THE SPECTRUM OF MERCURY BELOW THE IONIZATION POTENTIAL

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ABSTRACT

Spectrum of mercury excited by electrons of energy 7 to 10.4 volts.—When mercury vapor is bombarded by electrons of energy below the ionizing potential 10.4 volts, previous spectroscopic investigation has detected the emission of only the lines $1S-2p_2$ and $1S-2P$, whereas according to the Bohr theory there are many other lines which correspond to changes of orbit involving less energy change than 10.4 volts, which should be emitted line by line as the impacting energy is increased so as to be sufficient to take the electrons to the proper orbits. The failure to observe these lines is now shown to be due to the effect of space charge in lowering the energy of the impacting electrons except at the immediate surface of the anode, and by focussing light from the surface of the anode onto the slit of a quartz spectrograph, spectrograms have been secured showing the development of the spectrum of mercury in the stages predicted by the theory and at approximately the theoretical voltages. At 7 volts only $1S-2p_2$ appears, at 8.4 volts 4 new lines due to electrons returning from the $2S$ or $2s$ levels, at 8.9 volts 8 new lines due to electrons returning from the $3d_1$, $3d_2$, $3d_3$, $3D$ levels; at 9.9 volts 16 more lines; etc., in full agreement with the theory and with the photo-electric experiments of Franck and Einsporn.

THE complete spectrum of the normal mercury atom appears when the mercury vapor is ionized. Below the ionizing potential Franck and Hertz obtained a single line spectrum λ2536 and from analogy with other metals there can be little doubt that the line λ1849 also appears without ionization. According to the most obvious interpretation of the Bohr theory all of the lines should appear, group by group, below the ionization point, but other lines have not been observed.[1] Accordingly, a peculiar importance was formerly attached to the orbits $2p_2$ and 2P the orbits associated with these two lines. The electron could apparently be directly displaced by electronic collision from its normal position to these orbits but not to any others; the other orbits were apparently entered only by foreign electrons as they united with an ionized atom, and the complete spectrum, since it appeared at ionization, was naturally considered to be caused by the ionization of the gas.

[1] McLennan and Henderson, Roy. Soc. Proc. **91,** 485-491 (1915); McLennan and Ireton, Phil. Mag. **36,** 461-471 (1918). After the present work was begun Hertz announced somewhat similar results (Naturwissenschaften **11,** 778 (1923). Hertz did not use a quartz spectrometer and obtains therefore only four of the lines which are found in the present paper.

This somewhat unsatisfactory picture was discredited by the remarkable experiment of Franck and Einsporn. Using photo-electric rather than spectroscopic methods, they showed that the photo-electric current suddenly increased as the critical voltage for each of the known (as well as some unknown) orbits was reached. This result was extremely interesting but also somewhat puzzling, the most puzzling question being, if electrons are indeed displaced to these orbits without ionization, why do they not betray themselves to the spectroscopist? Until this was answered the theory was in a rather unsatisfactory state.

The answer seems to be that in the usual spectroscopic arrangement conditions are such that the space charge in the tube depresses the effective voltage below that of the electrodes and below that necessary to excite any but most easily excited lines. If conditions are such that the effect of space charge is minimized, all the lines come out group by group at these critical voltages, giving a beautiful demonstration of the truth of the fundamental Bohr theory.

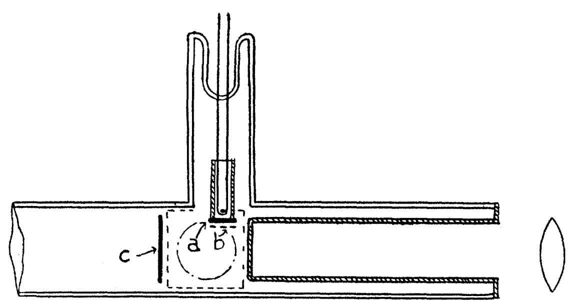

Fig. 1. Diagram of discharge tube.

The discharge tube used is shown in Fig. 1. The main tube was glass, about 3 mm in diameter, and was lined with nickel gauze to make the interior (ostensibly) a constant potential region. Re-entrant in one end was a quartz tube, the end being close to the region of discharge, and through this the spectrum could be observed with little absorption by the mercury vapor. The mercury was excited by slow electrons which, coming from the constant potential oxide coated platinum source *a*, were accelerated to the grid *b*, and entered the "constant potential region." The dashed circle in the figure represents a side tube extending several inches below the discharge chamber and forming a mercury well. Heating elements were provided about the mercury well and the discharge chamber to maintain a suitable vapor pressure (probably about .05 mm). The currents used were of the order of 1 milliampere.

It being the object of the experiment to detect, if possible, the spectrum below the ionization point, it was necessary to determine quite definitely the beginning of ionization. For this purpose the electrode *c* was placed behind the nickel grid at one end of the chamber. When the potential of this is kept equal to that of the thermionic source only positive ions can reach it. Such an electrode gives a small photo-electric current when illuminated, but this is always negligible in comparison with the positive ion current at ionization. The current to the electrode was measured as a function of the accelerating voltage (between source and grid). Fig. 2 shows that ionization set in when the impressed voltage reached 11 volts. The ionization potential of mercury is 10.4 volts; potential drops in the leads and contact potentials explain the discrepancy. The potentials as given later in this paper have been corrected by 0.6 volts to give the true potentials in the tube.

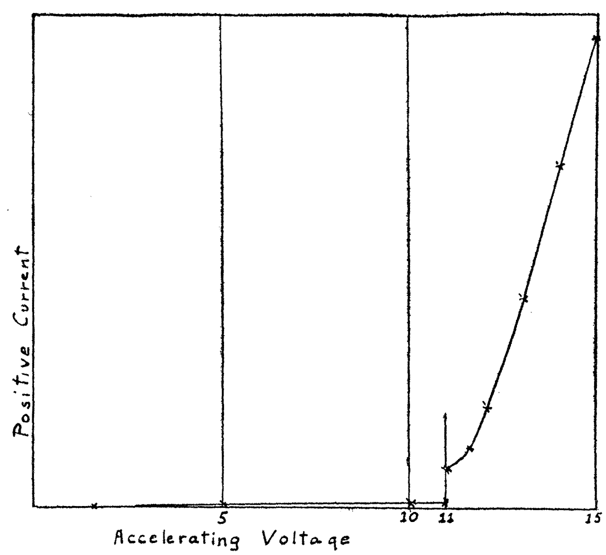

Fig. 2. Current-voltage curve showing ionization point.

While it was thought necessary to make this direct measurement of ionization, as a matter of fact the discharge suddenly alters its appearance when ionization sets in, so markedly that there can never be any doubt concerning the incidence of ionization. As the voltage is raised the tube appears to the eye at first dark; when the potential is within 2½ volts of the ionizing potential, a green glow appears bordering the electrodes, at first very thin but extending further and further into the tube as the voltage is raised, the color changing somewhat at the same time. Just as the glow seems about to fill the entire tube, ionization suddenly sets in (as measured by the galvanometer connected to c) with a complete change in the appearance of the tube. Above the ionization point, the visible glow is confined to a column proceeding from the cathode directly across the tube, the electron stream being sometimes so well directed as to preserve the pattern of the accelerating grid along the whole length of the column.

The obvious explanation of this behavior is that when there is no ionization the tube is so filled with negative space charge that only in their immediate proximity is the potential equal to that of the electrodes. Consequently only here are the various spectrum lines excited when the electrode reaches their respective critical potentials. The positive ions when they occur completely neutralize this space charge and allow light-producing collisions to occur at all points in the path of the electron.

Mercury Spectrum Below Ionization

In consequence of the space charge it is essential in examining the spectrum as a function of the exciting voltage, to focus upon the slit of the spectrometer light coming from the immediate proximity of the electrode. In the tube used one part of the gauze which lined the tube was flat and this was focused upon the spectrometer. A Hilger monochromator was adapted to serve as spectrometer by substituting a camera for the telescope; this gave sufficient dispersion for the purpose and was fairly rapid.

In Fig. 3 are shown spectrograms obtained with exciting electrons of different velocities, given in volts at the left of each spectrogram. To the right is given the usual energy level diagram so arranged that the various possible transitions are shown opposite the spectrogram to which they apply. In this diagram the vertical line *1S* represents the stable orbit of the valence electron; the other vertical lines representing the outer unoccupied orbits are drawn at distances proportional to the energies of these orbits, reckoning from the *1S* orbit as zero.[2] The scales at the bottom of the figure give the symbolic name of the orbit (Paschen's notation) and the energy of the orbit in volts. The symbols above the diagram N_k^j give the quantum numbers as assigned by Bohr, N being the total quantum number, k the azimuthal and j the inner quantum number.[3] It will be remembered that the selection principle allows all transitions in which k changes by one unit and in which j changes by 1 or 0 (except that the transition between orbits for each of which $j=1$

[2] For clearness it has been necessary to exaggerate the separations of the levels d_1, d_2, d_3 and D.

[3] Compare Bohr, Ann. der Phys. May 1923

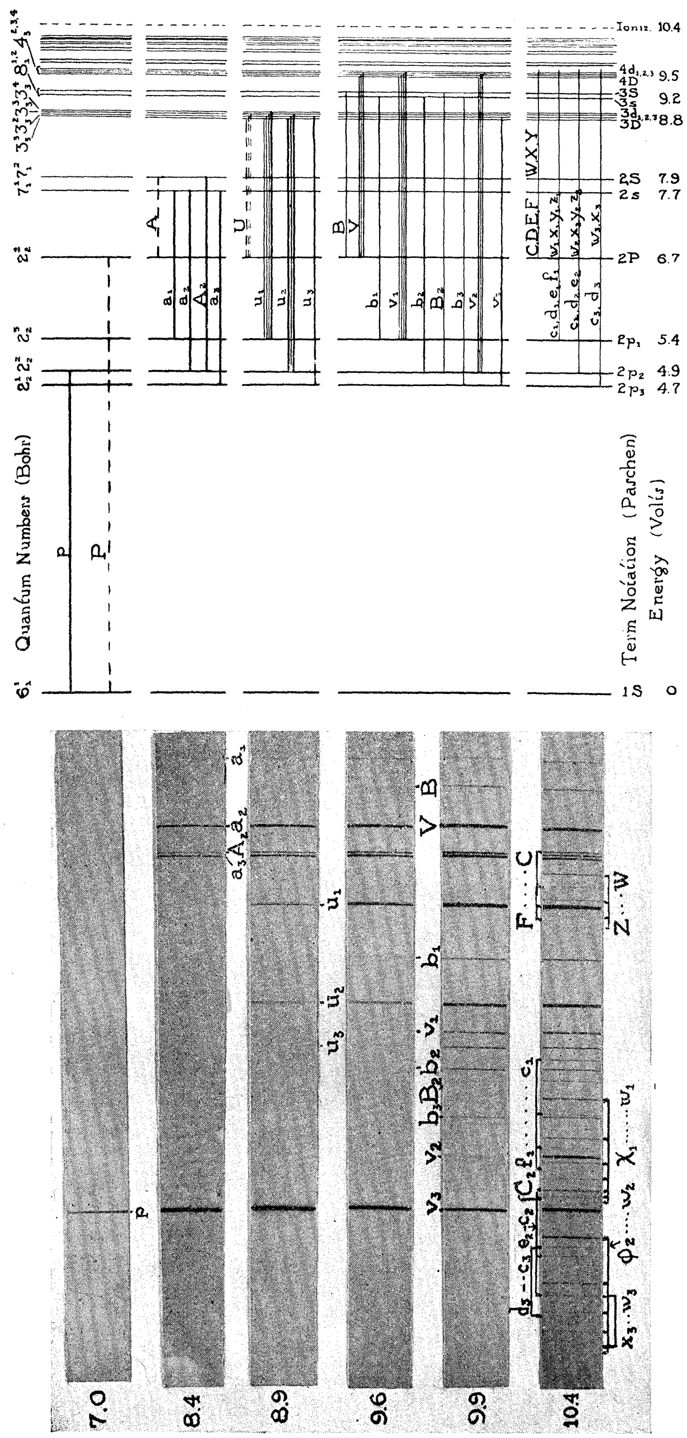
Quantum Numbers (Bohr)
Term Notation (Paschen)
Energy (Volts)
Ioniz. 10.4
4D 9.5
3S 9.2
3D 8.8
2S 7.9
2s 7.7
2P 6.7
2p₁ 5.4
2p₂ 4.9
2p₃ 4.7
1S 0
7.0
8.4
8.9
9.6
9.9
10.4

Fig. 3.

is barred). To simplify the figure all levels of the p_1, p_2, p_3, or P type of higher order than the first have been omitted since there is no line involving levels of this type that falls within the range of sensibility of the photographic plates used. All other levels are represented and all light producing transitions permitted by the theory are given by the horizontal lines. Such of these transition lines as are dotted correspond to spectrum lines which fall in the infra-red or ultra-violet outside of the range of the plate and so are not represented in the spectrogram.

The notation which has been used should explain itself by reference to the energy diagram, but it may be summarized here:

2nd subordinate series

Triplets	$a_1 \ldots f_1$	represent	$(2p_1-ms)$	$m=2\ldots7$
	$a_2 \ldots e_2$	"	$(2p_2-ms)$	$m=2\ldots6$
	$a_3 \ldots d_3$	"	$(2p_3-ms)$	$m=2\ldots5$
Singlets	$A \ldots F$	"	$(2P-mS)$	$m=2\ldots7$
Combination	$A_2 \ldots C_2$	"	$(2p_2-mS)$	$m=2\ldots4$

1st subordinate series

Triplets and combination	$u_1 \ldots \chi_1$	represent	$2p_1-md_{1,2,3}$; $2p_1-mD$	$m=3\ldots10$
	$u_2 \ldots \phi_2$	"	$2p_2-md_{2,3}$; $2p_2-mD$	$m=3\ldots9$
	$u_3 \ldots \chi_3$	"	$(2p_3-md_3)$	$m=3\ldots6$
Singlets	$U \ldots Z$	"	$(2P-mD)$	$m=3\ldots8$

The topmost spectrogram shows the single line λ 2536, the only line which appears below 7.7 volts. The impacting electron has here enough energy to displace the atomic electron to the $2p_1$, $2p_2$, $2p_3$ or $2P$ orbits. The selection principle forbids the return from $2p_1$ or $2p_3$ and so the only lines which may be emitted at this voltage are $1S-2P$ and $1S-2p_2$ and of these the former falls too far in the ultra-violet to affect the plate. At 8.4 volts (the 2nd spectrogram) displacements of electrons to the $2s$ and $2S$ orbits are possible which result in the production of five more lines as shown in the diagram. The line $2P-2S$, λ10139 is the strongest in the spectrum but is in the infra-red. The others appear in the spectrograms.

In the third spectrogram, excited by electrons falling from the $3d_1$, $3d_2$, $3d_3$ or $3D$ levels eight additional lines should appear. With the small dispersion used the multiplet character of the lines is not completely shown; on the original spectrograms three components of $2p_1-3d_{1,2,3}$ (D) are shown and two components of $2p_2-3d_{2,3}$ (D). In the next two spectrograms the lines from the $3s$, S levels are not completely separated from those originating in electrons coming from the $4d$, D levels and these two spectrograms are best considered together. The last spectrogram shows the appearance of the spectrum just after ionization has set in, all the earlier lines of the subordinate series appearing.[4]

It will be realized that it is difficult to get sharp differentiation between the different groups of lines. This difficulty is due to three factors: (1) The velocity distribution of the electrons as they leave the source is nearly a volt. (2) The lens which focusses the tube upon the spectrometer slit is not achromatic; a blurred image of the light source is therefore obtained and when any new line appears as a narrow layer of light about the electrodes the image of this layer upon the slit is vanishingly weak. (3) It is likely that the probability of excitation of any state increases at least for a short range as the critical voltage is exceeded. This all makes it quite difficult to obtain the various lines with any suddenness as the critical voltages are reached. The best results were obtained by making the voltages as low as practicable and taking exposures of several hours.

Discussion of Results

It is very satisfying to have obtained the various groups of lines appearing at approximately the potentials predicted by the theory. The Bohr theory assigns certain energies to the different orbits. It is known from flourescent phenomena that light quanta of exactly these energy values can effect a displacement of the valence electron to these orbits (line absorption). The question arises whether it is actually possible for an electron with energy greater than that of some particular orbit to displace an electron to it. Hitherto the spectroscopic evidence has seemed to show that this was possible only in the case of the displacement $1S \rightarrow 2p_2$ and possibly in the case $1S \rightarrow 2P$. The present work, confirming the photo-electric results of Franck and Einsporn, shows that such a displacement is much more generally possible. It seems likely that a displacement of an electron from the normal ($1S$) orbit to any other is possible when the energy of an impacting electron equals or exceeds the energy of that orbit. It must be remarked however that the present experiment does not prove that this is the case because, for in-

[4] In the energy level diagram it has been impracticable to show all of the transitions from each of the outer levels corresponding to the many new lines in the last spectrogram. So by the single transition line shown terminating at the $2P$ level and drawn in the figure out to just beyond the $4d$ levels a multiplying of lines is to be understood starting respectively from the $4S$, $5D$, $5S$, $6D$, $6S$ etc. levels. All the lines given in the table are found but these are not all named in the energy diagram. The nomenclature here is obviously an extension of that in the upper spectrograms, C, D, E, F representing lines of the same series as A, B (i.e. $1P - mS$), W, X, Y, Z a continuation of the series whose earlier members are U, V, etc.

stance, if direct displacement were possible from the *1S* orbit to only some of the *d* orbits, nevertheless the other *d* orbits would become filled through collisions of the excited atom with neighboring atoms (collisions of the second kind of Rosseland and Klein.)

However this may be, it is certain that many, possibly all, of the lines of the spectrum are excited by electrons with velocities only slightly exceeding those calculated by the quantum relation. The transition $1S \rightarrow 2p_2$ has hitherto been considered specially prominent; in all inelastic collision experiments, even those of Franck and Einsporn where other deflection points were observed, it is this type of collision which dominates the whole shape of the curve. From the present work, on the other hand, it would appear that not only do the other lines appear below ionization but that the stronger of them are quite comparable in intensity with the line $1S - 2p_2$.

In addition to the inelastic collisions which Franck and Einsporn found corresponding to the most prominent spectroscopic terms there were a number of these collisions observed which had no spectroscopic counterpart. Of the collisions at lower voltage where the interpretation of their curve is quite definite, about half of those observed were in remarkable agreement with the spectroscopic terms, but half were equally definitely not to be associated with any known spectroscopic term. At that time with their results unsupported by spectroscopic observations, these anomalous types of collision could be considered as casting doubt upon the validity of the results; in view of the present work there can now, however, be little doubt as to their validity, and we must consider the meaning of those unexplained types of collision.

It appears possible that they are indeed real energy levels, whose orbits are quite incapable of functioning in spectroscopic emission since transitions both to and from them violate the selection principle. Such terms could not be detected by the spectroscopist, but only by an experiment such as that of Franck and Einsporn.

University of Wisconsin,
February 2, 1924.

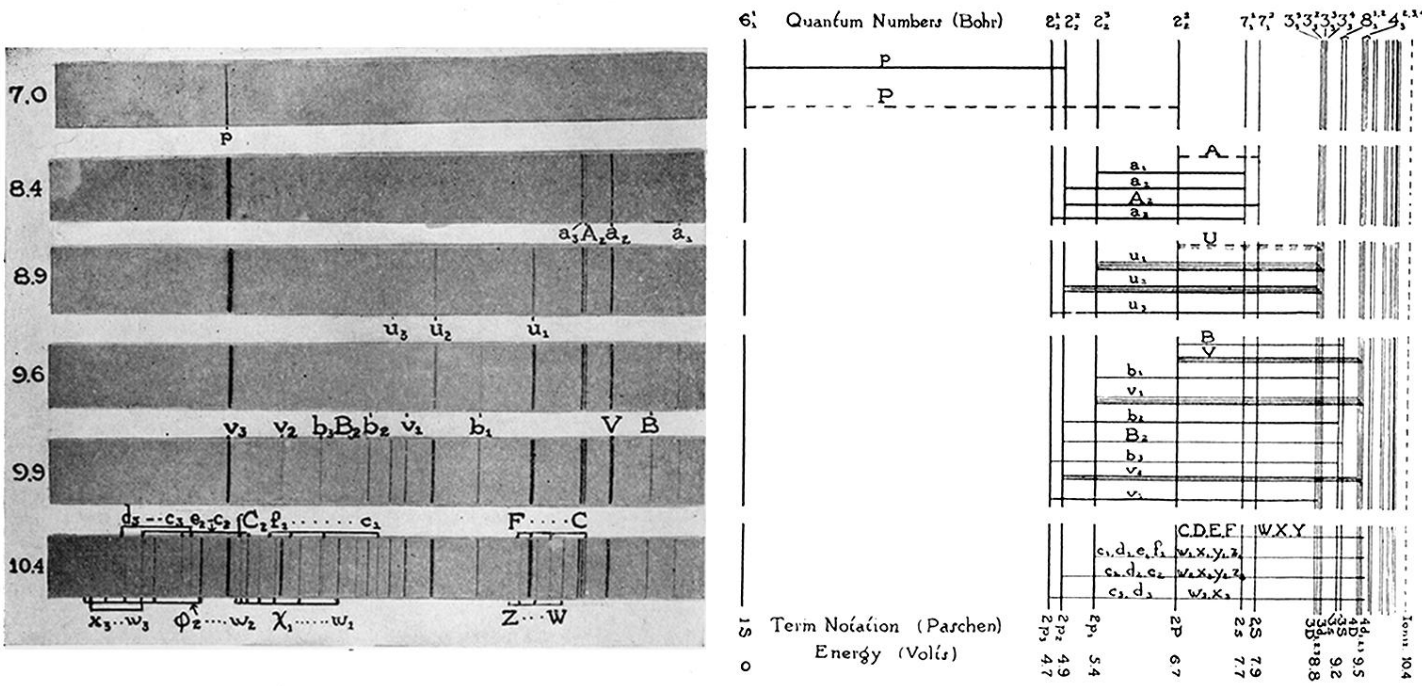
7.0
8.4
8.9
9.6
9.9
10.4
Quantum Numbers (Bohr)
Term Notation (Paschen)
Energy (Volts)
P
A
U
B
V
C.D.E.F
W.X.Y
F · · · C
Z · · W

Fig. 3.