THE SPECTRA OF MERCURY ABOVE THE IONIZATION POTENTIAL

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Abstract

Excitation of arc spectra of Hg by electrons having velocities above the ionization potential. Effect of recombination.—Electrons in mercury vapor with velocities greater than the ionization potential were confined into a beam by a magnetic field. The light produced was projected on the slit of a spectroscope with the direction of the beam at right angles to the slit. Perpendicular to the beam an electric field withdrew positive ions before they recombined. The intensity of the arc lines was found to be independent of the electric field which indicates that recombination contributes very little to the formation of these lines. These results are contrary to the previously accepted explanation given for the complete arc spectrum appearing above the ionization potential. Consequently in addition to simple excitation the arc spectrum can be explained in the two following ways, (1) as being due to the return to the 1^1S_0 state by an electron which has been displaced from an inner energy level to a virtual orbit while simultaneously one of the electrons of the valency group falls in to fill the vacated level; (2) due to a special type of recombination which is called initial recombination.

Intensity variation of the spark lines due to the motion of the positive ions.—Spark lines due to singly and doubly charged ions show a variation of intensity along their length in such a manner that it is possible to distinguish them from the arc lines. It is also possible to differentiate between the lines of the first and the second spark spectrum.

SINCE the complete arc spectrum of the normal mercury atom appears when the mercury vapor is ionized it was formerly supposed to be due to the ionization of the gas or rather due to the recombination of the free electrons with the atomic ions. However, Eldridge[1] has found that important lines of the arc spectrum can be produced below ionization which is in accord with the Bohr theory and in agreement with the photoelectric experiments of Franck and Einsporn. In previous experiments on the spectrum of mercury vapor excited by the higher velocity electrons, effects due to the direct impacts and to recombination have not been separated. The question arises as to which of these processes contributes the more to the production of the arc lines. The purpose of this work is to obtain the mercury spectrum with and without recombination occurring and to determine the role which recombination plays in the production of the arc lines and also to study some of the characteristics of the mercury spark spectrum given out by ions having a particular direction of motion.

Experimental Arrangement and Procedure

In Fig. 1 is shown the arrangement of electrodes which were mounted in a bulb containing mercury vapor at a pressure of 0.001 mm of Hg. Elec-

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

trons from the heated tungsten filament F were accelerated through the slit system S_1 with velocities greater than 40 volts. The electrons passed through the opening in S_2 and were given an additional velocity which carried them into the Faraday cage C. The purpose of the field between S_2 and C was to prevent the return of secondary electrons from C. The filament was a straight wire whose cross section is shown at F. A uniform magnetic field of several hundred gauss produced by Helmholtz coils was in the direction indicated at H and served to confine the electrons into a well defined beam. The light coming from the region indicated by the dotted circle was projected on the slit of the spectroscope in such a manner that the direction of the beam was perpendicular to the slit. An electric field parallel to the slit placed between the two parallel plates served to withdraw the ions before they recombined. This field was not made greater than 200 volts per cm. It can be shown that when the electrons are under the influence of this transverse electric field they will not be deviated appreciably from their original path and that their velocity will not be altered by more than a fraction of a volt. The positive ions on the other hand will be drawn over to the plate while their path will describe an arc of a cycloid of very large diameter compared with the dimensions of the apparatus, that is, the ions will move practically in a straight line in going to the plate. Galvanometer G_2 gave a measure of the current reaching the edges of S_1. This was small compared to the total current of the beam collected by C as measured by G_6. G_5 indicated a small number of scattered electrons which reached S_2. Either G_3 or G_4 could be used for measuring the positive ion current. The region midway between the parallel plates which was occupied by the beam was kept at the same potential as S_1 and S_2. The two parallel plates were kept positive and negative respectively by the same amount with reference to S_1, S_2. Without this cross field we have the electrons moving in a region free from external electric fields and hence the ions and free electrons are able to recombine. The procedure was to apply an electric field of such an amount that a saturation positive-ion current was obtained, so that every ion formed was removed before it was allowed to recombine. Photographs of the spectrum were taken with and without the cross field applied.

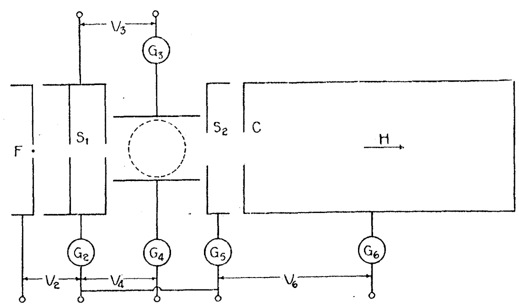

Fig. 1. Diagram of apparatus.

Experimental Results and Discussion

Fig. 2 shows a typical plate. The velocity of the electrons in this case was 300 volts. The top exposure was taken with the cross field applied and the lower one without. Beneath the lines indicated by the circles are spark lines (2847A, 2947A, 3208A) classified by L. and E. Bloch[2] as due to singly charged ions and called by them E_1. The dots mark lines of the second spark

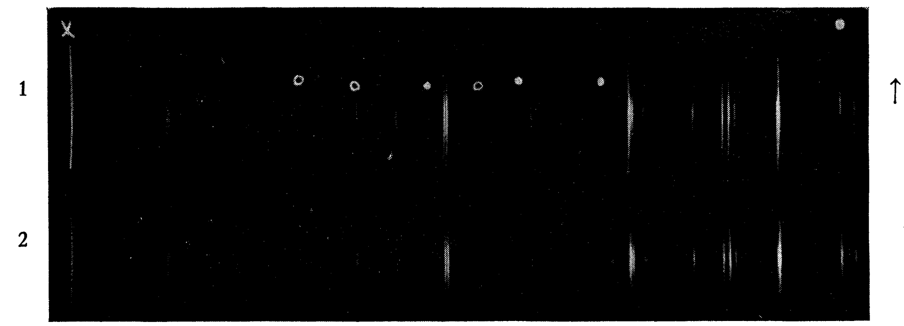

Fig. 2. Spectra of mercury (1) with the cross field applied and (2) without. The direction of motion of the positive ions is given by the arrow.

spectrum which have been designated as E_2 by L. and E. Bloch. One of them (4797A) can easily be seen while the others are very much fainter but could be readily observed on the original negative. The other lines belong to the arc spectrum. Some of them such as the one indicated by the cross (which is the 2537A line) are much longer than the others and actually extend beyond the region of the beam. The light coming from the part outside the beam is thought to be due to resonance radiation.

It is noticed that the arc lines and the lines of the first spark spectrum are unaffected by the field while the lines due to the doubly charged ion show a change in their intensity distribution. Curve 1 in Fig. 3 shows more clearly the intensity of the 4797A line with respect to the beam. On the ordinate is plotted intensity in arbitrary units and on the abscissa the position with respect to the center of the beam. Curve 2 represents one of the arc lines belonging to the sharp series which showed but little resonance radiation and gives the variation of the electron current in the beam. The direction of motion of the ions is indicated by the arrow and it is seen that the spark line is actually displaced in this direction.

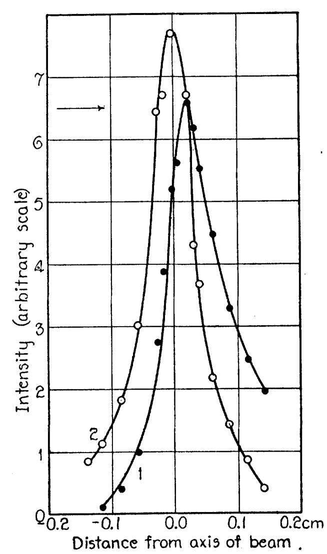

Fig. 3. Experimental curves showing intensity variation of (1) the 4797A line of Hg^{++}, and (2) an arc line which gives the width of the beam.

By altering the size of the filament and the openings in the diaphragms a beam of much greater width could be produced so that the ions in their

[2] L. and E. Bloch, Jour. d. Physique **4**, 333 (1923).

journey through it would be more apt to experience a second collision. The photographs obtained show the arc lines still unchanged in the presence of the electric field, but the lines of the singly charged ions now exhibit a change in intensity as is shown by Curve 1 in Fig. 4. Curve 2 represents the intensity for an arc line which gives the width of the beam. As to whether these E_1 spark lines show a change in intensity because of the electric field

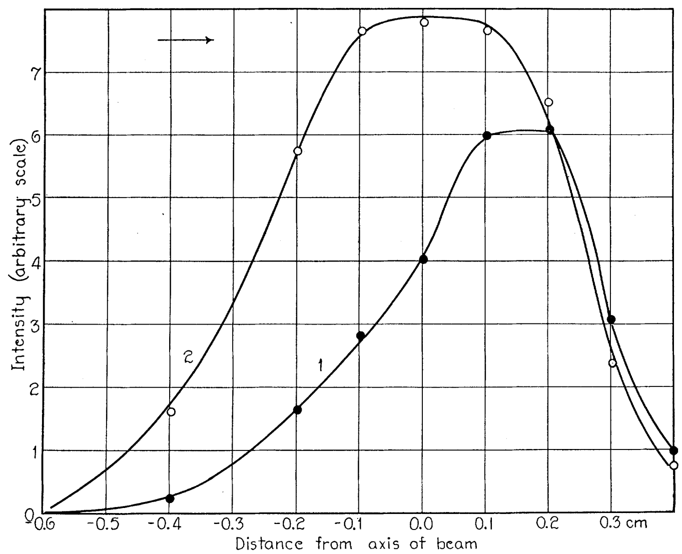

Fig. 4. Experimental curves showing intensity variation of (1) the 2847A line of Hg^+ and (2) an arc line which gives the width of the beam.

is found to be determined by the size of the beam. We are led to believe that the light observed with the wider beam is due to a double collision while that of the other is brought about by a single impact. Since the arc lines are always unaffected by the external field we are able by suitably adjusting the size of the beam to distinguish between the spark and arc spectrum and also are able to differentiate between the spark lines of the first and second spark spectrum.

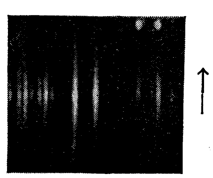

Fig. 5. Showing two exposures taken close together on the same plate with and without the cross field.

Fig. 5 shows two exposures taken on the same plate with and without the cross field. The line beneath the dot which is the 4797A E_2 line shows the effect of the field. The densities of the other lines which belong to the arc spectrum were found to be the same for the two exposures. We therefore conclude that recombination does not contribute to the production of the arc spectrum under the conditions of this experiment, since recombination would be much less effective with the electric field than in its absence. The electron current in the beam was of the order of 10^{-4} amperes/cm^2 while the positive ion current was 10^{-5} amperes/cm^2. The electron current and the pressure in the tube could be kept constant over a period of four hours which was the time necessary for the two exposures. For testing the constancy of conditions two photographs were taken with all conditions the same and the density of the lines were found to be equal.

Recently Mohler[3] has shown that recombination spectra do occur but he found it necessary to use high concentrations of ions and slow electrons. As is to be expected he found continuous bands terminating sharply on the high wave-length side. Thus to obtain spectra due to recombination a relatively large number of ions and slow electrons must be assembled together.

Having now definitely shown that in this experiment recombination does not occur of sufficient amount to account for the formation of the arc lines it is necessary to resort to collision processes to explain their existence. Since the velocity of the electrons is of the order of 200 volts it has much energy in excess of that which it would be necessary for it to lose in order to excite only the arc spectrum. Eldridge[4] has shown, on measuring the energy losses at electron impacts, that in mercury vapor when the electron has a velocity slightly above 4.9 volts it is then most likely to lose that amount of energy; but when it is increased to 16.5 volts very few electrons suffer this energy loss. This experiment as well as others has shown that the efficiency of excitation for these small velocities reaches a maximum slightly above the critical potential and then decreases, so that if the curve representing probability of excitation, were extrapolated to the higher velocities it would indicate that 200 volt electrons would not be likely to lose only these small amounts of energy. We should therefore not expect that these high velocity electrons would be able to produce the arc spectrum by simple excitation. The experiments of Bricourt[5] and also Seeliger in which the intensity of lines of the arc spectrum have been measured as a function of the velocity of the electrons, show that the intensity of the light starting sharply from the threshold value reach a maximum and then decrease as would be predicted by the experiments on the efficiency of excitation. Their results also give that the light intensity increases again for the higher velocities to a second maximum which is about equal to the first and comes at about eighty volts. It seems reasonable to suppose that this second rise of the curve is due to the appearance of a new phenomenon in which the electrons of the filled inner groups play a part.

Fricke[6] and others in measuring x-ray absorption have shown that several of the absorption limits have a definite fine structure. Kossel[7] has accounted for this as being due to the transport of an electron from its shell to the periphery and to certain virtual orbits which lie outside of the atom. The amount of energy for the latter process is of course the greater and hence we find the lines of the fine structure appearing on the high frequency side of

[3] F. L. Mohler, Phys. Rev. **31**, 187 (1928).
[4] John A. Eldridge, Phys. Rev. **20**, 456 (1922).
[5] P. Bricourt, Comptes Rendus **185**, 846 (1927).
[6] H. Fricke, Phys. Rev. **16**, 202 (1920).
[7] Kossel, Zeits. f. Physik **1**, 124 (1920).

the absorption band. More recently Chamberlain and Lindsay[8] in determining outer x-ray energy levels for the elements from antimony to samarium have postulated three possible transition combinations which can be expected for antimony, tellurium and iodine, to explain the L_{I} absorption limit. (1) An electron ejected from the L_{I} orbit might go to infinity and a valence electron from the $O_{II\ III}$ group drop in to fill the vacated place. (The O_{II-III} is for these elements what might be called the incompletely filled valency group.) (2) The L_{I} electron could stop in the O_{II-III} level and then fall back again to its original level. (3) The electron ejected from the L_{I} level might go to a virtual orbit and then one of the electrons in the O_{II-III} level drop back to fill the vacancy in the inner energy level while at the same time the electron in the virtual orbit falls back to the O_{II-III} group. Processes analogous to (1) and (2) would not give out the arc spectrum while (3) by virtue of the electron going from the excited state to the normal valency level could emit lines of the arc spectrum. To explain the second maximum of Bricourt's intensity-voltage curve and to account for the production of the arc lines by the high velocity electrons in the present work, we suggest that transition combinations similar to (3) are taking place.

The formation of arc lines may be due to a special type of recombination which is called initial recombination. Formerly initial recombination was thought to be a recombination between two ions generated from the same molecule. According to this hypothesis an electron ejected from a molecule goes only a small distance from the ion. The electron, however, is still attracted to the ion and will return again to recombine unless there exist external fields of sufficient strength which can remove the electron completely from the ion. Recently Franck[9] has proposed an initial recombination which he describes as being a recombination between an ion and its own electron under the condition in which the electron is not free. He considers the process as not being appreciably affected by external fields because the electron is assumed to be always under the influence of the intense field of the ion. In the present investigation the external fields were not great enough to prevent initial recombination as defined by Franck and consequently the observed intensity of the arc lines may be due to this type of initial recombination.

The writer desires to express his thanks to Professor John T. Tate for proposing this method of producing spectra without recombination and to Professor W. F. G. Swann for his suggestions during the course of this work. Also the writer wishes to thank Professor James Barnes for the privilege of using the densitometer at Bryn Mawr College. The investigation was begun in the Physical Laboratory of the University of Minnesota.

BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE,
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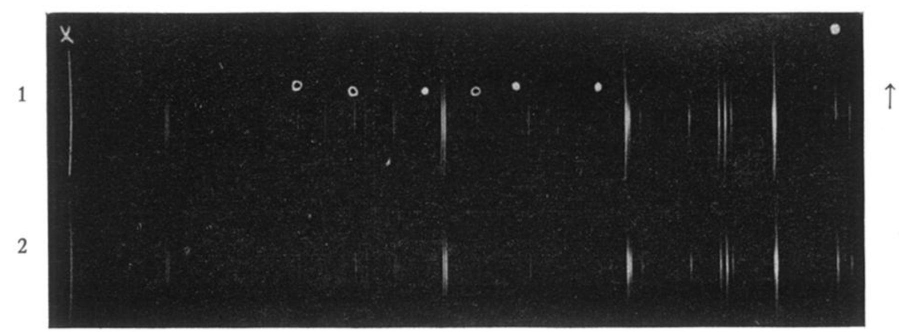
July 16, 1928.

[8] Chamberlain and Lindsay, Phys. Rev. **30**, 369 (1927).
[9] Franck, Jour. Franklin Inst. **205**, 473 (1928).



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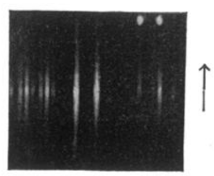

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