure after necessary temperature stabilization of the instrumentation and the beam involved measurement of the 100-cps ion current and dc electron beam currents at 50, 100, 200, 300, 400, and 500 V. With the electron gun off, the 100-cps surface ionization current was measured with the wire at a temperature above 1900°K. For each electron energy, I_i/I_{sd} was thus determined using the same amplifier and detector system. (Note: $I_{sd}/I_i\approx10^4$.) The ionization efficiency of the surface detector E at the above temperature was determined by stopping the chopper (the dc current equaled the amplitude of the square wave current in the chopped measurement) and then simultaneously reducing the temperature of the wire to 1500°C while adding oxygen. The ionization efficiency was then determined

$$E=I_{sd}/I_{sd}(1500°\mathrm{C},\ 10^{-6}\ \mathrm{Torr}\ \mathrm{O_2}).$$

Two such efficiencies are shown as crosses in Fig. 2 at absolute temperatures of 1925 and 2375 degrees. The efficiency at the higher temperature compares with Datz and Taylor's results for lithium on tungsten and with calculation of the efficiency using the Saha-Langmuir equation.[5] This calculation required the assumption that all reflection coefficients equal zero, which was more restrictive than the previous assumption that 100% ionization was observed for lithium on oxidized tungsten, as it required only that the reflection coefficient r_i of the incident atoms on the hot wire be zero.

Obviously, the observation that efficiencies determined by the two different methods are equal does not of itself prove the validity of the assumption of reflection coefficients equaling zero. The alternative, however, that they remain constant through 1000° temperature range for a surface changing in degree of oxidation, seems even less likely.

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[5] S. Datz and E. H. Taylor, J. Chem. Phys. **25**, 389 (1956).

[6] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, No. 6, 310 (1927).

It should be noted that all biasing potentials were fully investigated for interdependent effects. Collection and acceleration potentials were determined such that they not interfere with each other or the electron beam at energies in excess of 50 V. A barium-impregnated, indirectly heated cathode was used in this work to take advantage of its low electrical noise operation and reduction of surface charging as compared with oxide-coated cathodes.

RESULTS AND DISCUSSION

The absolute ionization cross sections for lithium are presented in Fig. 3. These are superimposed upon a relative cross section curve previously measured by Brink.[1] Each 100-V point is the average of 16 measurements made with different oven loadings, cathodes, temperatures, and geometries, and with three different sizes of wires etc. The scatter of the values is indicated by the error bars. Brink's relative curve was normalized at the 500-V absolute value where the relative probable error in the absolute measurement was 8%. The 50-V value corresponds to the average of only two measurements.

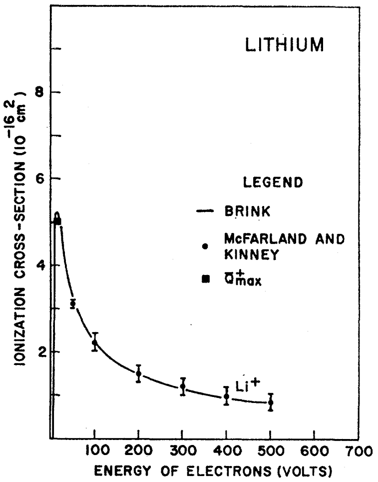

FIG. 3. Ionization cross section of lithium versus electron energy.

Figures 4 through 7 summarize measurements which have been completed for sodium, potassium, rubidium, and cesium using the same procedure. Each datum point represents the average of at least three different runs. $\bar{Q}^{+}_{\mathrm{max}}$ is determined as an average of the five extrapolated 100-V Q^{+}_{max} values determined by using the solid-line curves. Since the present measurements are fundamentally total cross section measurements, their interpretation, except for lithium, is dependent upon obtaining information from other sources[1,2] concerning the relative abundance of the various ionization species. With normalization at 500 V, there is quite good agreement in relative ionization for sodium with both sources. With potassium, best agreement is with Brink's work although Tate and Smith's work agrees at both high and low energies. Agreement with Tate and Smith is again good for rubidium but is somewhat less good for cesium. Specifically, the Q^{+} absolute values presented have been calculated by determining the value of $\sum n\alpha_n$ for lithium and potassium from Brink's measurements and for sodium, rubidium, and cesium from Tate and Smith's work.

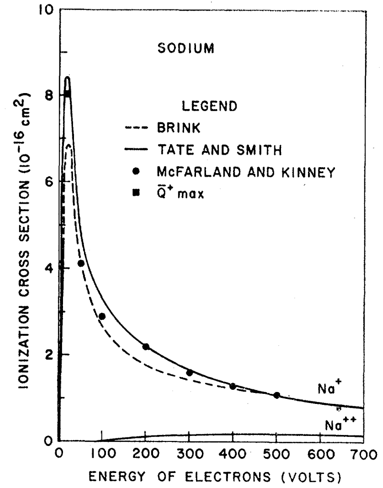

FIG. 4. Ionization cross section of sodium versus electron energy.

Table I indicates the degree of agreement between the current work and that of Brink.[4] Fite and Brackmann's[7] measurement of hydrogen has been included for comparative purposes. Again agreement is good except for the maximal values which reflect the averaging used in the current work. Brink's equal values for cesium at 300 and 500 V are the result of an error in computation. Correction of the 500-V value gives qualitative agreement with the current work.

The departure of Tate and Smith's relative measurements for K^{+} and Cs^{+} from these new measurements and those of Brink for K^{+} is in excess of experimental

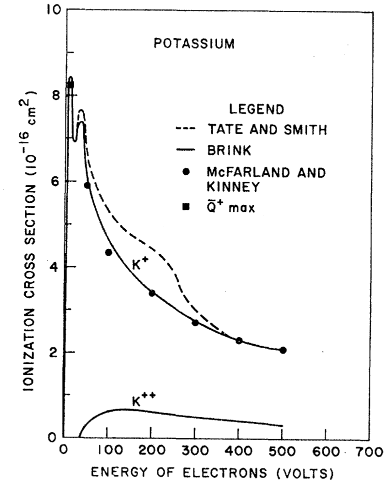

FIG. 5. Ionization cross section of potassium versus electron energy.

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[7] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).

TABLE I. The absolute cross sections for ionization by electron bombardment of the alkali metals. Comparative values including hydrogen are given and referenced. Values of Q^+ are given in units of 10^{-16} cm^2.

Element	50 eV	100 eV	200 eV		300 eV		400 eV		500 eV		(Max)	
H												0.7[a]
Li	3.1	2.2	1.5	...	1.2	...	0.99	...	0.83	...	4.9	...
Na	4.1	2.9	2.1	2.1[b]	1.6	1.7[b]	1.3	...	1.1	1.5[b]	7.6	8.6[b]
K	5.9	4.5	3.5	3.5[b]	2.7	3.3[b]	2.3	...	2.1	2.4[b]	8.2	9.6[b]
Rb	6.8	4.1	2.9	3.0[b]	2.4	2.6[b]	2.0	...	1.6	1.8[b]	8.8	9.6[b]
Cs	8.8	7.0	5.45	...	4.0	4.5[b]	3.4	...	2.8	4.5[b]	9.4	11.2[b]

[a] From Ref. 7. (Note change in units.)
[b] From Ref. 4.

error. That they should disagree for cesium is not entirely unexpected as the $\sum n\alpha_n$ play an important role in the calculation of Q^+_{Cs} and afford a source for significant error. Indeed the agreement for the cesium total ionization which does not involve this sum is excellent. For K$^+$, the agreement between the authors' measurements and those of Brink leads one to suspect the Tate and Smith results at intermediate energies. The unusual shape of their curve in this energy range lends support to this suspicion. It is perhaps needless to remark that the system of measurement used by Tate and Smith is quite different from the crossed-beam method, which virtually rules out the possibility of multiple-stage processes. Also, having had available the experience of the previous workers including the data and calculations of Brink, the authors have expended effort toward resolving apparent conflicts in measured values. Indeed, potassium has been the most widely measured element in this laboratory.

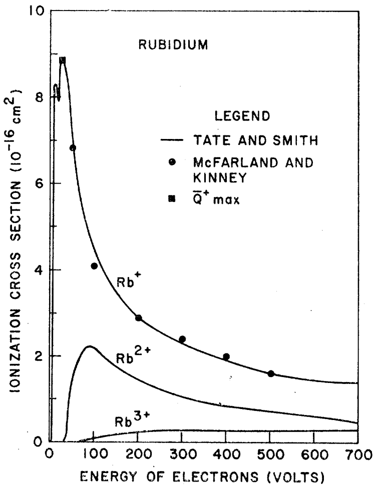

FIG. 6. Ionization cross section of rubidium versus electron energy.

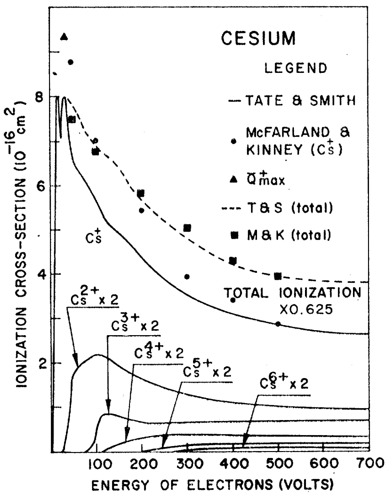

FIG. 7. Ionization cross section of cesium versus electron energy.

In conclusion, the absolute ionization cross sections for the alkali metals have been determined to an estimated relative probable error of less than 10% by assuming 100% surface ionization of alkali-metal beams on oxidized tungsten. Should future research invalidate this assumption, correction of the tabulated values will result from multiplication by the corrected efficiency factor as the velocity is a slowly varying function of efficiency. Preliminary work presently under way in this Laboratory which measures E directly should lead to cross-section values which are independent of the above assumption.

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