at approximately 15 Mev, the reported[18] photofission resonance energy for U^{238}. The resonance is expected to be at approximately the same[19] energy in the case of Th^{232} and U^{235}. The ratios from the proton bombardment of normal uranium[7] are considered to be upper limits since the fission product selected in the work, Ag^{111}, is probably not at the bottom of the trough. These data are presented with downward arrows. With two exceptions, the remaining points lie on a reasonably smooth curve. The ratio for the thermal neutron fission[14] of Pu^{239} is definitely higher than the other data at comparable excitation. The other striking deviation is the lone experiment[4] reported on the photofission of U^{235}. It is possible that in this work the betatron energy was not sufficiently greater than 15 Mev to take advantage of the photofission resonance.[20] Within the accuracy of our knowledge of the energy of the Li+D neutrons causing fission in this study, the results reported here lie on the curve.

Figure 2 indicates the strong energy dependence of symmetrical fission and can be interpreted as an excitation curve for the formation of symmetrical products relative to asymmetrical ones in the fission of heavy elements. It would indicate, for example, that the yield of symmetrical products in spontaneous fission (if the main peaks are well separated) would be immeasurably low.

Table I and Fig. 1 also illustrate that the increase in neutron energy from pile neutrons to Li+D neutrons has a much less drastic effect on the low yields on the light side of the light peak. The yield of Ge^{77} has increased 2.7-fold; that of Br^{83} only by 40 percent. The increase in yield in this region in the case of Th^{232} can be explained semiquantitatively by the postulate that an appreciable fraction of the fissions with Li+D neutrons involve the emission (before or after fission) of one or two more neutrons than in the case of pile neutron fission. This insensitivity to energy in this region of the yield curve confirms the data of Newton.[6] In his work the same two mass chains had approximately the same yields from U^{236} excited by about 33 Mev as in U^{236} formed from thermal neutrons on U^{235}. Newton's work on U^{236} excited by 33 Mev also shows little increase in yields on the heavy side of the heavy group. Thus, both the work on Th^{232}+37.5-Mev alphas[6] and this work emphasize the difference between the restrictions preventing symmetric and very asymmetric fission.

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Ionization Probability Curves for Krypton and Xenon near Threshold

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The shapes of the ionization probability curves of krypton and xenon have been determined near the ionization potential by measuring the ionization produced by nearly monoenergetic electrons in a mass spectrometer. Ionization processes associated with the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ ground states of the ions are clearly resolved. Ions are observed which are attributed to auto-ionization of atoms excited to the higher states having the $^2P_{\frac{1}{2}}$ core configuration.

I. INTRODUCTION

LITTLE information is available concerning the true shapes of ionization probability curves near threshold. This is largely owing to the difficulty in obtaining an electron beam with a sufficiently narrow energy spread. Lawrence,[1] and later Nottingham,[2] in their study of the ionization probability of mercury used a magnetic analyzer to reduce the energy spread of the electron beam. In this type of experiment where total ionization is measured precautions are necessary to distinguish photoelectric effects and true ionization and to eliminate impurities in the gas sample. If, however, only the shape of the ionization probability curve is to be determined, one may use a mass spectrometer in which a positive analysis of the ions produced largely eliminates the need for these precautions.

On the other hand, the problems associated with the production of a sufficiently monoenergetic electron beam in a mass spectrometer were solved only recently. With the use of this new method it was demonstrated[3,4] that within the experimental accuracy then attainable, the ionization produced was directly proportional to the excess energy of the bombarding electrons in the region near the threshold.

In the earlier work,[3] it was reported that a slight break sometimes observed in the ionization probability curves for krypton might be attributed to the doublet ground state of the krypton ion. Since then, an increase in sensitivity, due in part to a new pulsing circuit,[5] has permitted a more detailed study of ionization prob-

[1] E. O. Lawrence, Phys. Rev. **28**, 947 (1926).
[2] W. B. Nottingham, Phys. Rev. **55**, 203 (1939).
[3] Fox, Hickam, Kjeldaas, and Grove, Proc. of the Symposium on Mass Spectroscopy in Physical Research, Natl. Bur. Standards Circular 522, January, 1953.
[4] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. **84**, 859 (1951).
[5] To be published.

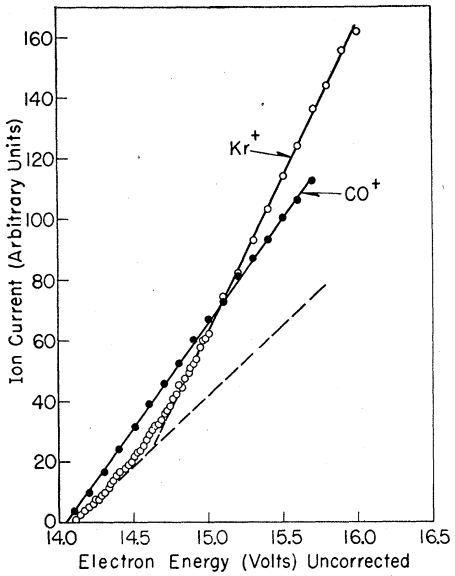

FIG. 1. Relative ionization probability curve for Kr and CO. The slight corrections necessary to establish the absolute energy scale have not been applied. The experimental probable error is indicated by the size of the data points.

ability curves. The results of studies on krypton and xenon, to be presented in this paper, reveal detailed structure of the ionization probability curves. It will be shown how these hitherto unobserved details can be correlated with information about the energy levels concerned.

II. EXPERIMENTAL PROCEDURE

The gas samples used were purchased from the Air Reduction Sales Company and were of the "spectroscopically pure" grade. No further purification was necessary since a scan of the mass spectra for these samples indicated that there were no conflicting impurities present. A pressure less than 10^{-4} mm of mercury was maintained in the ion source during observations.

The ionization studies were made using a 90° sectored magnetic field mass spectrometer similar in design to the type L-V manufactured by Westinghouse. The ion source was modified for use of the "retarding potential difference method" described in the earlier papers.[3,4] This method utilizes a retarding electrode between the filament and the ionization chamber which serves to chop off sharply the low energy electrons from the original distribution. The sharp lower boundary energy in this chopped distribution can be varied by changing the potential of this retarding electrode without appreciably affecting the rest of the distribution. The *difference* in the ion currents for two values of the retarding potential is therefore the ion current produced by electrons monoenergetic to within this change in the retarding voltage. This method then serves to eliminate effects resulting from the thermal energy spread of the electrons as well as the unknown contact potential between the filament and the ionization chamber. Since an auxiliary magnetic field is employed to align the electron beam, those electrons which have an initial transverse velocity move through the electron gun with a spiraling motion. The energy contained in this spiraling motion is adequately limited by making the slits through which the electrons pass sufficiently narrow. The effect on the electron energy owing to the electric field employed for ion removal from the ionization chamber was eliminated by giving this field and the electron beam a properly phased pulsed time dependence, so that electrons reach the ionization chamber only when the ion removal field is zero. Employing these techniques, the effective electron beam possessed a maximum energy spread of 0.06 ev and the total kinetic energy of the electrons was known to within 0.1 ev whenever an ion source with fresh surfaces was used. It was found, however, that a contact potential between the retarding electrode and the ion chamber, presumably the result of deposits from the filament, would build up with time. In the earlier work,[3,4] where ionization potentials were measured on an absolute basis, only fresh surfaces were used to minimize errors resulting from this source. Since the purpose of the present studies was to investigate the shapes of the ionization probability curves near threshold, a knowledge of the absolute energy scale was not essential; therefore, this contact potential was allowed to build up to about 0.3 volt before the ion source was removed and cleaned. For the same reason the correction for space charge in the electron beam employed in the earlier

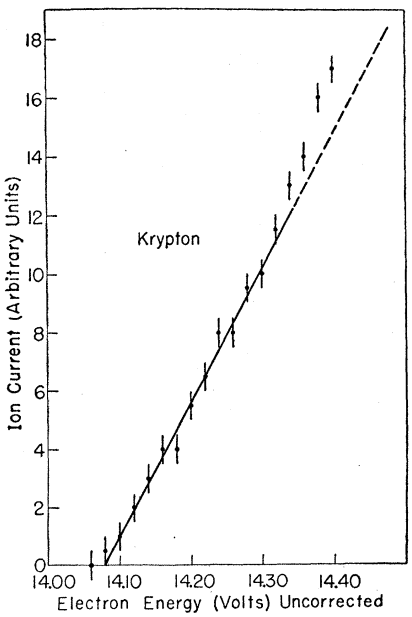

FIG. 2. The initial portion of the relative ionization probability curve for Kr on an expanded scale. The experimental probable error is indicated by the height of the lines through the data points.

work was not made. The curves shown in this paper therefore give the electron energy as uncorrected. The over-all magnitude of these corrections are small however, as can be seen by a comparison of the measured appearance potentials with the spectroscopically determined ionization potentials.

III. EXPERIMENTAL RESULTS

In Fig. 1 are shown the curves obtained for krypton and carbon monoxide. The carbon monoxide (observed at mass 28) curve is used to illustrate the linearity of ionization probability curves obtained by this method when only a single ionization process is involved. A further purpose of including the carbon monoxide curve in this figure is to indicate that the structure shown by the krypton curve cannot be caused by instrumental effects since the two curves were taken under identical conditions. It is seen from Fig. 1 that the ionization probability curve for krypton exhibits a linear portion extending from the appearance potential at 14.08 volts to about 14.3 volts. The linearity of this initial portion is demonstrated in Fig. 2 where the data have been plotted on a greatly expanded scale. It is clear that within the experimental probable error, indicated by the height of the line through the data points, this portion of the curve is indeed linear. Near 14.3 volts the curve departs from linearity for a region of about 0.6 volt after which a new linear slope is obtained (see Fig. 1).

The shape of the ionization probability curve for xenon is shown in Fig. 3. This curve exhibits a pronounced break occurring at about 1.2 volts above the onset of initial ionization. The trend of the points just below this break indicates that there may be a slight deviation from linearity in this region, although the experimental accuracy of the instrument was not sufficient to definitely establish this point. For a number of runs, the trend of the points in this region was always above the straight lines best drawn to fit the data. Here the probable error of a single measurement is indicated by the size of the data points.

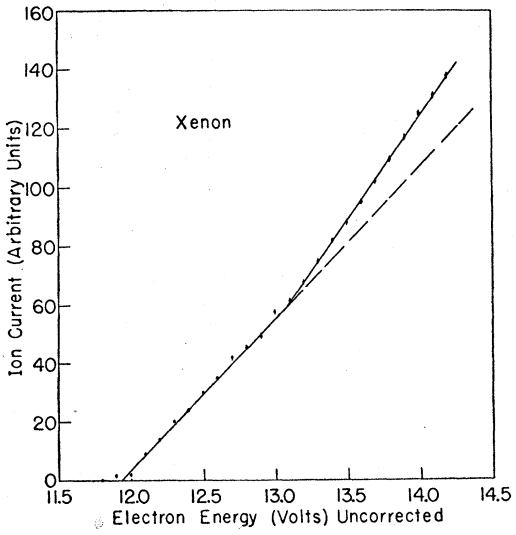

FIG. 3. Relative ionization probability curve for Xe. The probable error is indicated by the height of the data points.

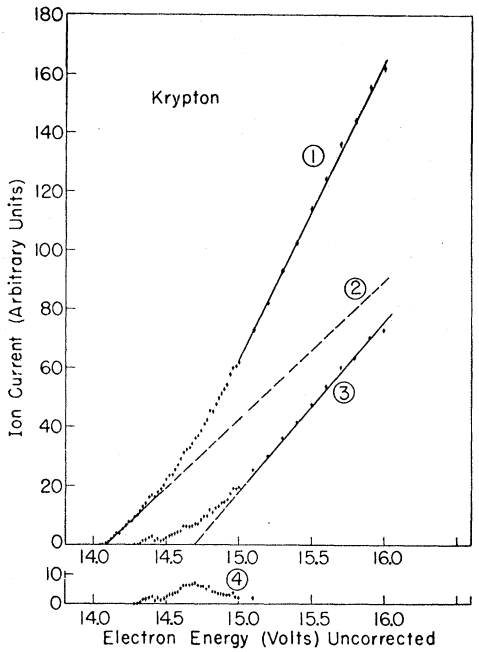

FIG. 4. Analysis of the relative ionization probability curve for Kr. (1) A typical experimental curve. (2) The straight line extrapolation of the initial linear portion of curve 1. (3) The curve obtained by subtracting curve 2 from curve 1. (4) The curve obtained by subtracting the linear portion of curve 3 and its extrapolation from curve 3.

Ionization probability curves for these gases were observed over a period of several months and under a wide range of experimental conditions. The magnetic field used for aligning the electron beam was varied by a factor of two. The pressure in the ion source was varied by a factor of five. Several electron gun-ionization chamber designs were used. The pulse frequency ranged from 50 to 200 kilocycles. The shapes of the ionization probability curves were found to be invariant under these changes.

IV. DISCUSSION

The energy level diagram of any singly charged rare gas ion, with the exception of helium, shows that the ground state of the ion is a doublet. The lowest energy state of this doublet, i.e., the true ground state of the ion, is a $^2P_{\frac{3}{2}}$ state, the other member being a $^2P_{\frac{1}{2}}$ state. In the cases of krypton and xenon, the energy separations of these doublets are[6] 0.666 ev and 1.31 ev, respectively, as determined by spectroscopic measurements.[7] The ionization probability curve for krypton

[6] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1950), Vol. I, Part 1.

[7] Based on 8066.83 cm^{-1} per electron volt; J. W. M. DuMond and E. R. Cohen, Phys. Rev. 82, 555 (1951).

is analyzed into its components in Fig. 4. Curve 1 of this figure shows a typical curve for krypton. The initial linear portion of this curve arises from ionization to the $^2P_{\frac{3}{2}}$ state. For gases whose ions have a single ground state the ionization probability curves obtained by the authors were linear functions of the excess energy of the bombarding electrons. On this basis it is assumed that the linear relationship holds for each member of the doublet ground state. The dashed curve 2 is then a linear extrapolation of the initial portion of curve 1, and a point by point subtraction of these curves yields curve 3. The linear portion of this curve is then the ionization to the $^2P_{\frac{1}{2}}$ state and a linear extrapolation of this curve to zero ion current yield its appearance potential.

The nonlinear portion of this curve will be discussed below. The difference between the two appearance potentials should then equal the energy separation of the doublet. And indeed, twelve runs on krypton yielded an average value for this separation of 0.66 $\pm$0.01 ev, in excellent agreement with the spectroscopic value of 0.666 ev.

A similar analysis was made on xenon. Five runs on this gas yielded an average value of 1.27$\pm$0.03 ev, as compared with the spectroscopic value of 1.31 ev.

It is interesting to compare the relative probabilities of ionization to the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states. It is apparent from Figs. 3 and 4 that the probability is higher for the $^2P_{\frac{1}{2}}$ state in krypton, while for xenon the reverse seems to hold. This somewhat surprising result has consistently been obtained from the experimental data. It may be noted that the ratio of these slopes was obtained by a subtraction method similar to the one employed in making a quantitative analysis employing ionization probability curves of a carbon monoxide and nitrogen[8] mixture, wherein the constituents were determined to better than one percent.

For the purpose of discussing the nonlinear portion of curve 3, Fig. 4, a further analysis has been made. Since the linear portion of curve 3 and its extrapolation are the result of ionization to the $^2P_{\frac{1}{2}}$ state, its contribution is subtracted from the curve yielding curve 4, Fig. 4. This curve then results from ionization not accounted for by direct ionization to the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states. This ionization is interpreted as arising by the mechanism of auto-ionization proposed by White[9] in connection with certain peculiarities observed in the optical spectra of these gases. A reference to an energy level diagram for any of these gases[9] will show that there are certain discrete excited states of the atom which lie above the beginning of that continuum resulting in ionization to the $^2P_{\frac{3}{2}}$ state. Owing to an interaction between the excited electron and the ionic core, it is possible for this ionic core to undergo a spontaneous radiationless transition to the $^2P_{\frac{1}{2}}$ configuration, the excited electron carrying off the excess energy resulting in ionization. It is this mechanism which White proposed to explain the absence of radiation arising from these levels. More recently, Beutler[10] has observed unusually strong and diffuse absorption to some of these energy levels. The absence of emission lines from, and the presence of strong and diffuse absorption lines to these levels is good evidence for the mechanism of auto-ionization.

It would be desirable to correlate the apparent structure in curve 4 with the energy levels responsible for auto-ionization. However, the accuracy of the present results does not justify this. A comparison of Figs. 3 and 4 shows that the contribution from auto-ionization is much greater in krypton than in xenon. In fact, in the latter case the auto-ionization is so small as to be barely discernible above the experimental error. This may have some relationship to the result that the ionization probability to the $^2P_{\frac{1}{2}}$ state as compared to the $^2P_{\frac{3}{2}}$ state was smaller in xenon than in krypton.

Similar studies have been made on argon. However, since the ground state doublet separation for this ion is only 0.18 ev the present accuracy of the instrumentation was not sufficient for a detailed study. It can be reported, however, that a break located at about the right energy was observed in the ionization probability curves.

SUMMARY

Relative ionization probability curves for krypton and xenon have been determined near threshold using nearly monoenergetic electrons. The detailed structure of these curves has been correlated with the energy levels obtained from spectroscopic information. The linear ionization near threshold, found to exist where ionization can proceed by a single process to a single energy level, has been applied to the analysis of the more complicated case of the singly charged ions of krypton and xenon. On the basis of a linear threshold law for each energy level, the data yield the proper energy spacing between the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ ground states for these ions. Additional structure in the ionization probability curves for these ions is interpreted as arising from the process of auto-ionization.

Studies are now in progress on the doubly charged rare gas ions which possess four energy levels near the ground state. In the preliminary curves, breaks are observed which can be correlated with these energy levels on the basis of a linear threshold law for each energy level.

The authors wish to thank their colleagues in the Physics Department, especially Dr. T. Holstein, Dr. M. A. Biondi, and Dr. A. V. Phelps, for their many helpful suggestions and discussions.

[8] W. M. Hickam and R. E. Fox, J. Chem. Phys. **20**, 1055 (1952).
[9] H. E. White, Phys. Rev. **38**, 2016 (1931).
[10] H. Beutler, Z. Physik **93**, 177 (1934).