THE SINGLE-LINED AND THE MANY-LINED SPECTRUM OF MERCURY.[1]

By T. C. Hebb.

FRANCK and Hertz have shown[2] that under certain conditions a single-lined spectrum of mercury can be obtained. They found that one of the necessary conditions was that the vapor of mercury be bombarded by electrons having a speed equal to or greater than that produced by falling through 5 volts. As they had already shown that the ionizing potential of mercury was 4.9 volts they were led to an application of the relation $Ve = h\nu$ where $h = 6.56 \times 10^{-27}$ erg. sec. and ν is the frequency of the single-lined spectrum $\lambda = 2536.72$ Å. U. The experiments of Franck and Hertz are exceedingly suggestive and would appear to offer new light on the structure of the atom.

These results have since been repeated and extended by McLennan and Henderson.[3] They found that they could get the single-lined spectrum of mercury for any potential difference between 5 and 12.5 volts, but that with a potential difference below 5 volts they obtained no spectrum and that with a potential difference of 12.5 volts or higher they always obtained the many-lined spectrum of mercury. In order to explain the occurrence of the many-lined spectrum at 12.5 volts they suggest that possibly a new type of ionization occurs at this point. They have further shown that they can obtain single-lined spectra of both cadmium and zinc. In a still later article McLennan has shown[4] that he can also obtain a single-lined spectrum of magnesium. As the ionizing potentials of cadmium, zinc and magnesium have not been determined directly the authors apply the above quantum relation $Ve = h\nu$ in order to determine the value for each of the metals.

The results embodied in this paper are considered worthy of publication even though the work is incomplete. The writer had occasion to spend a limited time at the Ryerson Physical Laboratory during the spring of 1916 and at a suggestion from Professor Millikan attempted

[1] This and the following paper were presented before the American Physical Society at the Chicago meeting, December 1, 1916.

[2] Deutsch. Phys. Gesell. Verh., 16, 11, pp. 512–517, June 15, 1914.

[3] Roy. Soc. Proc., 91, pp. 485–491, Aug. 2, 1915.

[4] Roy. Soc. Proc., 92, pp. 305–312, Mar. 1, 1916.

to repeat the experiments of Franck and Hertz and of McLennan and Henderson and if possible throw light on the relations of the single-lined and the many-lined spectrum of mercury.

The results to be stated later were obtained with the following apparatus:

A (Fig. 1) was a quartz tube 20 cm. in length, 1.9 cm. internal diameter and 2.1 cm. external diameter. *B* and *C* were iron caps which were joined to the tube with Khotinsky cement. Through *B* passed a glass tube which was connected to the air pump and through which also passed the wire leading to the platinum anode *D*, mounted on the end of the glass tube. Passing through *C* were two glass tubes through which passed the iron electrodes which held the cathode *E*. The latter was attached to the iron electrodes with clamps. The glass tubes were fastened to the iron caps *B* and *C* with Khotinsky cement. The above arrangement of apparatus made it possible to renew the platinum cathode and also to vary the distance between the anode and cathode. The central part of the tube was placed in an asbestos gas-heated furnace with a sheet-iron bottom. The collimator of the spectrograph passed through a hole in the furnace and the slit was placed directly against the quartz tube. *B* and *C* were surrounded with copper water jackets and the iron electrodes at *F* were cooled with a stream of air in order to prevent the cement from softening. With this arrangement and with the iron electrodes 1/8″ in diameter it was found possible to use 20 amperes through the cathode and heat the furnace with a gas flame and not have the cement connections soften even after hours of operation. It should be stated that the diagram shows a horizontal section and that the mercury usually stood directly under the anode and cathode. To prevent the heat from passing along the mercury and melting the cement at *C* or *B* the tube was inclined so that the mercury always stayed in the *C* end of the tube and at *G* there was placed an iron stop which prevented it from reaching the end of the tube. The cathode consisted of a piece of platinum .0025 cm. thick and about 1.5 cm. long. The width varied in different cases from 2 mm. to 4 mm. and the current to heat it from 10 to 20 amperes. The platinum was either used bare or coated with barium oxide. The photographs were taken with a small quartz spectrograph. The slit was directed towards some point between the anode and cathode. The lens was of such size that it gathered light from all points between the anode and cathode if they were placed 1.5 mm. apart.

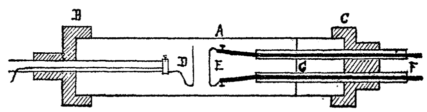


Fig. 1.

With the apparatus outlined as above one of the first difficulties encountered was due to the occurrence of the many-lined spectrum. It was found almost impossible to make exposures at voltages used by other experimenters for any considerable length of time without having an arc strike and then the plate showed the many-lined spectrum. In order to obviate the striking of the arc the potential difference between the electrodes was lowered step by step, until finally at a little under 5 volts it was found that it was possible to photograph for hours without the appearance of the many-lined spectrum. It thus appears from these experiments that the many-lined spectrum can be obtained for any potential difference above 5 volts. As the other experimenters, as well as the writer, have obtained the single-lined spectrum above 5 volts we have the interesting fact that both the single-lined and the many-lined spectra of mercury may be obtained above 5 volts. McLennan and Henderson (l.c.) obtained the single-lined spectrum for potential differences as high as 12.5 volts. The writer has been able to obtain it for potential differences as high as 21.5 volts. No attempts have been made, as yet, to obtain it at higher voltages, but there seems to be no reason why it could not be obtained.

The fact that the many-lined spectrum of mercury can be produced for the same potential differences for which the single-lined spectrum has been obtained raises the question as to whether there is such a thing as a true single-lined spectrum of mercury above 5 volts. Or to put it another way can the radiation $\lambda = 2536.72$ Å. U. be produced above 5 volts without the appearance of any of the other radiations of mercury? The writer restricts the question to a potential difference greater than 5 volts for reasons which will appear later. Further, if either the single-lined spectrum or the many-lined spectrum can be produced independently of one another above 5 volts, what are the conditions necessary in order to bring out either the one or the other? The spectrogram labelled I. in the accompanying plate is submitted relative to the above questions. This spectrogram was taken under the following conditions. The maximum and minimum potential differences between anode and cathode were 9.0 and 8.4 volts. The distance between the anode and cathode was between 2 and 3 mm. The temperature immediately outside of the tube was about 160° C. The slit of the spectrograph was arranged so that part of it received light from between the anode and cathode and part from below them. The time of exposure was 3 hours. That part of the plate which received light from between the anode and cathode shows the many-lined spectrum with the line $\lambda = 2536.72$ Å. U. relatively stronger than the others, whereas, that part of the plate which received light from below the anode and cathode shows only the line $\lambda = 2536.72$ Å. U. Further, the lines other than the line $\lambda = 2536.72$ Å. U. have blunt ends showing no tapering effect. It is hoped that this appears in the reproduction. In as much as the lines other than the line $\lambda = 2536.72$ Å. U. show no tapering effect, this spectrogram seems to indicate that the single-lined spectrum can be produced without any of the other radiations being present. The spectrogram also seems to show that the occurrence of the single-lined spectrum or the many-lined spectrum depends upon the density of the electronic discharge. From the bluntness of the lines it would also appear as if there were a minimum density of electronic discharge which was necessary in order to produce the many-lined spectrum. It should be pointed out that no variation in the density of the mercury vapor could be present to explain the above spectrogram.

Another spectrogram bearing on the above questions is shown in II. of the plate. The maximum and minimum potential differences in the case of this spectrogram were 21.5 and 20 volts. Ordinarily such a voltage would produce an intense arc, but in this case the cathode consisted of uncoated platinum which had been heated in a good vacuum for 30 or 40 hours. As a consequence the electronic discharge from it was very small. In no other way did the experiment differ materially from others where strong spectra were obtained. The spectrogram shows only the line $\lambda = 2536.72$ Å. U.

Spectrogram III. also bears on the above questions. It was taken under the following conditions. The maximum and minimum potential differences were 5.5 and 4.7 volts. The cathode was coated with barium oxide. The distance between the anode and cathode was about 3 mm. The temperature immediately outside the tube was about 165° C. The time of exposure was 4 hours. The plate shows the line $\lambda = 2536.72$ Å. U. very plainly and some of the other stronger lines of the many-lined spectrum faintly. The writer is unable to decide whether the many-lined spectrum in this case came in slowly or whether it was produced by some sudden increase in the density of the electronic discharge.

Although the above spectrograms are conflicting in their evidence, the writer is of the opinion that it is possible to produce the radiation $\lambda = 2536.72$ Å. U. without any of the rest of the radiation of mercury being present. Further, in order to produce the single-lined spectrum for potential differences greater than 5 volts, it seems to be necessary to keep the density of the electronic discharge below a certain minimum value and the greater the potential difference used the smaller must this minimum value be.

In endeavoring to locate the lowest potential difference at which the many-lined spectrum was produced, it was found possible to obtain the single-lined spectrum for potential differences considerably below the minimum as obtained by the other experimenters. Spectrogram IV., for instance, was obtained with maximum and minimum potential differences of 2.5 and 1.9 volts. The plate in this case was exposed 3 hours. Slight traces of the line were seen on a plate exposed 4 hours with maximum and minimum potential differences of 2.0 and 1.4 volts. These results raise a question relative to whether a potential difference across the electrodes is necessary in order to produce the single-lined spectrum. The writer is not able to answer this question. Whatever may cause the single-lined spectrum, it decreases in intensity very rapidly with decreasing voltage. In order therefore to get it at these low voltages every means for increasing the intensity of radiation must be used. But even after the radiation has been made as intense as possible a point is reached where the fogging of the plate masks the effect looked for. Spectrogram V. shows how intense the radiation can be obtained for maximum and minimum potential differences of 4.1 and 3.5 volts. The plate in this case was only exposed 2 hours. A comparison of spectrograms IV. and V. will give an idea relative to the decrease in intensity of the radiation $\lambda = 2536.72$ Å. U. with the decrease in voltage.

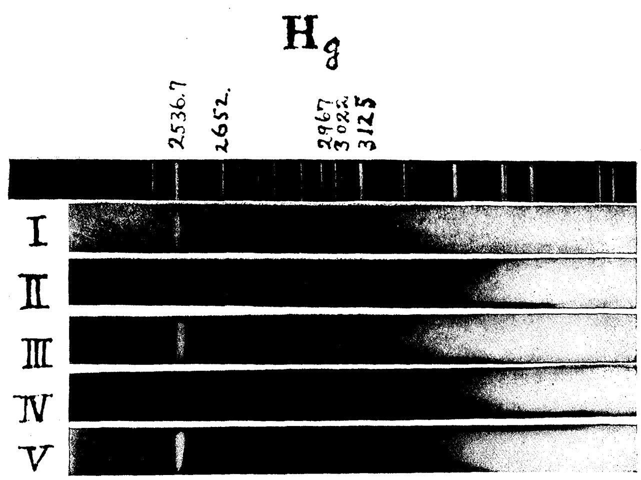
The production of the single-lined spectrum of mercury at such low voltages as recorded above seems to cast doubt on the deductions of Franck and Hertz. These experimenters came to the conclusion that ionization was necessary in order to produce the single-lined spectrum and as ionization occurs at 4.9 volts for mercury they did not believe that the single-lined spectrum could be produced below that voltage and their experimental results seemed to bear out their theory. If ionization is necessary to produce the single-lined spectrum then we must conclude that the electrons leave the hot body with a velocity greater than has been supposed. The velocity of emission would have to be of the order of 2 or 3 volts. Richardson and Brown have determined the velocity of emission from platinum and from platinum coated with an oxide.[1] In the case of platinum they never found the velocity greater than 0.6 volt and in the case of the oxide-coated platinum the greatest velocity obtained was 1.2 volts.

As these results seemed to point to an explanation it was thought worth while to try and measure the velocity of emission right in the tube under observation. For this purpose the anode was connected to the one pair of quadrants of an electrometer with the other pair grounded.

[1] Phil. Mag., Vol. 16, p. 353 (1908).

The negative end of the cathode was joined to the earth through a variable potential difference, so that its potential could be varied with respect to the earth. If the hot cathode gave out only electrons then by raising its potential a value could be reached for which no charge could pass to the electrometer. As is well known both positive and negative particles are given out from a hot body. With the two streams of particles coming from the cathode it was found that by raising the potential of the negative end of the cathode a value was reached which gave no deflection of the electrometer. This means that the positively charged particles forced out by the potential of the cathode just balanced the negatively charged particles which, owing to their initial velocity, overcame this same potential. If the potential of the cathode was raised above this point the electrometer acquired a positive charge and if it was lowered below this point it acquired a negative charge. Were the positive stream to be eliminated then the potential would have to be still higher in order to prevent the electrometer from acquiring a charge. In the case of the writer's apparatus it was found that twenty or thirty hours of heating and pumping were not sufficient to greatly reduce the positive stream. This was probably due to the great amount of matreial from which it was necessary to drive the occluded gases. In only one case was the positive stream reduced to small proportions. This was for the case of pure platinum. As time was limited no effort was made to overcome the difficulties. The general results obtained, however, were these. With pure platinum for both anode and cathode the potential necessary in order to get zero deflection of the electrometer after 20 or 30 hours of heating was about .25 volt. Had there been no positive stream this value would have been raised. This result agrees quite well with that of Richardson and Brown for uncoated platinum. With platinum coated with barium oxide the potential necessary to get zero deflection of the electrometer was very much greater than for pure platinum. After long heating and pumping a value as high as 2.3 volts was obtained. As there was still a large positive stream this value would have to be raised considerably, perhaps to 3 volts, in order to stop the negative stream. To conclude from the above results that the velocity of emission is of the order of 3 volts would, it appears, be unsafe for there are a number of uncertain factors. The results, however, are suggestive and the phenomena need further investigation.

As the velocity obtained for pure platinum could not be much in doubt an attempt was made to find the potential difference for which the single-lined spectrum appeared for uncoated platinum electrodes which had been heated in a vacuum for 30 or 40 hours. It was found, however, that no trace of a line appeared for voltages in the vicinity 4.9.



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Even potential differences as high as 20 volts gave only a very weak line after 4 hours' exposure. (See II. of the plate.) This was no doubt due to the smallness of the electronic discharge. It is evident that the question relative to whether ionization produces the single-lined spectrum is still unanswered.

Another result obtained in connection with these experiments which needs explanation is the fact that an arc was made to operate at a potential difference as low as 3.2 volts. The arc was never found to strike at a potential difference lower than 5 volts but after it was once in operation there were times when the maximum voltage across it was as low as 3.2 volts. The spectrum from it then showed the many-lined spectrum of mercury. If a velocity of emission of the order of 2 volts be assumed for the electrons then the arc at these voltages can be explained, otherwise it must be assumed that the arc itself produces the nceessary ionization to keep itself in operation. If the velocity of emission of the electrons is of the order of 2 or 3 volts then it appears that the arc should be capable of striking at 2 or 3 volts if ionization is all that is necessary. This result has not been observed.

The experiments outlined in this paper have shown: (1) that the mercury arc can be made to strike at any potential difference greater than 4.7 volts, thus producing the many-lined spectrum; (2) that the arc having been made to strike will operate as low as 3.2 volts, producing the many-lined spectrum. This needs a special explanation for the production of its ions unless it is shown that the velocity of emission is sufficient to account for the discrepancy; (3) that the single-lined spectrum can be obtained for all potential differences between 2.5 and 21.5 volts. In order to explain its production below 5 volts it must be assumed that there is a large velocity of emission or else the idea that ionization is necessary for the emission of light must be abandoned. It may be that ionization is necessary to produce the many-lined spectrum but that a jarring effect is all that is necessary to produce the single-lined spectrum; (4) that whether the many-lined or single-lined spectrum of mercury appears above 5 volts depends upon the density of the electronic discharge.

The writer wishes to express his gratitude to the staff of the Ryerson Physical Laboratory, University of Chicago, for placing at his disposal the facilities for doing these experiments, and especially to Professor Millikan, whose interest in this subject inspired the work.

Since doing the above experiments the writer has become associated with the University of British Columbia and expects to continue this work.

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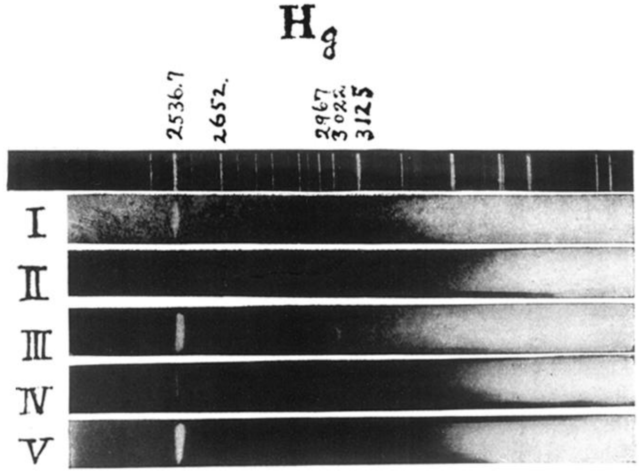
Hg
2536.7
2652.
2967
3022
3125
I
II
III
IV
V