Ionization Probability Curves Near Threshold for Zn, Cd, and Hg

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The ionization probability curves near threshold of the closely related elements zinc, cadmium, and mercury have been obtained using nearly monoenergetic electrons. Structure observed in the curves is interpreted as the result of autoionization of states of the atom which arise from the excitation of a single inner shell electron. In the analysis of the results, it is necessary to consider both the optically allowed and forbidden excited states. The energy levels of the optically allowed states of this system have been identified by Beutler, but the locations of the optically forbidden states are unknown.

I. INTRODUCTION

SINCE the work of Lawrence,[1] many investigations have been made of the structure in the ionization probability curve for Hg by electron impact.[2] Of these results, the most precise measurements are probably reported by Nottingham.[3] Using a magnetic analyzer to provide electrons of a narrow energy spread, he obtained the ionization probability curve near threshold for mercury in great detail. It is the purpose of this paper to report the curves obtained within some three volts of threshold for the closely associated elements, zinc, cadmium, and mercury and to suggest an explanation for the observed structure.

II. EXPERIMENTAL PROCEDURE

The experiment was carried out using a 90° sectored type mass spectrometer. Ions formed by nearly monoenergetic electrons of known energy were obtained by the retarding potential difference method previously described.[4] The samples of Zn, Cd, and Hg were introduced into the mass spectrometer by a simple furnace arrangement.

It was possible to introduce into the mass spectrometer a gas sample simultaneously with the metallic vapors to check the operation of the instrument. The ability to reproduce the previously reported curves of krypton and xenon[5] was considered an indication of satisfactory performance. Mercury could be introduced simultaneously with either cadmium or zinc for direct comparison of the curves under similar conditions. The relative absence of any structure in the mercury curve at electron energies which resulted in pronounced structure in the cadmium and zinc curves is further evidence that the reported structure is truly associated with the ionization probability and is not instrumental.

Measurements of the mercury pressure using an ion gauge located outside the ionization chamber indicated that the mercury pressure in the ionization chamber was approximately 10^{-5} mm Hg. Since the vapor pressure of zinc and cadmium was appreciable only in the region of the heated ionization chamber, these could not be measured with the gauge. However, assuming the ionization cross section for these elements to be the same as that for mercury, the pressure in the ionization chamber determined by the mass spectrometer was of this same magnitude. At these low pressures only single electron-atom collision processes are considered significant.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We shall present and discuss the results beginning with the simplest case, that of Zn. The initial portion of the ionization probability curve for zinc is shown in Fig. 1. The curve rises linearly for approximately 1.4 ev. Pronounced structure is then observed over a region of one electron volt. This is followed by an approximately linear rise. The voltage scale on this and other curves to be presented was adjusted so that the measured appearance potential agreed with the spectroscopic ionization potential.[6] The necessary adjustment was 0.2 volt or less.

The curve for zinc is interpreted in a similar manner to that suggested in previous work.[5,7,8] There it was possible to attribute the deviations from linearity in

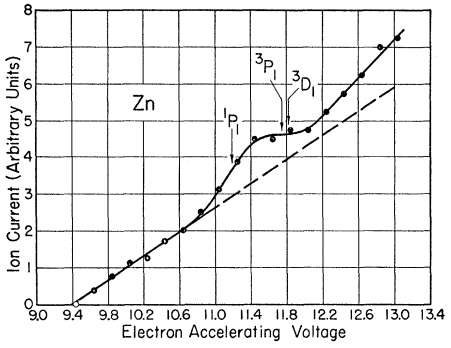

FIG. 1. Relative ionization probability curve for Zn. The states noted are those of Zn I[b].

[1] E. O. Lawrence, Phys. Rev. **28**, 947 (1926).
[2] O. M. White, Proc. Phys. Soc. (London) **66**, 641 (1953).
[3] W. B. Nottingham, Phys. Rev. **55**, 203 (1939).
[4] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. **84**, 859 (1951).
[5] Fox, Hickam, and Kjeldaas, Phys. Rev. **89**, 555 (1953).
[6] Atomic Energy Levels, National Bureau of Standards Circular 467 (1950), Vol. 2, and Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1950), Vol. 1. The conversion factor used is 8066.8 cm^{-1} per volt from J. W. M. Du Mond and E. R. Cohen, Phys. Rev. **82**, 555 (1951).
[7] Hickam, Fox, and Kjeldaas, Phys. Rev. **90**, 386 (1953).
[8] Kjeldaas, Hickam, and Fox, Phys. Rev. **90**, 386 (1953).

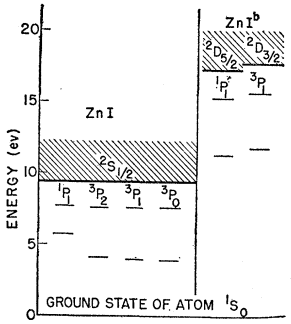

FIG. 2. Simplified energy level diagram for zinc atom. The states arise from the excitation of either a single valence electron (Zn I) or a single inner (d) shell electron (Zn I^b).

the ionization probability curves near threshold to the presence of excited states of either the atom or the ion. Excitation to such states may introduce a mechanism for ionization in addition to direct excitation to the ion ground state. When this occurs, one must consider the ionization probability curve as the summation of a number of ionization processes, each of which has a definite threshold energy.

We shall now consider the energy levels of zinc as a basis for such an interpretation. A simplified energy level diagram for the zinc atom is shown in Fig. 2. The electronic configuration of the $^1S_0$ ground state is $3d^{10}4s^2$. The states associated with Zn I arise from the excitation of a single valence (s) electron. The states all converge to the $^2S_{\frac{1}{2}}$ state of the ion at 9.39 ev. The Zn I^b states are those identified by Beutler[9] from absorption spectroscopy as arising from the excitation of a single inner (d) shell electron. An example of this type transition is $3d^{10}4s^2\ ^1S_0 \rightarrow 3d^9 4s^2 4p\ ^1P_1$. These states are observed only in absorption spectra because of autoionization, i.e., atoms excited to such levels undergo radiationless transitions to the ground state of the ion with the ejection of an electron. The absorption lines resulting from optical excitation to some of the states of Zn I^b are very diffuse (half-width $\sim$0.05 ev) indicating a short lifetime compared to radiative lifetimes. Accordingly, it is expected that the ionization resulting from this excitation is a true measure of the probability of exciting to these atomic states.

The only identified states which arise from the excitation of a single electron and fall within the energy range investigated are those of the I^b group shown on the curve of Fig. 1. The initial linear rise and the dashed extrapolation is interpreted as ionization by direct excitation to the $^2S_{\frac{1}{2}}$ ion ground state. Ionization in excess of this linear rise is believed to result from the process of autoionization associated with the I^b states. It does not seem possible to attribute the autoionization threshold to the $^1P_1$ state which is located approximately 0.5 volt higher. We propose that this threshold indicates the presence of states which are not observed in absorption spectroscopy because of forbidden transitions. In particular, to be included in the optically forbidden states are those of J value 0 and 2. Since the autoionization curve may be a composite of excitation curves associated with several states, it is difficult to obtain much information on the excitation for the individual states. However, the curve does show that a maximum excitation probability must occur for one or more of the states close to threshold. The shape of excitation curves associated with different states will be discussed later.

The discussion of the zinc ionization probability curve is equally applicable to cadmium (Fig. 3). The structural details of the autoionization curve can be related in an identical manner to the Cd I^b states identified by Beutler[10] and here also an additional state is required to explain the autoionization threshold.[10] Only the energy displacement of the structure from the ionization threshold is significantly different in the two curves.

In the case of mercury the relative location of the I^b states[11] with respect to the $^2S_{\frac{1}{2}}$ ground state of the ion should be particularly noted (Fig. 4). The lowest-lying $^1P_1$ state of this group falls below the $^2S_{\frac{1}{2}}$ state and so is not capable of contributing to the ionization. Furthermore, the lowest-lying $^3P_1$ state is only some 0.6 ev above the $^2S_{\frac{1}{2}}$ ion ground state.

The ionization probability curve for mercury (Fig. 5) is in satisfactory agreement with that of Nottingham[3] and can be analyzed in an identical fashion to that just discussed. The pronounced structure near threshold is interpreted as autoionization superimposed on a linearly rising excitation curve associated with the $^2S_{\frac{1}{2}}$ ion ground state. In this particular case there is no interference from the $^1P_1$ state and so the pronounced maximum is believed to be associated with the optically forbidden levels of the I^b group. The experimental data indicate that the state in question is located very close to the $^2S_{\frac{1}{2}}$ ion ground state. The location of the $^3D_1$ state on a linear portion of the curve suggests that the probability of exciting to this particular state is relatively small.

The interpretation of the structure of the ionization probability curves given above requires that the excita-

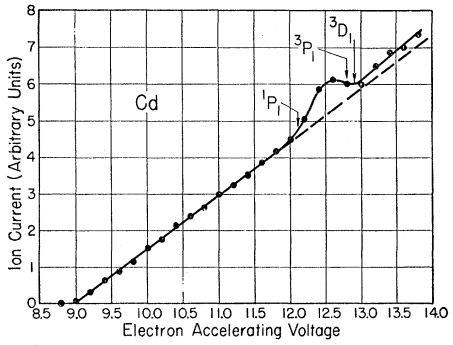

FIG. 3. Relative ionization probability curve for Cd. The states noted are those of Cd I^b.

[9] H. Beutler, Z. Physik **87**, 176 (1933).

[10] H. Beutler, Z. Physik **87**, 19 (1933).

[11] H. Beutler, Z. Physik **86**, 710 (1933).

tion function for the optically forbidden state has a maximum within approximately one electron volt of threshold. Investigations on the cross section for excitation of spectral lines by electron impact have been carried out for zinc, cadmium, and mercury by a number of workers.[12] In general, the excitation function associated with the lowest-lying partially forbidden $^3P_1$ state of the normal spectrum reveals a pronounced maximum near onset while the maximum observed for the optically allowed $^1P_1$ state is many electron volts above threshold. These results are in agreement with the theoretical calculations of Penny[13] on mercury, which in addition show a maximum near threshold for the optically forbidden $^3P_0$ and $^3P_2$ states.

The interpretations of Lawrence[1] and Nottingham[3] of the structure in the mercury curve are difficult to extend to the curves for zinc and cadmium. Lawrence inferred that the probability of exciting any type of atomic transition involving ionization by a slow electron reached a maximum when the electron had just enough energy to excite the process. Nottingham based his interpretation on the shapes of the excitation curves of the lowest-lying $^1P_1$ and $^3P_1$ states of Hg I which have been discussed. He suggested that the observed ionization probability curve is the sum of two curves. The peak at 10.8 volts was to be associated with the triplet system and the broad maximum at 32 volts was characteristic of the singlet mode of ionization. Since the excitation curves of the $^3P_1$ state for zinc and cadmium resemble closely that of mercury, Nottingham's explanation implies that such structure would appear within one volt of threshold in the ionization probability curve of these elements.

Another interpretation considered was that the structure resulted from states[6] associated with the excitation of both valence electrons. Since these states

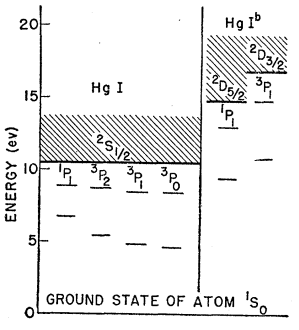

FIG. 4. Simplified energy level diagram for mercury atom. The states arise from the excitation of either a single valence electron (Hg I) or a single inner (*d*) shell electron (Hg I[b]).

[12] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 55.

[13] W. G. Penny, Phys. Rev. **39**, 467 (1932).

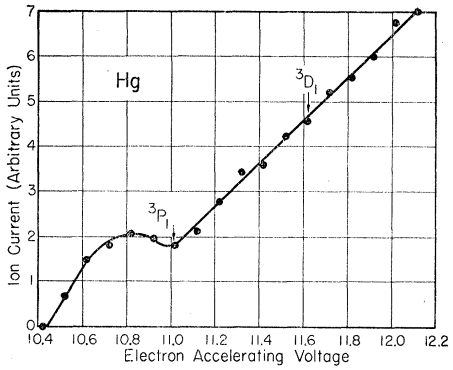

FIG. 5. Relative ionization probability curve for Hg. The states noted are those of Hg I[b].

are identified by emission spectra, it is doubtful that they would contribute significantly by the autoionization process. In the experimental results this is evidenced by the fact that these states fall on a linear portion of the curves and reveal no pronounced peaks.

Of the interpretations advanced, it appears that the one proposed in this paper is most consistent in explaining the observed structure.

SUMMARY

Zinc, cadmium, and mercury ionization probability curves near threshold have been obtained using nearly monoenergetic electrons. As in a number of previous gases, it has been shown that where ionization by excitation to the ionic ground state is the only process which can occur, a linear threshold law is observed. Structure in the three curves is closely correlated with the optically allowed states of the atom arising from the excitation of a single inner (*d*) shell electron. The states contribute by the process of autoionization. In order to account for details of the observed structure by this process, it is necessary to postulate the presence of optically forbidden states which can be excited by electron impact. This results in the proposed location of a new state which most likely has a J value of 0 or 2 and further suggests that the excitation to such a state reaches a maximum very close to onset.

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