IONIZATION OF ALKALI METAL ATOMS BY SLOW ELECTRONS

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An improved technique for studying ionization in crossed atomic and monoenergetic electron beams is described. The ionization cross sections are measured for all alkali metals at electron energies from threshold to 30 eV. The linear increase of the cross sections that is predicted by Geltman's theory at the ionization threshold is observed, and the linear interval is determined for each atom. The complex structure observed in the cesium, rubidium, and potassium ionization curves can be accounted for consistently and uniquely by p-electron excitation of the alkali atom followed by its ionization with ejection of the p electron.

INTRODUCTION

The ionization of alkali metal atoms by electron impact has been investigated frequently. Tate and Smith were the first to measure the ionization functions of sodium, potassium, rubidium and cesium, using volumes of the metal vapors. Using a variant of that technique, one of the present authors measured the ionization cross sections of potassium and cesium. The crossed beam technique was used to measure the cross sections for ionization of alkali atoms by electrons from 50 to 500 eV, and to obtain the cross sections in the region (10-30 eV) of maximum efficiency.

The behavior of the ionization function at threshold for different alkali atoms has been studied and by the volume of gas technique, and by means of crossed beams. However, these publications contain no discussion of the threshold behavior. Theoretical studies had previously indicated two different dependences of the ionization cross section on the excess energy possessed by the electrons above threshold. Geltman predicted a linear law, while Wannier predicted a power law with the exponent 1.127. It therefore became necessary to perform new experiments in which alkali atom ionization by low-energy electrons would be investigated systematically and thoroughly. Our work was undertaken to develop a sufficiently reliable means of determining the absolute ionization cross sections and to perform careful ionization measurements for all alkali atoms near threshold, including the region of maximum efficiency.

APPARATUS AND EXPERIMENTAL TECHNIQUE

Our experiments were based on the crossed beam technique, which was first used by Funk and later by other workers, to investigate the ionization of atoms. We made further improvements by using electron beams having a small energy spread and also a new means of measuring the neutral particle density in the atomic beam.

The main units of the apparatus are: 1) an atom furnace, 2) a detector of neutral atom density, 3) a 127-degree electrostatic electron selector, and 4) an ion registration unit. The first three of these units were placed inside the vacuum chamber (Fig. 1), which was made of stainless steel with metallic seals. Following the requisite heating of the chamber the residual pressure during measurements was (0.5-1) x 10^-7 Torr. The sources of neutral atoms were effusion chambers which are of simple construction and furnish a very stable atom beam for a protracted period of time. Metal atoms evaporated from the chamber; a beam was formed with the aid of two hot slits and one cold slit, having the respective dimensions 0.2 x 1 mm and
5 x 6 mm. Stainless steel was used for both the effusion chamber and the slits, and the atom beam spread was at most six degrees.

The techniques described in the literature for measuring atom intensities in beams\(^\text{11}\) suffer from several deficiencies, including low accuracy and limited applicability. We therefore used an electronic technique, determining the mass of atoms condensed on the surface of a piezoelectric quartz crystal (cooled by liquid nitrogen) from the change of natural vibrational frequency. This change is directly proportional to the mass \(M_k\) of condensed material.\(^\text{12,13}\)

\[
\Delta f = (\nu/S)^2 M_k, \tag{1}
\]

where \(S\) is the area of the condensate on the crystal and \(k_f\) is a constant that depends on the crystal cut and frequency. We used AT-cut quartz having the natural frequency \(f_0 = 4.79 \times 10^9\) Hz.

The circuit used to determine the frequency change (Fig. 2) consists of a quartz measuring oscillator 1, a reference oscillator 2, a frequency mixer 3, a difference frequency amplifier 4, a frequency meter 5, and an oscillograph 6 for monitoring the shape of the low-frequency signal. The measuring and reference crystals were attached to a liquid nitrogen trap (Fig. 1). We obtained \(\pm 5\) Hz frequency stability during a period of 5 minutes (the usual experimental period). The constant \(k_f\) was calculated\(^\text{(12)}\) and also determined experimentally with a torsion balance; agreement, with \(3\%\) error, was obtained for the value \(1.9 \times 10^{-8}\) g-Hz\(^{-1}\)-cm\(^{-2}\).

The density of atoms in the collision region was determined from the equation

\[
n = \frac{M_k}{\nu lb m}, \tag{2}
\]

where \(l\) and \(b\) are the dimensions of the atom beam (2.5 x 6 mm) where it is crossed by the electron beam, \(\nu\) is the time during which atoms condensed on the piezocrystal, \(\bar{v}\) is the mean velocity of beam atoms, and \(m\) is the atomic mass.\(^\text{11}\) The atom concentration in this region was varied, by changing the source temperature, between the limits \(1 \times 10^{15}\) and \(6 \times 10^{14}\) atoms/cm\(^3\).

A monoenergetic electron beam was formed by an apparatus that included a 127-degree electrostatic selector.\(^\text{14}\) A flat beam with a velocity spread of only 0.5 eV for 90% of the electrons was obtained from a conventional electron gun with an indirectly heated oxide ribbon cathode. All parts of the electron monochromator, made of stainless steel, were specially treated, and then assembled and adjusted under a microscope. This type of monochromator provided electron beams with a spread of at most 3-5%. The absolute values of the ion current \((10^{-12}-10^{-11}\ A)\) were measured, as a rule, at the ionization maximum, when the contribution from residual gas ionization was negligible (< 1 for \(p = 0.5-1\))

\[
Q = \frac{i_{\text{ion}} T}{M_k l_v T} \tag{3}
\]

where \(M_k\) is obtained from (1), \(i_{\text{ion}}\) is the ion current, \(l_v\) is the electron current, \(T\) is the absolute temperature of the metal vapor in the source, and \(c = 2.2 \times 10^{-8}\ \text{cm-sec}^{-1}\text{-g}^{-1}\text{-deg}^{-1/2}\) is the constant of the method. Relative ionization curves were obtained with a spread of at most 3-5%. The absolute values of the ion current \((10^{-12}-10^{-11}\ A)\) were measured, as a rule, at the ionization maximum, when the contribution from residual gas ionization was negligible (< 1 for \(p = 0.5-1\))

\[\text{FIG. 3. Ionization cross sections of lithium and sodium. 1—our results; 2—obtained by Tate and Smith [1]; 3—obtained by Kochevol and Przhonskii [1]; 4—calculated using Gryzin's approximation.}\]

\[\text{FIG. 4. Ionization cross section of potassium. 1—our results; 2—obtained by Tate and Smith [1]; 3—obtained by Kochevol and Przhonskii [1]; 4—calculated using Gryzin's formula.}\]
The relative error of the absolute cross sections is ± 15%, and the rms error is ±12%.

Control measurements showed that our technique for investigating atomic ionization cross sections is characterized by high sensitivity \((10^{14}-10^{15} \text{ atoms/sec})\), universality, satisfactory accuracy, and very good energy resolution of the ionization curve structure.

RESULTS AND DISCUSSION

We investigated the ionization of five alkali atoms at energies from threshold to 30 eV. The behavior of the ionization curves was investigated especially thoroughly at threshold and at the ionization maxima. Most of the relative and absolute measurements were visual readings of a precision pointer-type instrument; other measurements (of the ionization curves) were obtained with a recording electronic potentiometer. In the last instance the electron energy was given by a special potentiometer which was rotated by a synchronous motor.

The absolute cross section measurements were repeated nine or more times while varying the electron and atom densities and with different geometries for the beam crossing region.

Our principal results are presented in Figs. 3–8 and in the table. The horizontal axis of the drawings represents the electron energy in electron volts with 0.1–0.2 eV uncertainty. The vertical axis in Figs. 3–6 represents absolute ionization cross sections in cm\(^2\), and in Figs. 7 and 8 represents relative cross sections in arbitrary units.

1. Complex structure of ionization functions and its origin

We shall first consider the ionization functions of the atoms. The curves for different atoms are characterized by an absence of similarity in their behavior at low energies. The ionization functions of lithium and sodium exhibit the simplest form, with one broad peak; the curves for potassium and rubidium have two maxima, and that for cesium has three. We observe a gradual shift toward lower energies of the first peaks as the atomic number increases. A similar tendency of the second maxima for K, Rb, and Cs is also observed.

It is obvious that the clear first peak (at 9.5 eV) of the ionization function of cesium, which was first discovered by us, along with the improved sharpness and accuracy of all other ionization maxima of alkali atoms result directly from the more advanced technology used in our experimental work.

The ionization functions of all the atoms are collected in Fig. 7 for convenience in connection with further discussion. We believe that the complete and unequivocal explanation of the complexity of these curves can be derived from the fact that when electrons collide with...
alkali metal atoms the kinetic energy of the electrons is transferred both to s electrons and to inner p electrons of the alkali atoms.

Let us therefore consider the most complex ionization, which is observed in the case of cesium. The first peak (see the table) can here reasonably be attributed to ordinary s-electron ionization:

$$A + e^- \rightarrow A^+ + 2e,$$

where $A$ and $A^+$ are the neutral atom and the ordinary ion. The second and third maxima arise through p-electron excitation and ionization:

$$A + e^- \rightarrow A^+_p + e^- \rightarrow A^{++} + 2e,$$

where $A^+_p$ and $A^{++}$ are the excited atom and the ion (minus a p-electron).

The foregoing account is confirmed, first of all, by the level scheme of Cs in the case of p-electron excitation. The group of the lowest excited levels is here 12.3, 13.5, 14.1, and 14.2 eV. Autoionization then converts these excited atoms into states of ordinary ions, and at about 12–13 eV the ionization curve begins to rise steeply to a maximum at 15 eV. On the other hand, the four ionization limits of Cs for the detachment of a p electron are 17.2, 17.5, 18.8, and 19.1 eV. This type of ionization obviously causes the third maximum of Cs ionization, beginning at 18–20 eV.

Secondly, the maximum at 15 eV is clearly revealed in all the excitation functions of cesium lines from the 2S, 2P, and 2D levels, whose relative roles increase with the higher principal quantum number of the level. This maximum is also uniquely associated with the aforementioned group of excited Cs levels (p-electron transitions). Some of the excited states of $A^+_p$ undergo cascade transitions to ordinary excited states of cesium.

![FIG. 8. Ionization curves of alkali atoms near threshold.](image)

For rubidium the excitation energy involving the analogous group of p levels is considerably higher (15.2, 16.2, 17.0, and 17.3 eV); this leads to a corresponding shift of the second ionization curve maximum. The location of the second maximum (and its beginning) is shifted still more in the case of potassium, whose excited p states encompass the interval 18.7–20 eV.

Since according to Moore the limits of the excited p levels of lithium and sodium are 34 and 54 eV, respectively, we can understand why the ionization functions of these elements exhibit no nonmonotonic behavior (in our energy range).

From the foregoing we conclude that ordinary ionization (the detachment of an s electron) is observed in its pure (simple) form only in the cases of lithium and sodium, but that in the heavier alkali atoms it is masked by additional ion-formation processes, for which p electrons are responsible.

We note here that the hypothesis of p-electron participation in the ionization of potassium and rubidium was previously presented by Kaneo and by Brink, who were unable, however, to extend the hypothesis to cesium. (It is now clear that their failure to do this resulted from very crude measurements of the cesium ionization curve in earlier work.) Therefore the character of cesium ionization that we have observed furnishes a clue to a consistent and unequivocal explanation of the ionization-curve behavior for all the alkali atoms near threshold.

The dashed lines in Fig. 7 distinguish simple ionization from the other processes for potassium, rubidium, and cesium. We observe, on the one hand, that the cross sections for ordinary ionization of all fire atoms have very similar energy dependence. On the other hand, for certain incident electron energies the p electrons make very large contributions to the ionization of Cs, Rb, and K.

2. Ionization cross sections at low energies

The absolute ionization cross sections for the greatest maxima are given in the table, while Figs. 3–6 show the cross sections for the entire energy interval. Our results are in good general agreement with those in and especially with the first of these. The differences between the results obtained in the three investigations lie practically within the limits of experimental error, although in the absolute cross sections are a little too large and the positions of the maxima were determined with considerably less accuracy.

The fact that three investigations using very different techniques are in agreement, within experimental error limits, indicates that we now have reliable ionization cross sections of alkali atoms both at low energies (our results), and in the region 30–500 eV.

Figures 3–6 also show that the experimental results are in satisfactory general agreement in the regions of the maxima with the cross sections that we calculated of course, these curves have been plotted with a certain degree of arbitrariness.

We did not measure the absolute cross section for rubidium ionization; the obtained ionization function was normalized in accordance with the results given in [1] for the principal maximum.
Ionization of alkali metal atoms by slow electrons

Ionization of atoms by electron impact has thus been found to be considerably more complex than had been anticipated. A comprehensive and careful investigation could therefore obtain valuable and extensive knowledge regarding the characteristics of inelastic electron-atom collisions.

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