Probability Curves near Threshold for the Formation of He^+, Ne^{++}, A^{++}, Kr^{++}, and Xe^{++} by Electron Impact

W. M. Hickam, R. E. Fox, and T. Kjeldaas, Jr.
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

(Received June 23, 1954)

The formation of He^+, Ne^{++}, A^{++}, Kr^{++}, and Xe^{++} as a function of electron energy is studied with essentially monoenergetic electrons. The He^+ curve obtained in this way for an energy range of eight volts above the ionization threshold does not exhibit any detectable departure from linearity. The accuracy is such that the difference between a 1.0 and 1.1 power curve is detectable for this energy range. The ionization probability curves of the doubly charged ions is interpreted as the superposition of linear excitation curves arising from each of the $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, and $^1S_0$ states of the ions.

I. INTRODUCTION

IONIZATION probability curves obtained with monoenergetic electrons[1,2] for singly charged ions exhibit a threshold law which varies linearly with the excess electron energy. When this linear threshold law was applied to the analysis of ionization probability curves of Xe^+ and Kr^+ it was demonstrated that the observed structure could be correlated to energy levels of the ions.[3] For at least a few volts above threshold, the total ionization cross section could be treated as the sum of linearly increasing cross sections for each state of the ion. Certain departures from linearity over restricted regions were adequately explained by the autoionization of excited states of the atoms. More recently, Wannier[4] has extended the work of Wigner to ionization processes and has given theoretical arguments for a general threshold law applicable to singly charged ions formed by direct electron impact. Since the earlier reported work, instrumental modifications have made it possible to study ionization probability curves over a somewhat wider energy range. Because the singly charged helium ion has no energy levels within some 40 volts of the ionization potential, it was chosen for a further study of the threshold law.

A natural extension of these studies is the examination of ionization probability curves resulting from the formation of doubly charged ions of the rare gases. Curves obtained for doubly charged rare gas ions by other investigators[5–7] exhibited a considerably larger amount of curvature or "tailing" near the ionization threshold than did those for the singly charged ions. Since the tailing due to the electron energy spread should have been comparable for the two cases, the excessive tailing for doubly charged ions was believed to be characteristic of the formation of these ions.

The retarding potential difference method[8] developed by the authors[1,2] substantially reduces the effects of electron energy spread and thus makes possible a detailed examination of the structure of ionization probability curves. The fact that the doubly charged rare gas ions (except He^{++}) have five energy levels near the ground state allows one to extend the studies of the effects of energy levels on these curves.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The experiments were performed with a mass spectrometer employing the RPD method of obtaining relative ionization probability curves. The instrument and procedure was similar to that employed in the study of singly charged ions[1,3] with the exception that an electron multiplier was used as the ion detector in order to obtain greater sensitivity.[9]

1. Ionization Probability of He^+

The ionization probability curve for He^+ is shown in Fig. 1 for an energy range of some 8 ev. The energy scale of this curve, as well as all subsequent curves, has been adjusted so as to make the appearance potential agree with the spectroscopically determined ionization

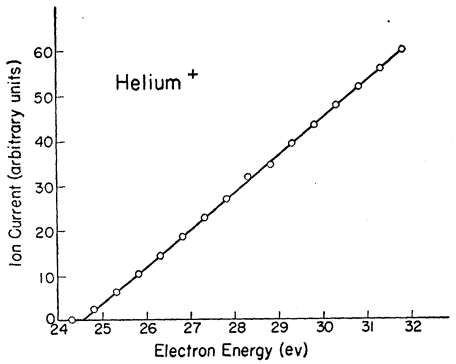

FIG. 1. Ionization probability curve for He^+. The onset has been made to agree with the spectroscopically determined ionization potential.

[1] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. **84**, 859 (1951)
[2] Fox, Hickam, Kjeldaas, and Grove, National Bureau of Standards Circular 522 (U. S. Government Printing Office, Washington, D. C., 1953), p. 211.
[3] Fox, Hickam, and Kjeldaas, Phys. Rev. **89**, 555 (1953).
[4] G. Wannier, Phys. Rev. **90**, 817 (1953).
[5] W. Bleakney, Phys. Rev. **36**, 1303 (1930).
[6] D. P. Stevenson and J. A. Hipple, Phys. Rev. **62**, 237 (1942).
[7] Dibeler, Mohler, and Reese, Bur. Standards J. Research **38**, 617 (1947).
[8] Hereinafter referred to as the RPD method.
[9] A detailed description of the apparatus and method is being prepared for publication as a separate paper.

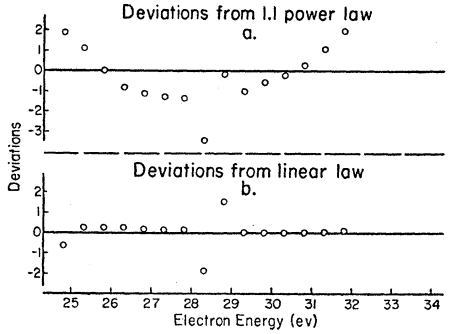

FIG. 2. (a) The deviation of the experimental points of Fig. 1 from the best fit by least squares to a 1.1 power curve. (b) The deviation of the same points from a linear (1.0) curve.

potential. In general, this correction was 0.3 ev or less. Figure 2 was prepared to exhibit quantitatively the degree of linearity obtained. The bottom curve shows the deviations of the points from a linear law, while the top curve shows the deviations of these same points from a 1.1 power law. These deviations were determined by least-squares fit in both cases. Wannier's[4] theory for a threshold law predicts that for an energy range small compared to the Rydberg energy,

$$I^+ = AE^{1.127},$$

where A is a constant of proportionality, and E is the electron energy in excess of the ionization potential. The curves in Fig. 2 definitely show that the 1.1 power law does not fit the data as well as the linear law. It must be noted, however, that this curve covers an energy range of 8 volts and thus may not be a true test of Wannier's law. If the energy range is limited to one or two electron volts, the scatter in the experimental points makes it impossible to determine which of the two power laws gives the best fit to the data. Thus, a comparison of the 1.1 power law and the linear law for other gases did not lead to a definite conclusion.

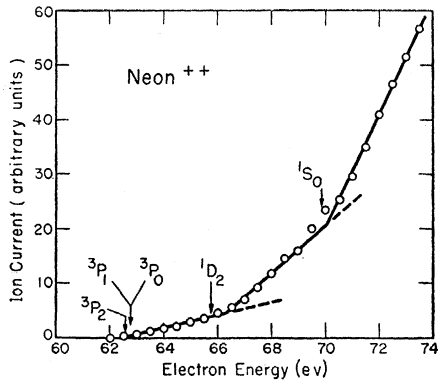

FIG. 3. An ionization probability curve for the formation of Ne^{++}. The onset has been made to agree with the spectroscopically determined ionization potential. The location of the energy levels are determined by spectroscopic data.

2. Ionization Probability of Ne^{++}, A^{++}, Kr^{++}, and Xe^{++}

The ionization probability curves for Ne^{++}, A^{++}, Kr^{++}, and Xe^{++} are shown in Figs. 3, 4, 5, and 6, respectively. The positions of the energy levels above the $^3P_2$ ground state as given by spectroscopic data[10] are shown on each curve by appropriately placed arrows.

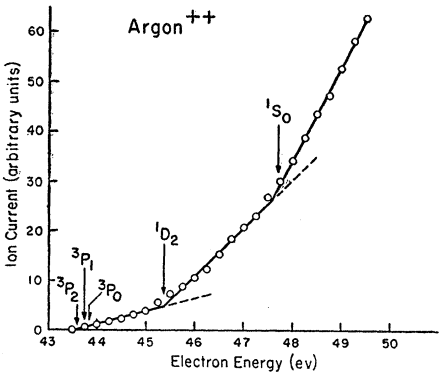

FIG. 4. Ionization probability curve for the formation of A^{++}. The energy scale has been adjusted to make the designated energy states agree with the spectroscopically determined values.

Actually, several runs were made for each gas, the curves shown here are believed to be typical. The curves are analyzed on the same basis as were the singly charged ions, i.e., the assumption is made that they are the sums of linearly rising cross sections for each level of the ion formed. In the present case, however, five states are involved: $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, and $^1S_0$; and since the

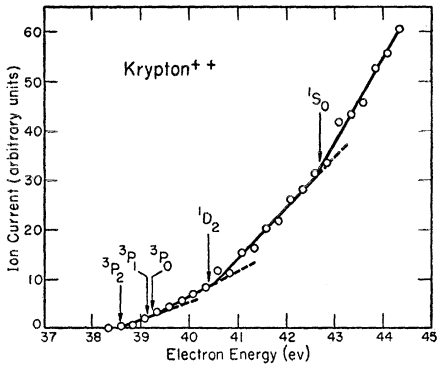

FIG. 5. Ionization probability curve for the formation of Kr^{++}. The energy scale has been adjusted to make the designated energy states agree with the spectroscopically determined values.

scatter is more severe, the correctness of this assumption cannot be demonstrated by using it to locate the energy levels and then comparing the results with spectroscopic

[10] All identified states are taken from C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1952); Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1950), Vol. I. The conversion factor used is 8066.8 cm^{-1} per volt from J. W. M. DuMond and E. A. Cohen, Phys. Rev. 82, 555 (1951).

data. Instead, the levels are located on the curves from the spectroscopic information, thus dividing the curves into successive energy regions. Within any one energy region the points should fall on a straight line. Figures 3 through 6 were prepared by fitting the best straight line to the data within each energy region. The relatively good fit of the points to the straight lines, and the agreement of the intersections of these straight lines with the marked levels is an indication that the assumption is at least approximately valid. The largest discrepancy occurs in the Ne^{++} curve where the average of three runs disagrees with the $^1D_2$ and $^1S_0$ levels by about 0.5 ev. In the other cases the agreement was usually better than 0.2 ev. Furthermore, a certain amount of departure from linearity is evident in the vicinity of the breaks for the neon and argon curves. Perhaps these deviations may be explained on the basis of contributions from autoionization. This effect would be similar to that observed in the case of the singly charged ions.[3]

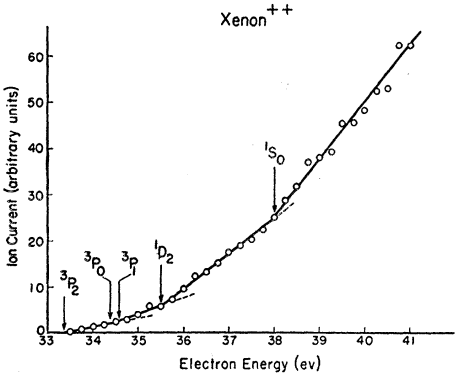

FIG. 6. Ionization probability curves for the formation of Xe^{++}. The energy scale has been adjusted to make the designated energy states agree with the spectroscopically determined values.

This method of analyzing the data implies that the threshold law for the formation of doubly charged ions in a single state goes linearly with the excess electron energy just as for singly charged ions. The initial portion of the ionization probability curve for Xe^{++} was studied in great detail and is shown in Fig. 7. This curve gives the most direct information of the group studied since the first excited energy level of this ion is about one volt higher than its ground state. A number of curves were taken in this region of which Fig. 7 is typical. It is apparent from the curve that there is no evidence for other than a linear threshold law. Wannier has reported in a private communication that the arguments which led to the 1.127 power law[4] for single ionization would

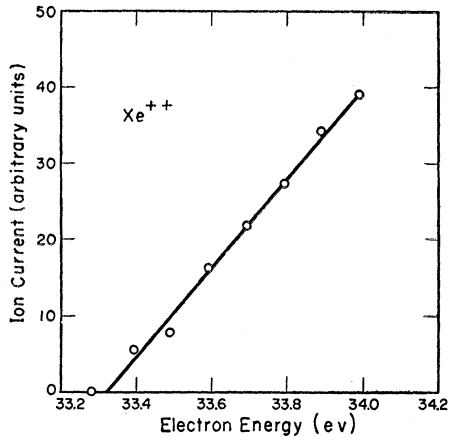

FIG. 7. The ionization probability curve for the formation of Xe^{++} taken between the $^3P_2$ ground state and the $^3P_0$ state to demonstrate the linearity of the ionization threshold law. The energy scale has been adjusted to make the onset of the curve agree with the spectroscopically determined ionization potential.

lead to a threshold law which varies approximately as the square of the excess electron energy in the case of double ionization.

Additional evidence for a linear rather than a higher power law is found in the early work of Bleakney[5] on the multiply charged ions of argon and neon. In his work the straight line sections of the ionization probability curves for A^{+++} and Ne^{+++} yield pronounced breaks which are in good agreement with the spectroscopically determined energy levels for the removal of two p electrons and a single s electron.

The results of the work reported here coupled with Bleakney's work provide evidence that a linear threshold law holds for doubly as well as singly charged ions. The deviations of the points from linearity in some of the curves are attributed to additional ionization processes such as autoionization. It is evident from the data that an appreciable electron energy spread would yield a smoothly varying curve and hence result in a loss of information concerning the ionization processes associated with the energy levels. The most positive test of the threshold law for the formation of doubly charged ions would be obtained from a study of He^{++}. Unfortunately, however, interferences from a background current of H_2^+, coupled with the low ion yield for $(He)^{++}$ prevented this investigation. It is hoped that in the near future such a study can be made using He^3.

The authors wish to express their appreciation to Dr. D. J. Grove for his many helpful discussions, and to other colleagues in the Physics Department for their critical review of the manuscript.