VOLTAGE-INTENSITY RELATIONS IN THE MERCURY SPECTRUM

By William D. Crozier

Abstract

Voltage-intensity curves have been obtained for twenty lines of the mercury spectrum, when excited by electron impact. The range of accelerating voltage was from excitation to fifty volts, the discharge tube being designed to eliminate most of the disturbance due to positive ion formation. The components of four of the triplet groups were resolved and investigated separately. No significant change appears in the number of atoms in a given energy state as the ionization potential is passed. The components of each of the dD groups of energy levels are excited at practically the same voltage but have quite different excitation functions. *The excitation functions* for d_1, d_3, and s levels and for the $2p_2$ level appear to be similar in form and to have sharp maxima within a few volts of the excitation voltage. The excitation functions for d_2 and D levels also appear similar, increasing uniformly to 30 or 40 volts where they have broad maxima. *The voltage-intensity characteristics* of lines originating in transitions down from the same initial level agree in type but sometimes show certain differences in shape. It appears that the probability of different transitions down from a given energy state may not be independent of the way in which this state is excited. There is evidence that a large number of excitations of $2p_2$ by transitions down from higher levels are not followed by $1S-2p_2$ transitions.

Introduction

This work was undertaken with the object of collecting some information as to the nature of the excitation function for certain of the energy levels of mercury. The excitation function is here defined as the fraction of collisions between an electron and an atom which result in the excitation of a given energy level, expressed as a function of the accelerating voltage on the electron. Information as to the nature of the excitation function for a certain energy level may be obtained by studying the variation of intensity with voltage of the spectral lines resulting from transitions down from this level. The exact form of the function may sometimes be somewhat modified by the effect of transitions from higher levels to the one in question and of radiationless transitions out of it.

At the time of starting this problem practically the only information available on voltage intensity relations was for hydrogen[1] and helium.[2,3,4] It had been noticed by Eldridge[5] that the intensities of different lines in the mercury spectrum varied in different ways as the velocity of the exciting electrons was varied over a short range above ionization. During the

[1] Hughes and Lowe, Phys. Rev. **21**, 292 (1923).
[2] Hughes and Lowe, Proc. Royal Soc. **A104**, 480 (1923).
[3] Udden and Jacobsen, Phys. Rev. **23**, 322 (1924).
[4] Bazzoni and Lay, Phys. Rev. **23**, 327 (1924).
[5] Eldridge, Phys. Rev. **23**, 294A (1924).

progress of the work a paper appeared by D. R. White,[6] showing extremely interesting details in the voltage-intensity curves below the ionization potential. This was deemed sufficiently important to warrant a careful exploration of this region with the view of confirming the results and extending them to the lines of the triplet groups which had not been resolved. A paper has also appeared by J. Valasek[7] giving voltage-intensity curves for a few mercury lines in the voltage range 15-300.

Apparatus

The discharge tube is a modification of one described by Eldridge[8] and is shown in cross section in Fig. 1. In front of the flat equipotential cathode were two grids G which were kept at the same potential. The grids were

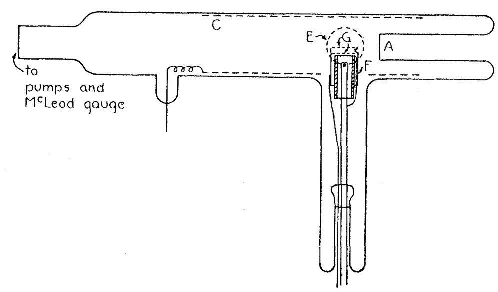

Fig. 1. The Experimental tube.

separated by about 2 mm, the first being about 1 mm in front of the cathode. Blackening of the quartz window A by platinum evaporated from the hot cathode was eliminated by using as the grid support a nickel cylinder F which enclosed the cathode. A side tube indicated at E projected on what was the lower side and contained mercury. The whole tube was enclosed in an oven with an electric heater to maintain the desired mercury vapor density. The pressure of the residual gas was maintained at all times below 10^{-5} mm as indicated by a McLeod gauge.

It was found necessary to limit the current passing through the grids to 0.1 or 0.2 milliamperes to avoid excessive local alteration of potential by space charge. With the currents used the potential over the region between the grids was constant to within 0.1 volt.

A voltage correction of approximately 2 volts was necessary in order to give the true volt-velocity of the electrons. This was determined approximately by the point of appearance of positive ions as described by White. However, if the voltage scale was shifted to make one of the lines appear at its theoretical voltage, then in general the others appeared at their theoretical points. This method is used for a slight final adjustment of the voltage scale for the curves shown. The uncertainty as to the value of the voltage probably does not greatly exceed 0.1 volt.

[6] White, Phys. Rev. **28**, 1125 (1926).
[7] Valasek, Phys. Rev. **29**, 817 (1927).
[8] Eldridge, Phys. Rev. **23**, 685 (1924).

With this arrangement of elements, the tube was reasonably free from disturbances caused by the production of positive ions as the ionization potential was passed. Neither the total emmission from the cathode, nor the current collected by the cylinder *C*, nor the intensity of the light emitted, showed any discontinuity as the ionization potential was passed. The curves between grid voltage and current showed only a slight change in slope. These characteristics of the tube made it possible to carry the observations across the ionization potential with assurance of their correctness.

The final curves were taken with the tube maintained at temperatures from 85°C to 115°C, except in the case of the λ2537 line, which was taken at 28°C. The higher temperatures were used to shorten the time of exposure for the weaker lines. Preliminary observations were made with temperatures ranging from 0°C to 130°C and no appreciable difference was noted in the shape of the curves obtained. It is not certain that the mercury pressure in the tube was exactly that characteristic of the temperature, as some condensation was taking place in the tube leading to the pumps and in the side tube carrying the leads.

The light from between the grids, after passing through the quartz window *A*, was focused on the slit of a quartz spectrograph. Most of the work was done with a spectrograph of aperture F11 having a dispersion of 14.5 A per mm in the region of 3300 and 6.5A per mm in the region of 2600. Exposures ranged from a fraction of a minute to twenty minutes.

Measurement of the density of the lines on the photographic film was made by means of a microphotometer with a photographic recorder. The film was calibrated by taking a series of spectrograms on one film, using different exposure times. The reciprocity law was then assumed to get the density-intensity relation. This method of calibration gave sufficiently good results, voltage-intensity curves taken with different exposures agreeing reasonably well in shape. The precision of the density measurements was for the most part probably within five percent. Practically all the points appearing on the curves are averages of several determinations, partly on different films taken under similar conditions, and partly on the same film.

Results and Discussion

General comments on curves. The curves in Figs. 2 to 11 present the results of some three thousand microphotometer measurements on twenty lines of the mercury spectrum.

Below the ionization potential the results of different measurements on different plates and at different temperatures were very concordant and it is usually possible to draw a smooth curve passing through nearly all the points. Above 10.4 volts the points become somewhat scattered. Most of the irregularities are probably due to some slight instability of current or voltage distribution, associated with the production of positive ions. It was possible to get smoother curves by working at lower temperatures, but then the exposure times became inconveniently long.

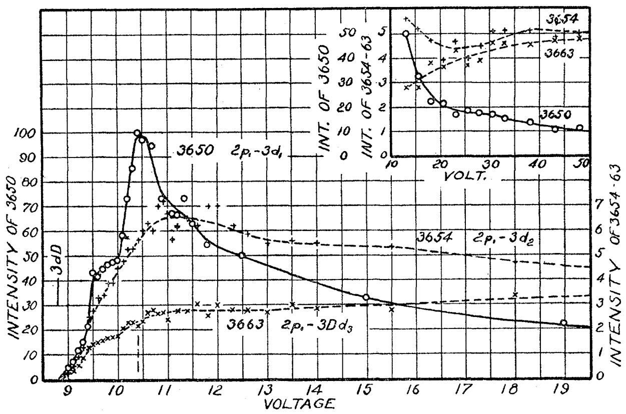

Fig. 2. Voltage-intensity curves of the λ3650 group.

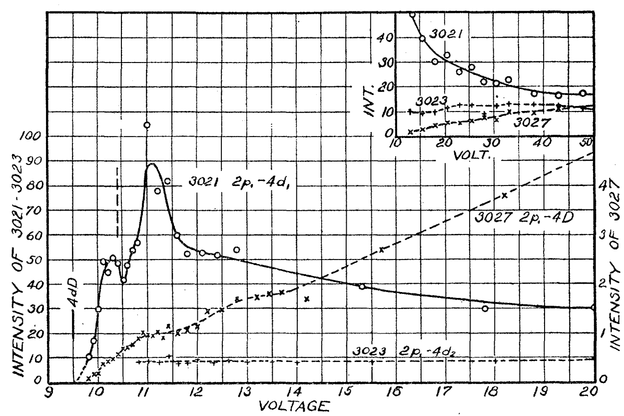

Fig. 3. Voltage-intensity curves of the λ3021 group.

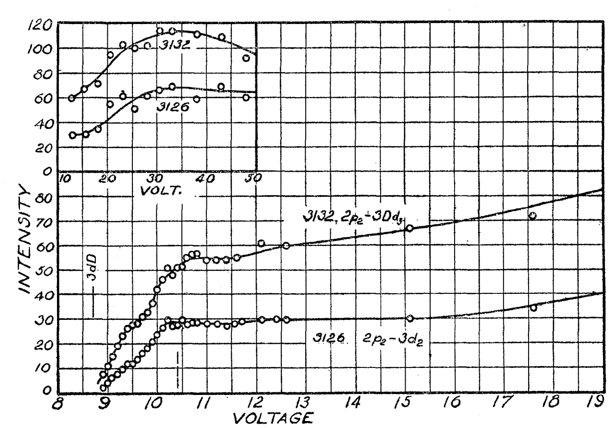

Fig. 4. Voltage-intensity curves of the λ3126 group.

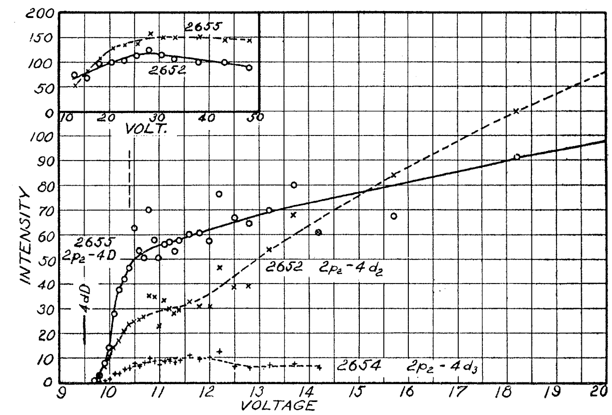

Fig. 5. Voltage-intensity curves of the λ2652 group.

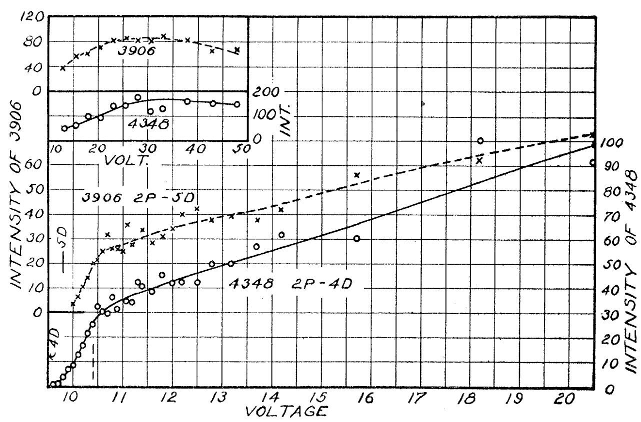

Fig. 6. Voltage-intensity curves of λ4348 and λ3906.

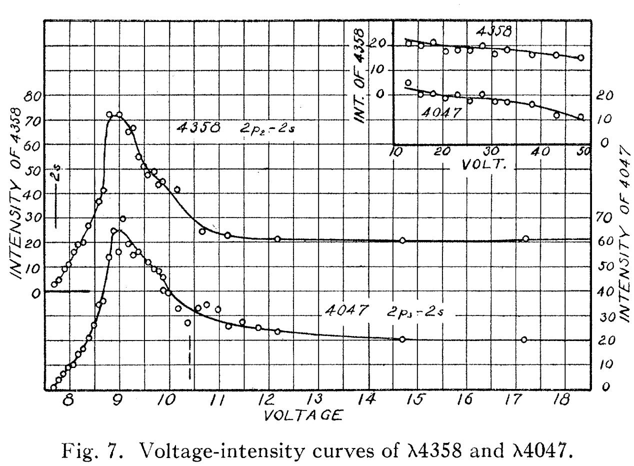

Fig. 7. Voltage-intensity curves of λ4358 and λ4047.

Where the results are comparable with the results of White and of Valasek they are, in general, in excellent agreement with them. In confirmation of the general results of other investigators, it was found that all the lines but one appeared at their respective theoretical voltages, including the components of the triplet groups which have not heretofore been

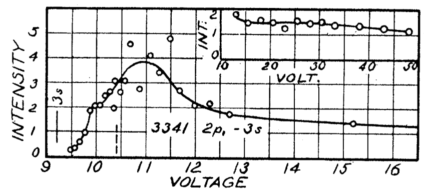

Fig. 8. Voltage-intensity curve of λ3341.

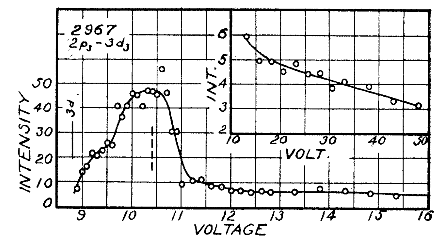

Fig. 9. Voltage-intensity curve of λ2967.

investigated individually, at least photometrically. The exception to this result was in the line 4078, ($2p_2-2S$).[9] In agreement with the result of White, it was found that this line did not appear in any appreciable strength below about 8.5 volts. The curve in Fig. 10 does not show this as conclusively as

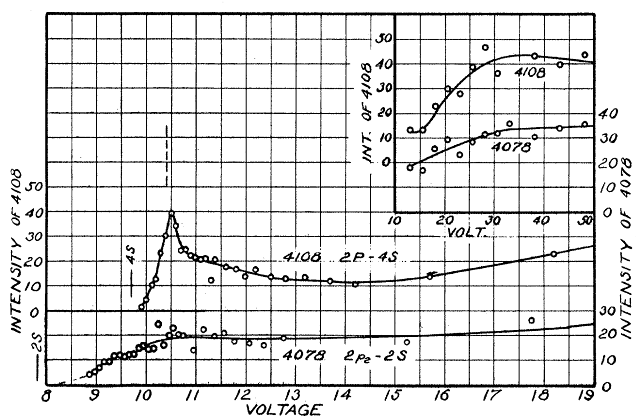

Fig. 10. Voltage-intensity curves of λ4108 and λ4078.

visual observations which were made on plates where the exposure time was sufficient to give a much greater intensity.

Specific results and their interpretation. Non-significance of the ionization potential. In one respect it will be observed that the curves differ from previous curves of the sort, and this is in the fact that in practically no case does a break occur in them at the ionization potential. There is a possible exception in the curves for $2p_1-3d_1$, $2p_3-3d_3$, and $2P-4S$, appearing in Figs. 2, 9, 10, respectively. However, it does not seem likely that the fact that this is the ionization potential has anything to do with this. This result

[9] The Paschen notation is used throughout this article.

is, for example, in sharp contrast with the results of White, which in all cases show a sharp upward break near ionization.

This result is taken to indicate that the role which ionization plays under these conditions in unimportant, at least at lower voltages, as compared with the role of the other inelastic collisions. Were a considerable part of the intensity of the lines due to electrons combining with the atoms after ionization, as was once thought to be the case, then the intensities of all the lines should show an increase at the ionization potential. After Hertz[10] and Eldridge[11] showed that all the arc spectrum could be produced by nonionizing collisions, it has been thought that the role of ionization is unimportant. The present work definitely confirms this conclusion.

This circumstance is extremely important in discussing the relation of our results to the excitation function. It is fundamentally important to show that the energy states are mainly excited by impacts and not by transitions down from higher levels.

Behavior of the triplet components. The components of four of the triplet groups were resolved, the curves being shown in Figs. 2 to 5. In two instances as indicated it was impossible to separate lines from the d_3 and D levels, but there is every reason to believe that the d_3 line is very weak in comparison with the D line and for the discussion it will be assumed that the composite line is due primarily to D. This assumption is justified by the curves for analogous lines where resolution was possible.

In each case it was found that the lines in each group appeared at practically the same voltage. This fact is important in that it has not been previously verified, at least photometrically, that these lines appear together.

The shape of the curves for different members of a group differs very markedly. This is particularly exemplified by the behavior of the lines from $3d_1$ and $4d_1$ in Figs. 2 and 3 as compared with that of those from the d_2 and D levels. In addition to the obvious difference over all the range of voltage, there is a particularly interesting difference in their behavior for a short range just above their appearance. The curves of Fig. 2 illustrate this best though those in Fig. 3 show a similar effect. After appearing at the same point the lines have an upward curvature of almost the same shape for about 0.4 volt, and then the line from d_1 shows a very rapid increase while the others do not. This is believed to be a true characteristic of the excitation function of the d_1 levels and not to be due to transitions from higher levels. The only other levels which are sufficiently close to the d levels are the $3sS$ and $4sS$ levels. Radiation transitions from these to d_1 are forbidden, and if the transitions were due to collisions of the second kind it would be expected that the relative intensity of the lines from the d_1 levels to lines from the s or S levels should increase with temperature. Some rough measurements were made on the relative intensity of 3341 $(2p_1-3s)$ and 3650

[10] Hertz, Zeits. f. Physik **22**, 18 (1924).

[11] Eldridge, Phys. Rev. **23**, 685 (1924).

($2p_1-3d_1$) at temperatures of 0°C and 130°C, which indicate that this is not the case and that possibly even the opposite is true.

The pronounced drop so characteristic of the d_1 curves at 9.5 and 10.3 volts in Figs. 2 and 3 respectively, may possibly have an explanation in the fact that at approximately these points higher levels are excited in preference to d_1.

Behavior of lines from similar initial levels. Perhaps the most striking characteristics of the curves in general are the sharp maxima which sometimes occur at low voltages. Curves showing this feature in every case, except that of the somewhat anomalous line, $2P-4S$, decrease continuously as the voltage is increased beyond the maximum point.

A second class of lines shows a less interesting behavior; the sharp maximum is missing, and after the initial rise just above the excitation voltage, the curve flattens out. In most cases these curves continue to rise gradually to 30 or 40 volts and then fall off. Adopting this classification it will be seen that, in general, lines from analogous initial levels belong to the same class. For instance, in Figs. 2 and 3 it will be seen that the analogous lines $2p_1-3d_1$, and $2p_1-4d_1$ are very similar and fall into the first class. In the same figures $2p_1-3D$ and $2p_1-4D$ are similar and fall into the second class. The resemblance of $2p_1-3d_2$ and $2p_1-4d_2$ is not so striking. Both show indications of a maximum at lower voltages but their behavior at higher voltages is characteristic of the second class, and they appear to fall naturally into this class. The exact shape of these two curves is not very certain as the lines are in close proximity to much stronger lines, which fact introduces errors due to a peculiarity of the photographic plate. A complete classification of the lines observed is found in Table I, together with the figures in which they are to be found.

TABLE I. *Classification of lines*

Lines of the first class		Lines of the second class	
Type of line	Figure	Type of line	Figure
$X-md_1$	2, 3	$X-md_2$	2, 3, 4, 5
$X-md_3$	5, 9	$X-mD$	2, 3, 4, 5, 6
$X-ms$	7, 8	$2p_2-2S$	10
$2P-4S$	10		
$1S-2p_2$	11		

The only instance of marked dissimilarity between the characteristics of lines resulting from transitions down from levels of the same kind is in the lines from the S levels. Since the line 4078, ($2p_2-2S$), seems to be exceptional in another respect, not appearing at the theoretical voltage for the excitation of $2S$, but about 0.5 volt higher, it seems reasonable to regard the S levels as anomalous.

Behavior of lines from the same initial level. We have several cases before us of lines which originate in transitions from the same initial level to different final levels. Table II shows the type of transitions where this occurs together with the numbers of the figures to which reference may be made.

The shape of curves from the same initial level is practically identical for voltages below ionization, in agreement with the result of White. Above ionization the curves, while showing great similarity in type, are not in general identical and in several cases show marked disagreement. The particularly bad case shown by the lines $2p_1-3d_2$ and $2p_1-4d_2$, in comparison with the lines $2p_2-3d_2$ and $2p_2-4d_2$, is perhaps not to be taken too seriously, as the curves for the first two are not entirely reliable as mentioned above. However, even in other cases where this difficulty is not present there is disagreement between curves for lines with the same initial level.

TABLE II. *Classification of lines*

Type of Line	Figures
$X-3d_2$	2, 4
$X-3d_3D$	2, 4
$X-4d_2$	3, 5
$X-2s$	7
$X-4D$	3, 5, 6

A good example of this is found in comparing the line 3027 ($2p_1-4D$) in Fig. 3 with the line 2655 ($2p_2-4D$) in Fig. 5. 3027 shows an increase in intensity of 12:1 in going from 11 to 50 volts, while 2655 shows an increase of less than 3:1. This fact together with some features to be mentioned in connection with the $1S-2p_2$ line, leads to the suggestion that probabilities of transition from an upper level to lower levels may sometimes depend upon the velocity of the electron which excited the upper level, and that the nature of the dependence may vary with the lower level to which the transition is to lead.

This suggestion while appearing somewhat unintelligible, especially in the light of the older quantum theories, may have an explanation in the fine structure of the levels concerned. By assuming a proper selection principle for the combination of the fine structure terms and proper excitation functions for each of the fine structure levels of the initial term it is easily seen that the probability of the transitons may be made to depend on the voltage of excitation and that the nature of the dependence may be different for different final levels.

It seems that consideration of the ordinary Zeeman sub-levels is not sufficient in this case, as the statistical weight of all the Zeeman sub-levels of the initial state is the same.

The curve of 2537 ($1S-2p_2$). This curve of Fig. 11 is discussed separately because it shows several interesting features, and its interpretation is probably not so simple as in the case of the other lines. The curve shows a great deal of detail below the ionization point. All the features shown were very closely reproducible, and the irregularities are not to be confused with those which appear on some of the other curves at higher voltages. Upward breaks appear at 7.7, 8.8, and 9.1 volts which may be interpreted as due to the excitation of $2p_2$ by transitions from $2s$, $3dD$, and $3s$, respectively, these levels being excited at approximately these voltages. A break appears at about 8.3 volts, the significance of which is not clear. It was not observed by White. Between 10.0 and 10.5 volts there are two maxima which were not observed by White, and of which the interpretation is also difficult owing to the great number of levels which can be excited at these voltages.

White observed a strong upward break at 5.4 volts which was attributed to transitions to $2p_2$ from $2p_1$ by collisions of the second kind. There is no evidence of such a break in our curve, and this is perhaps to be explained by the fact that our curve is taken at 28° where collisions of the second kind are less frequent than at the pressures presumably used by White.

It is believed that the peak between 6.0 and 7.5 volts is much broader than in the true voltage-intensity function. This is on account of resonance radiation produced in the space between the grids due to the 2537 radiation produced in the space beyond the second grid. Parts of this space

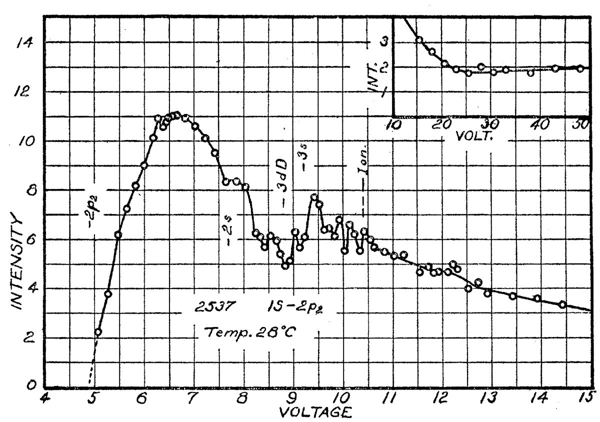

Fig. 11. Voltage-intensity curve of λ2537.

are at quite different potentials from the grids due to space charge, and the result is the same as if there was a rather wide velocity distribution in the electron beam.

Above ionization the intensity decreases as far as 25 volts, and then is constant. This is in qualitative agreement with the result of Valasek though there the intensity decreases to 100 volts.

This curve indicates that the excitation function for $2p_2$ has a strong maximum closely above 4.9 volts and then drops immediately to a very low value. This is in agreement with conclusions reached by Frl. Sponer[12] and by Eldridge[13] by retarding potential methods.

A difficulty arises in the interpretaion of this curve at voltages above the peak. As has been pointed out by Valasek,[7] the total intensity of the $1S-2p_2$ line appears to be much less than the combined intensity of the lines from transitions ending in $2p_2$. Analogous results have been obtained

[12] H. Sponer, Zeits. f. Physik **7**, 185 (1921).
[13] Eldridge, Phys. Rev. **20**, 456 (1922).

in other cases, and, in fact, no one has yet been able to show in any case a quantitative agreement between the number of transitions leading to a given state and the number leading from this state. It seems that the answer must be found in non-radiating transitions (collisions of the second kind). The effect does not appear to depend on pressure. If we assume the $2p_2$ state to consist of several fine structure states, some of which are metastable, we may find an explanation. The ratio of the non-radiating transitions to the radiating transitions will then depend only on the relative population of the fine structure levels and not on pressure.

The present curves render stronger the conclusions of Valasek and bring us more directly in contact with the difficulty. There appears a strong upward break in the intensity of 2537 at 7.7 volts which corresponds to contributions to $2p_2$ from $2s$. The evidence of these strong contributions does not extend to higher voltages. The peak in 2537 at 9.4 volts is much too weak to be associated with the peak which appears in the $2p_2-2s$ curve in Fig. 7. It appears that if $2s$ is excited by electrons having much more than the critical velocity the subsequent fall into the $2p_2$ state often results in an atom which is singularly unable to radiate. This may be explained if we assume as above that a different fine structure $2s$ state is excited by fast electrons from that by slow electrons. More of the first then go to the metastable $2p_2$ states mentioned above and there results a low probability of transition to $1S$ from $2p_2$. This explanation is not altogether improbable. Some recent work by Collins[14] has shown the possibility of influencing the relative population of different fine structure levels by different modes of optical excitation.

Bearing of the results on the excitation function. It is believed that we have here good evidence as to the general form of the excitation functions for the different series of the levels of mercury. The voltage-intensity curves undoubtedly depart to some extent from the true form of the excitation function, one reason being that some of the excitation is indirect, i.e., by transitions down from higher states. This is apparently not sufficient to entirely obscure the form of the curve even in the case of the excitation of $2p_2$, and for most of the other levels considered, it is known that most of the levels which lead into them are rather weakly excited. It is obvious from the curves that ionization contributes little. There may be non-radiating transitions out of some of the levels either by collisions of the second kind, or by the absorption of radiation. Collisions of the second kind do not appear to be of importance in most cases, especially as the preliminary observations showed the shape of the curves to be practically independent of pressure.

It is possible that the shape of the curves is influenced to some extent by absorption in the mercury vapor, some of the light being reemitted at different frequencies.

The discussion becomes somewhat complicated if we accept the method of treatment suggested above, that of considering the excitation of the

[14] Collins, Phys. Rev. **31,** 152A (1927).

fine-structure sub-levels separately. Then we must regard the excitation functions observed as composites of the excitation functions of the sub-levels of the initial level which are involved in the emission of the line observed.

It may be asked if a different curve would not have been obtained if the light had been observed in a different direction relative to the electron beam, since it is known that the light emitted is polarized. Some attempts to measure the polarization of the light in the direction observed indicated that in this tube it was not very strong. In any event the polarization with this type of excitation would not cause a great difference in the shape of the curves obtained looking in different directions and expecially would not account for the great differences in the two classes of curves.

In conclusion I wish to express my appreciation of the friendly interest and helpful attitude of the staff of the Physics Department at the University of Iowa, and of the facilities of the laboratory. I expecially wish to express my thanks to Professor Eldridge who suggested the problem and directed the work.

Hall of Physics,
University of Iowa,
August 12, 1927.*

* Received February 6, 1928.—Ed.