Ionization of Alkali Atoms by Electron Bombardment*

GILBERT O. BRINK
Lawrence Radiation Laboratory, University of California, Livermore, California
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The relative ionization cross sections of lithium, sodium, and potassium have been measured over an electron energy range of threshold to 500 eV by a crossed-beam technique. The results for sodium and potassium are found to agree with those of previous workers. An attempt is made to correlate the structure observed in the potassium curve to the known energy levels of the atom. While the rubidium curve was not measured in this experiment, structure observed in it by other workers is discussed.

INTRODUCTION

STUDIES of the ionization properties of the alkali atoms date back to the earliest days of electron-scattering experiments. The work has been limited, however, to those alkalis whose vapor pressures are high enough to provide a suitable density in the gas phase at reasonably low temperatures. Since most of the experiments were done by electron scattering in a volume of gas, no work was done on lithium as the temperature that would be required would be of the order of 600°C. Lithium lends itself very well, however, to a crossed-beam experiment since it is a simple matter to heat an atomic-beam oven to the necessary temperature.

A considerable amount of work has been done on the ionization properties of the various alkalis.[1–3] Tate and Smith[4] have measured all of the ionization cross sections except that for lithium and their results will be discussed later.

EXPERIMENTAL

The experiments described in this paper were done using a modulated crossed-beam technique.[5] The system is described in detail elsewhere[6] and only the relevant features will be discussed here.

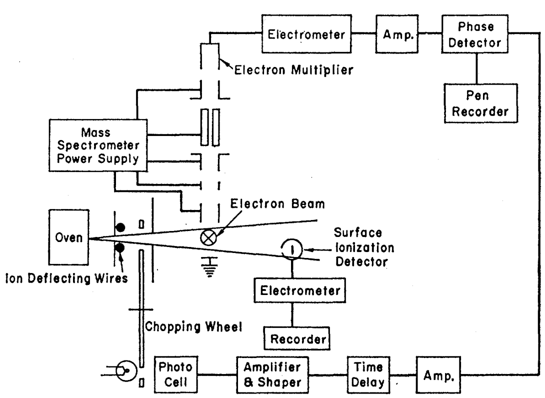

FIG. 1. Block diagram of experimental system.

A block diagram of the experimental system is shown in Fig. 1. The alkali atomic beam is produced by heating a stainless-steel oven containing the metal to the necessary temperature by electron bombardment. The atomic beam thus formed is modulated at 2 cps by a rotating wheel. The beam is crossed by a dc electron beam from a gun not shown in the figure. The ions formed are extracted from the interaction region by a weak electric field and focused into the entrance aperature of a Paul mass spectrometer.[7] After mass analysis the ions are focused onto the first dynode of a 14-stage electron multiplier.

The anode of the electron multiplier is connected to an electrometer whose input resistor serves as the anode load resistor. The electrometer separates the dc component of the signal due to background from the ac component due to the modulated beam. After suitable amplification the ac component feeds a phase detector whose output drives a pen recorder. In this manner a signal is obtained whose amplitude is proportional to the number of ions formed in the interaction region.

The electron gun is so designed that at least 98% of the total electron current used passes through the atomic beam. The electron beam is confined by a weak axial magnetic field that has no effect on the ions. All surfaces of the gun that are exposed to the ions are gold plated to minimize surface charging effects.

RESULTS

The relative ionization cross section of lithium is shown in Fig. 2. It shows the expected energy dependence for a simple ionization process. The experimental

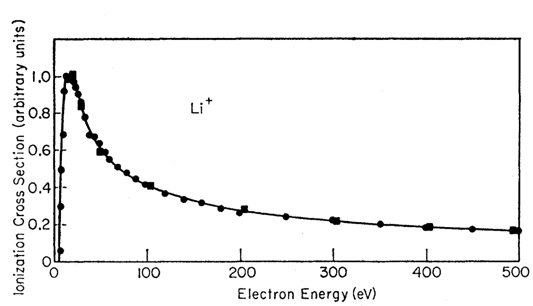

FIG. 2. Relative ionization cross section of lithium: ● experimental data; ■ equation $Q_i=6.41E^{-0.592}$.

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[1] R. B. Brode, Phys. Rev. **34**, 673 (1929).
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[3] A. L. Hughes and C. M. Van Atta, Phys. Rev. **36**, 214 (1930).
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[5] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).
[6] G. O. Brink, University of California Radiation Laboratory Report UCRL-6669, 1961 (unpublished).
[7] W. Paul and M. Raether, Z. Physik **140**, 262 (1955).

energy scale was adjusted so that the curve passed through the known ionization potential. This process, which corrected for contact potentials in the system, was applied also to the data for sodium and potassium. The amount of the correction was usually about 1 eV. A search was made for the Li^{++} ion but none was found. This indicates that it cannot have an abundance of more than a few percent of that of Li^{+}.

The curves for sodium and potassium are shown in Figs. 3 and 4. The present results agree generally with those of Tate and Smith.[4] The structure seen in the K^{+} curve was also observed by the previous workers. This structure and its interpretation will be discussed in the next section.

DISCUSSION

There is little theoretical work with which to compare the experimental data. A Born approximation for lithium has been calculated[8] and a comparison of this with the experimental data is shown in Fig. 5. The experimental data are arbitrarily normalized to the Born approximation at 500 eV.

It is interesting to note that over the region from 30 to 500 eV the lithium data lie on a straight line on the log-log plot. Below 30 eV the data deviate from this line as the ionization potential is approached. If the sodium data are normalized to lithium at 500 eV, they are seen to lie on the same straight line. This indicates that these cross sections have the same energy dependence over this energy range and differ only in absolute value.

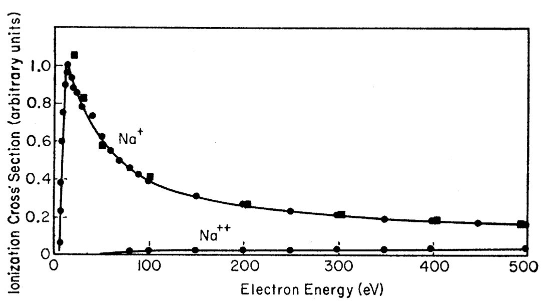

FIG. 3. Relative ionization cross section of sodium: ● experimental data; ■ equation $Q_i = 6.21E^{-0.592}$.

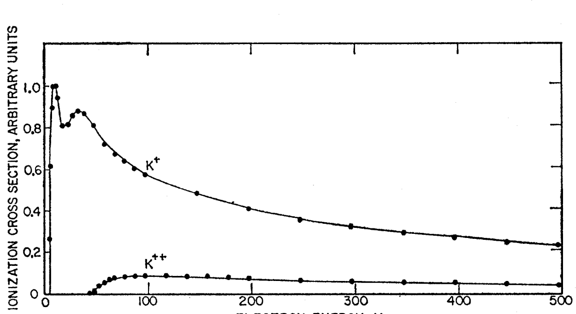

FIG. 4. Relative ionization cross section of potassium.

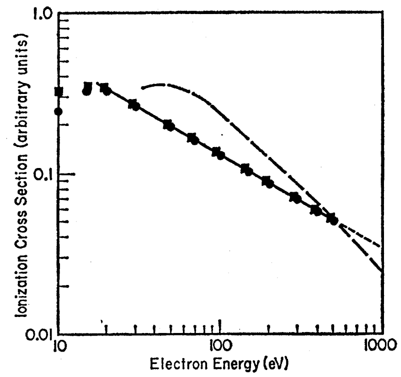

FIG. 5. Comparison of theory and experiment: Li data ●; Na data ■; dashed curve, Born approximation.

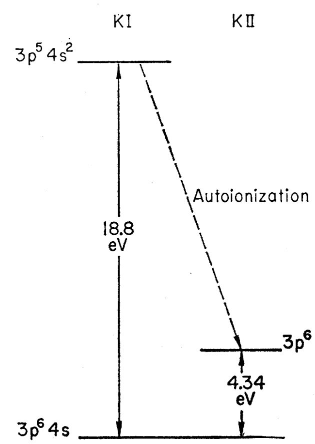

FIG. 6. Energy levels of the potassium atom.

The structure shown by the potassium curve can be discussed in terms of the energy levels of the atom,[9] some of which are shown in Fig. 6. At the time Tate and Smith first measured this cross section, they were unable to correlate the structure shown by it or the cross sections for rubidium and cesium to the atomic energy levels.

It can be seen from Fig. 6 that the ionization of potassium can proceed by two independent processes. The simple ionization corresponds to a transition from the electronic ground-state configuration $3p^6 4s$ to the ionic ground state $3p^6$. However, the ionic ground state can also be reached by the process of autoionization[10] through the $3p^5 4s^2$ excited state of the atom. The threshold for this second process is about 19 eV, and the

[8] M. R. C. McDowell and G. Peach, Phys. Rev. **121**, 1383 (1961).

[9] C. E. Moore, *Atomic Energy Tables*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D.C., 1948).

[10] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), Chap. XIX.

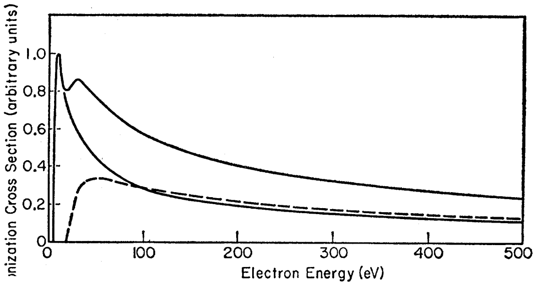

FIG. 7. Resolution of potassium curve: upper solid curve, total K^+; lower solid curve, simple ionization, $Q_i=4.94E^{-0.592}$; dashed curve, autoionization.

curve for the total ionization cross section to K^+ should exhibit a break at about this energy.

If it is assumed that the energy dependence of the cross section for simple ionization of potassium is the same as that for lithium and sodium, i.e., that cross-section points lie on the same straight line on a log-log plot, the total K^+ curve can be resolved into two curves as shown in Fig. 7. The lower solid curve corresponds to the cross section for simple ionization and the dashed curve corresponds to the autoionization process. It is seen that the lower curve exhibits the proper threshold of 19 eV.

The ionization cross section given by Tate and Smith[4] for Rb^+ exhibits similar structure to that of potassium and can be analyzed in a similar manner. The energy levels[9] are shown in Fig. 8 and it can be seen that the autoionization process should exhibit a threshold of about 15 eV. The Rb^+ ionization curve is shown resolved into its components in Fig. 9 and it can be seen that the autoionization component shows the proper threshold value.

The ionization cross section for Cs^+ obtained by Tate and Smith shows considerably more structure than the curves for K^+ and Rb^+. As of this writing the analysis of this structure has not been completed. There appear to be two atomic excited states which contribute to the autoionization process.

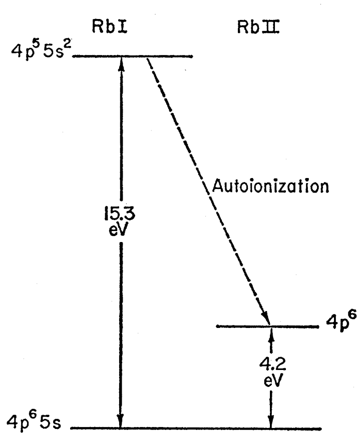

FIG. 8. Energy levels of the rubidium atom.

It is not the author's purpose to show that the resolutions of the above curves are unique, but only that they are consistent with the known experimental facts and energy levels. It is very difficult to experimentally distinguish between simple ionization and autoionization since they both lead to the same reaction product. Hence, no information is available on the ionization cross sections of the separate processes except that obtained by the above method.

It is interesting that the alkalis seem to exhibit the same energy dependence of their single ionization cross sections over such a wide energy range. This suggests that all of these cross sections can be expressed by a relation of the form

$$Q_i=\alpha E^{-\beta}, \qquad (1)$$

where α and β are constants. The constant β can be evaluated from the slope of the line shown in Fig. 5.

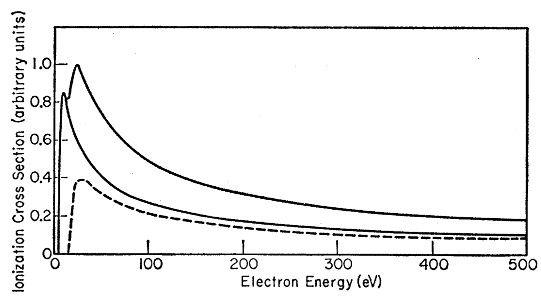

FIG. 9. Resolution of rubidium curve: upper curve, total Rb^+; middle curve, simple ionization, $Q_i=4.18E^{-0.592}$; lower curve, autoionization.

The best value that can be obtained from the graph is $\beta=0.592$. The constant α depends on the absolute value of the cross section and will be different for each case.

Equation (1) has been plotted in both Figs. 2 and 3 with the value of α chosen to make the points agree at 500 eV. The fit seems to be very good in both cases over the energy range from 30 to 500 eV. The values of α given are relative only and their correct values must wait until absolute values of the ionization cross sections are available. An experiment is being undertaken at this laboratory to measure these absolute values.

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