Absolute Ionization Cross Sections of the Alkali Metals*

G. O. BRINK†
Lawrence Radiation Laboratory, University of California, Livermore, California
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The absolute values of the cross sections for ionization by electron impact of sodium, potassium, rubidium, and cesium have been measured by a modulated crossed-beam technique. The values obtained for the maximum cross sections are tabulated and were observed to increase with increasing atomic number. An unsuccessful attempt was made to measure the ionization cross section of lithium.

INTRODUCTION

THE relative cross sections for the ionization of the alkali metals by electron impact have been measured by several different methods.[1–3] None of these experiments has been able to determine absolute values of these cross sections. The primary difficulty has been the determination of the density of the alkali vapor in the ionization region. The measurements described here were made by means of a crossed-beam technique in which the known properties of an atomic beam were used to determine the alkali-atom density in the ionization region. In this way it is possible to obtain an absolute value for the ionization cross section.

EXPERIMENTAL

A block diagram of the experimental system is shown in Fig. 1. With the exception of the ion-collection system the crossed-beam apparatus used in this experiment is the same as that used in the measurement of the relative ionization cross sections.[3] In this work the ions were simply collected on a metal plate that was biased with sufficient negative voltage to saturate the ion current. The ion current consists of two components: a dc current resulting from the ions produced from the background gas and an ac current at the chopping frequency resulting from the ions produced from the atomic beam. These two currents are separated by the electrometer and the ac signal is rectified by the phase detector and its amplitude recorded. This signal is, therefore, proportional to the total number of ions produced from the atomic beam. If the gain of the electronic system is known, this signal can be converted into a measure of the total number of ions formed from the atomic beam.

The intensity of the atomic beam is measured by means of a surface ionization detector. The beam is ionized by a heated tungsten wire and the resulting ac ion current is collected and measured by means of an electrometer. The negative potential on the ion collector is chosen such that the ion current is saturated indicating that all of the ions formed are being collected. If the ionization efficiency on the hot wire is known, this current may be converted into an absolute beam intensity at the position of the hot wire. The known properties of the atomic beam can then be used to calculate the atomic beam flux at the position of the electron beam.

In order to measure the beam flux it is necessary to know the ionization probability of the beam material on the hot wire. These probabilities for the alkalis on tungsten and oxidized tungsten have been measured by Datz and Taylor.[4] The shape of their curves of the fraction ionized versus temperature of the wire were reproduced in this experiment and this was taken as evidence that our conditions were about the same as those in their experiment. Their results were that all of the alkalis are completely ionized on oxidized tungsten and that rubidium and cesium are completely ionized on tungsten at a temperature of about 1300°K. In the measurements reported here both oxidized tungsten and oxide-free tungsten wires were used.

All of the data were taken at a high enough electron energy that the ion extraction field could not significantly perturb the electron beam. Care was taken to ensure that the entire electron beam passed through the atomic beam at all energies used. Generally data were taken at three electron energies with at least three measurements at each energy. All of these results were then combined to calculate the maximum value of Q^+ for each beam material.

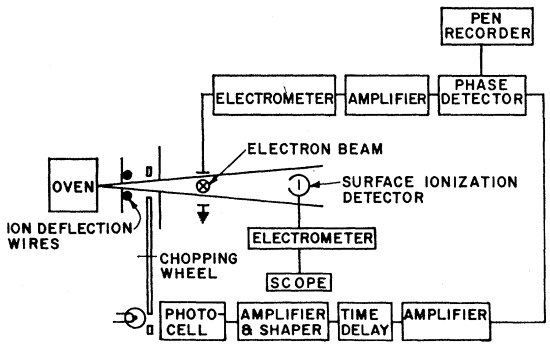

FIG. 1. Block diagram of experimental system.

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† Present address: Cornell Aeronautical Laboratory, Buffalo, New York.
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THEORY

The ion current in amperes resulting from the bombardment of an atomic beam by an electron beam can be written as follows:

$$I_i=\frac{\phi_e l I_e}{\bar{v}}\sum nQ^{n+}, \tag{1}$$

where ϕ_e is the atomic beam flux at the position of the electron beam, l is the path length of the electrons through the atomic beam, I_e is the electron current in amperes, $\bar{v}$ is the average velocity of the atoms in the beam, and Q^{n+} is the ionization cross section for the formation of ions of charge $n+$. Let the numbers α_n be defined by

$$Q^{n+}=\alpha_n Q^{+}. \tag{2}$$

Equation (1) can then be rewritten and solved for Q^+ to yield

$$Q^{+}=\bar{v}I_i/\phi_e l I_e\sum n\alpha_n. \tag{3}$$

The average velocity in the beam can be related to the ion current measured by the surface ionization detector by means of the following equation:

$$\bar{v}=GpE/MI_D, \tag{4}$$

where G is the constant containing apparatus parameters, p is the vapor pressure of beam material in the oven in mm of Hg, E is the probability of ionization of beam material on the hot wire, M is the molecular weight of beam material, and I_D is the ion current measured by the surface ionization detector.

Since the oven used in this experiment contained only a single chamber, it was not necessary to make a direct measurement of oven temperature in order to evaluate $\bar{v}$. The vapor pressure can be eliminated from Eq. (4) by means of the known vapor pressure versus temperature relations[5] and the equation

$$T=3.42\times10^{-9}M\bar{v}^2, \tag{5}$$

where T is given in °K. The result is

$$\ln\bar{v}=\ln\frac{GE}{MI_D}+\frac{2.92\times10^{8}A}{M\bar{v}^2}+B, \tag{6}$$

where A and B are the vapor pressure parameters as listed in Ref. 5. This equation can be solved to yield $\bar{v}$ for a given I_D.

The only remaining quantity in Eq. (3) that must be evaluated is ϕ_e. This can be obtained from the measured surface detector ion current by means of the following equation:

$$\phi_e=gI_D/E, \tag{7}$$

where g is a geometrical factor. Equations (3) and (7) can be combined with the measured value of l to yield

$$Q^{+}=2.55\times10^{-21}(\bar{v}I_iE/I_eI_D\sum n\alpha_n). \tag{8}$$

The values of α_n can be obtained from previous measurements[2,3] and the value of $\bar{v}$ is obtained from Eq. (6).

[5] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

TABLE I. Cross sections for ionization by electron collision.

Element	Values of Q^+ in units of 10^{-16} cm^2 200 eV	300 eV	500 eV	Q^+ (max)
Na	2.1	1.7	1.5	8.6
K	3.5	3.3	2.4	9.6
Rb	3.0	2.6	1.8	9.6
Cs	···	4.5	4.5	11.2

RESULTS

Table I shows the results of the cross-section measurement at several electron energies and the calculated values of the maximum cross sections. The results provide a reasonable fit to the relative curves.

An attempt was also made to measure the ionization cross section for lithium. While signals were seen it was not possible to obtain a sufficient signal-to-noise ratio to make a measurement. This was due to the fact that the cross section of lithium is smaller than those of the other alkalis. Also, the lithium atom-beam density was low at the limiting oven pressure due to the higher temperature and resulting higher atom velocity.

DISCUSSION OF ERRORS

It is difficult to assess the errors in an experiment of this type due to the large number of measured quantities that are used in the evaluation of the data. In addition to the errors accumulated in the actual measurement there are the errors that are present in the earlier work on the relative cross sections as well as the errors in the measurements of the ionization efficiencies on the hot wire. In this experiment there are a considerable number of geometrical measurements that were made in addition to the electrical measurements made in the actual taking of the data. For these reasons there is no reasonable way to evaluate the actual errors in the experiment.

About the best that can be done is to make an estimate of the error based on the scatter of the data. This, of course, says nothing about systematic errors in this or in the previous experiments. Based on these considerations it is reasonable to say that the data in Table I are probably good to within 20%.

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