Studies of the Afterglow in Mercury Vapor

II. Spectral Intensity Distribution‡

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The relative intensities of two hundred of the most intense lines of the spectrum of the afterglow in mercury vapor were measured photographically. The glow was observed in a stream of vapor which had previously passed through a region in which an arc discharge was maintained. By measuring the absolute intensity of the group of lines 3650–3663A radiated by one cubic centimeter of the vapor, the absolute intensities of these lines were determined and the total number of quanta radiated per second from unit volume calculated. From these results and from the measured rate of change of the positive ion concentration near the point of observation, it was shown that the total number of quanta radiated per second was much too great to be accounted for by assuming the afterglow to be produced by simple recombination of ions and electrons. Furthermore, a comparison of the number of quanta entering each atomic state by radiative transitions with the number similarly leaving this atomic state showed that the average energy possessed by the excited atoms emitting the line spectrum was about 9 electron volts. These results can best be explained by assuming that molecular particles with a mean life of about 10^{-3} second are formed by multiple impacts between the atomic ions produced in the arc, and neutral mercury atoms and that these particles dissociate to produce the excited atoms which radiate the afterglow. Some of the observed properties of the afterglow, especially the dependence of the intensity upon the pressure, are well accounted for by the assumption that this molecular particle is the excited molecule proposed by Arnot and Milligan.

INTRODUCTION

IN a preceding paper,[1] which in this paper will be referred to as "I" the present authors described an experimental study of the dependence upon vapor pressure of the intensity of the line spectrum of the afterglow in mercury vapor. They also made further observations on the "quenching" of the afterglow by auxiliary fields, and measured by electrical means the rate of disappearance of the ions. From these results they concluded that the bulk of the line spectrum in the afterglow does not result from "ion-electron recombination," by which is meant the direct union of a positive ion and an electron without any intermediate steps involving other bodies. They further interpreted the marked dependence upon pressure of the total intensity and of the distribution of intensity among the series lines of the spectrum as evidence that the process resulting in the line spectrum of the afterglow involves neutral atoms and is probably one in which molecular particles are formed from ions and neutral atoms, which particles later break up to furnish the excited atoms radiating the line spectrum. It was further concluded that metastable atoms are not directly involved in the production of these molecular particles, although they are intimately related to the diffuse bands which under special conditions were found in the afterglow with considerable intensity. The present paper describes further experiments with the afterglow which strongly confirm the conclusions of I.

EXPERIMENTAL

(1) Tube

The tube was in general similar to that described in I, but was considerably larger and did not have the electrodes *G*, *B* and *D*. The anode and a large oxide-coated cathode,[2] capable

* Now at Bell Telephone Laboratories.
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[1] R. C. Garth and G. E. Moore, Phys. Rev. **60**, 208 (1941).

[2] Acknowledgment is made to the Bell Telephone Laboratories, Inc., for their courtesy in furnishing this cathode.

of supporting an arc current of 25 amperes, were mounted in the vertical tube, 5 cm in diameter. The horizontal branch tube was 5 cm in diameter and 40 cm long, joining the vertical tube 3 cm above the anode. For observing the afterglow spectrum in the mercury stream, a fused quartz window, 2 cm in diameter, was attached to the branch tube about 9 cm from the center of the vertical tube. Immediately adjacent to this window was a probe of tungsten wire, 0.005 cm in diameter and 6 mm long, for the measurement of ion concentration and electron temperature at the point of observation. The concentration of mercury atoms was determined as in I.

(2) Intensity measurements

The intensities of the lines in the afterglow were too weak to measure with a thermocouple, even with arc currents of 25 amperes. Consequently the measurements were made in three steps: First, the relative intensities of seventeen reference lines emitted by a quartz mercury arc, operated under very constant conditions were measured to a precision of about one percent with a non-selective vacuum thermocouple.[3] This couple was so mounted on a screw driven carriage that the collector was maintained with its face perpendicular to the incident beam, in the focal plane of the quartz lens of a spectrograph (focal length = 30 cm; aperture = 2.5 cm), constructed to permit interchangeable use of couple and plate-holder. The voltage of the quartz arc was held constant to within ± 0.2 volt by a control device described in another paper.[4] The relative intensities of the lines emitted were constant to better than one percent over periods of several hours, while the absolute intensities of all but the resonance lines remained constant to within three percent, the changes being so slow that they could readily be corrected for. These measurements were corrected for the transmission of the spectrograph, which was determined for ten lines in the region 10,140 to 2537A, by a procedure essentially that described by Forsythe and Barnes.[5] The measurements were, however, much simplified by the use of the controlled arc, which

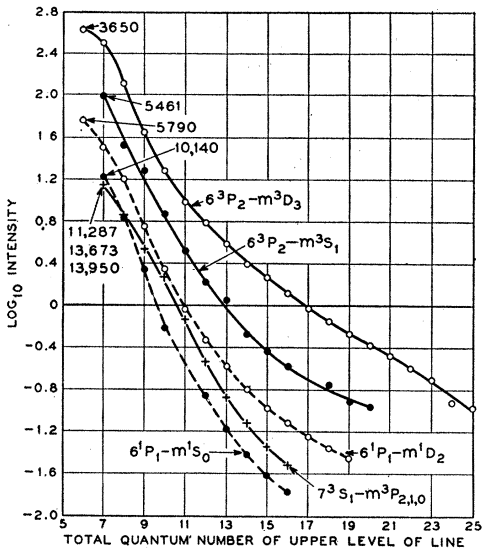

FIG. 5. Intensity relationships for five series in the mercury afterglow.

remained so constant throughout any one set of measurements that a single thermocouple could be used.

In the second step, the measurements of the relative intensities of the lines in the arc were used to determine the relative intensities of these same lines in the afterglow spectrum by determining for each line the ratio of its intensity in the arc to its intensity in the afterglow. The method of making this comparison has been described elsewhere[4] and will be only outlined here. On a single photographic plate one or more exposures of the afterglow and several of the controlled arc were taken, all with the same exposure times. The light from each source was diffusely reflected from a magnesium carbonate block into the slit of the spectrograph on which was mounted a calibrated sputtered step weakener of five steps. By varying the distance of one or both of the sources from the carbonate block, which was fixed with respect to the spectrograph, the intensity of the light entering the spectrograph could be controlled, since it was very closely proportional to the inverse square of the distance. Exposure distances were so selected that extrapolation was never necessary. Because of the step weakener, each exposure gave for each line five spectra of known intensity ratios. From the calibration of the weakener and the inverse

[3] G. E. Moore and H. W. Webb, Rev. Sci. Inst. **11**, 101 (1940).
[4] G. E. Moore and H. W. Webb, J. Opt. Soc. Am. **30**, 413 (1940).
[5] W. E. Forsythe and B. T. Barnes, Rev. Sci. Inst. **1**, 569 (1930).

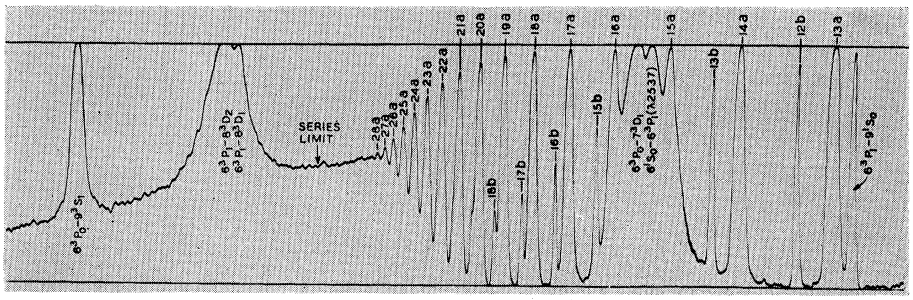

FIG. 6. Microphotometergraph showing convergence of triplet diffuse and sharp series. Series $a = 6^3P_2 - m^3D_{123}$; values of m from 13 to 28 inclusive are shown. Series $b = 6^3P_2 - m^3S_1$; values of m from 12 to 19 inclusive are shown. $6^3P_1 - 9'S_0 = 2563.88$; $6^3P_1 - 8^3D_1 = 2482.721$; $6^3P_0 - 7^3D_1 = 2534.771$; $6^3P_0 - 9^3S_1 = 2464.059$; $6^3P_1 - 8^3D_2 = 2482.008$.

square law, the relative intensities of the reference lines in the afterglow could be calculated from their relative intensities in the arc.

In the third step the ratio of the intensity of each of the weaker lines to that of the nearest of the seventeen reference lines was determined with a quartz spectrograph of higher dispersion, again with the step weakener over the slit. Since the ratio of the intensities of the strongest and weakest lines in the afterglow was of the order of 10^4, and the maximum ratio of intensities which could be measured with the step weakener alone was about five, this part of the measurements had to be performed in steps. For large ratios two auxiliary homogeneous weakeners were employed, whose spectral transmission had been measured with the spectrograph and thermocouple. These weakeners were made by sputtering platinum on quartz plates and each transmitted about 10 percent. By combining the homogeneous and step weakeners intensity ratios as large as 300 could be measured from three exposures, all taken on one photographic plate with constant exposure times. With the weaker lines thus measured as secondary reference lines, the above process was repeated and the measurements extended to lines whose intensities were 10^{-4} times that of the strongest lines in the spectrum. The measurements were repeated so that there were three to five separate measurements of the intensity of each line.

RESULTS

Energy distribution

The energy distribution in the spectrum of the afterglow was studied under conditions selected to give relatively high intensity. For the results described below, the arc was operated at 9.5 amperes and 6.5 volts. At a point in the stream opposite the window, the vapor pressure was 0.37 mm (10^{16} atoms per cc), the concentration of positive ions 6.7×10^{11} per cc, and the electron temperature 1890°K. There were approximately 200 lines of substantial intensity in the spectrum. Of these, 126 in twenty-two spectral series were measured directly, while the intensities of the remaining lines were evaluated by indirect methods.

The relative intensities of the lines in five of the more intense series are plotted in Fig. 5. Other data are given in Table I. Throughout this paper, the intensity of 5461A is arbitrarily taken as 100, whenever relative intensities are discussed. The most intense line was 3650A, $6^3P_2 - 6^3D_3$, the intensity of which was 350. The precision of the intensity determination of every directly measured line stronger than 5461A was on this scale between 1 and 3. For weaker lines it was in general better than 1; for example for 4916A the intensity was 6.4 ± 0.6, for 4970A, 0.065 ± 0.015.

The three series $6^3P_2 - m^3D_{123}$ are treated as one in Fig. 5 since the higher members could not be resolved by the spectrographs used. Similarly the two series $6^3P_1 - m^3D_{12}$ were measured as one beyond the second members. Twenty-two lines of the former series were separately measurable (under favorable conditions 24 lines[6] can be resolved) before the lines merged into the continuum about 10A on the long wave-length

[6] I. Walerstein, Phys. Rev. **46**, 874 (1934).

side of the series limit. A microphotometer trace showing the higher series lines and the continuum is shown in Fig. 6. Lines of the $6^3P_2-m^3S_1$ series are also clearly shown on the trace. The position of the series limit is indicated by an arrow.

Only the first six lines of the $6^3P_1-m^3D_{12}$ series were measured directly, since the higher members fell outside of the range in which the quartz arc was calibrated. As expected, the relative intensity distribution among these lines was very closely the same as for the corresponding lines in the $6^3P_2-m^3D_{123}$ series, and the intensities of the remaining lines in the series were therefore computed by assuming the same distribution throughout each series. The intensities for the other ultraviolet lines beyond λ2400 listed in the table were similarly estimated.

The intensity of 2537A ($6^1S_0-6^3P_1$) was measured but that of 1849A ($6^1S_0-6^1P_1$) could only be roughly estimated. Reversal is large with both lines so that their intensities could not be determined with precision. The higher members of the two series of which these lines are the first members lie too far in the ultraviolet to be photographed with the instruments available.

Of the numerous infra-red lines in the mercury spectrum, only eleven are listed in Table I as of sufficient intensity in the afterglow to be significant in this problem. No infra-red lines except 10,140A and 11,287A were observed on infra-red plates sensitive to 13,000A, and the direct photographic intensity determinations of these two lines were not very reliable. Since these lines were weak in comparison with the stronger lines in the visible and ultraviolet, their intensities could be estimated with sufficient accuracy. For example, the line 10,140A is the first member of the series $6^1P_1-m^1S_0$ of which the second and higher members were measured directly and found to have closely the same relative intensities as was observed for the corresponding lines in other series. Hence, from the intensity distributions in the other series, the intensity of 10,140A was computed as 17 ± 4. Approximately the same value was computed from the measured intensity of 4077A ($6^3P_1-7^1S_0$), which originates on the same upper level, by assuming that the ratio of the intensities of 10,140A and 4077A in the afterglow was the same as in the controlled arc, in which it was accurately measured with

TABLE I. *Intensities of lines not plotted in Fig. 5. Intensity of 5461 = 100.*

Term Designation	Relative Intensity
$6^1P_1-m^3D_2$	
$m=$ 6	48
7	10.2
8	3.8
	*
$6^3P_2-m^3D_2$	
$m=$ 6	52.0
7	30.0†
$6^3P_1-m^3D_2$	
$m=$ 6	151.0
7	99.0
8	48.0
9	25.0§
10	‡
$7^1S_0-m^1P_1$	
$m=$ 7	4.0
8	1.9
9	0.6†
10	0.29
11	0.17†
12	0.08
13	0.03
14	0.02
$6^3P_2-m^3D_1$	
$m=$ 6	39.2
7	14.0†
	*
$6^3P_1-m^3D_1$	
$m=$ 6	111.0
7	40.0
8	22.0
9	10.0§
10	‡
$6^3P_0-m^3D_1$	
$m=$ 6	91.0
7	48.0
8	20.0
9–16	‡
$6^3P_2-m^1D_2$	
$m=$ 6	26.4
7	12.5
8	6.6
9	1.8
	*
$6^3P_1-m^1D_2$	
$m=$ 6	96.0
7	25.0
8	9.8
	*
$6^3P_1-m^1S_0$	
$m=$ 7	3.7
8	1.8
9	0.75
10	0.24
11–16	‡

Term Designation	Relative Intensity
$7^3S_0-m^1P_1$	
$m=$ 7	0.63
8	1.15‖
9	0.44
10	0.17
11	0.065
$6^1P_1-m^3S_1$	
$m=$ 8	0.072
9	0.027
$7^3S_1-m^3P_{1,0}$	
$m=$ 8	1.7
9	0.86
10	0.29
11	0.096
12	0.043
$6^3P_0-m^3S_1$	
$m=$ 7	30.5
8	13.2
9	6.0
10	2.5
11–15	‡
$6^3P_1-m^3S_1$	
$m=$ 7	102.0
8	34.0
9	14.0
10	5.8
11	2.5
12–24	‡
Infra-red lines	
$6^1P_1-7^1S_0$	17.0
$7^3S_1-7^3P_2$	7.9
$7^1S_0-7^1P_1$	3.9
$7^3S_1-7^3P_1$	3.8
$7^3S_1-7^3P_0$	1.4
$6^1D_2-6^1F_3$	2.5
$6^3D_1-6^3F_2$	1.8
$7^3P_2-7^1D_1$	2.6
$6^3D_2-6^3F_3$	2.3
$6^3D_3-6^3F_4$	0.4
$6^1P_1-7^3S_1$	0.8
Other lines not listed above	
λ2537	62.2
λ1849	‡
λ1942	‡
λ6124	0.77

* Other lines of series not resolved.
† Estimated because of partial masking.
‡ Observed but not measured.
§ Estimated, only, because of short wave-length.
‖ Note: This line is apparently an exception to the general rule since it is more intense than the preceding line.

the thermocouple. Similarly, the intensities of 11,287A, 13,673A and 13,950A were computed by extrapolation from the intensities of the measured lines in their respective series as 10, 3.1 and 1.2, respectively. A satisfactory check on these computations giving values of 8.0, 3.8 and 1.4 was made with the above value for the intensity of 10,140A and the results of McAlister,[7] who measured the relative intensities of all the more prominent infra-red lines in a mercury arc. The intensities of the other seven infra-red lines, which were considerably weaker than these four, were similarly estimated as given in Table I.

Figure 5 gives the intensities of the lines of five of the more intense spectral series in the afterglow. The ordinates are the common logarithms of the intensities (intensity of 5461A = 100) and the abscissae the total quantum numbers of the levels from which the lines originate. The wavelength of the first member observed in each series is given on the curve to assist in identification. The intensities of the lines not plotted in the figure are given in Table I.

About 99 percent of the total radiation in the line spectra was in the first six members of the various series. Somewhat less than one percent of the total radiation was due to the series limit continua which were observed for eight different series.

The rate of direct excitation into each atomic level was computed by subtracting from the number of quanta leaving the level per second by radiative processes the number of quanta entering the level by radiation. These rates are given in Table II for most of the levels for which the values were sufficiently large to be of interest. The first and second columns give the series designations of the levels and the energies in wave numbers, respectively, the third and fourth give the quanta leaving and entering by radiative transitions, respectively, and the fifth column gives the difference, or the rate of direct excitation into the level. The scale in the last three columns was so chosen that the figures in the last column give the percent of the total number of direct excitation processes taking place into each level.

In computing these results, the values of the rates for the principal series levels m^1P_1 and m^3P_{012} have been taken as zero. Although no accurate measurement of the intensity or weakening by reversal of 1849 was made, the fact that it was comparable in intensity with the normally weak line 1942 suggests that most of the observed radiation was due to the transitions into the 6^1P_1 level from higher levels rather than to direct excitation. Similarly no accurate estimate was possible for the effect of reversal on the intensity of 2537A which was only one-sixth of that to be expected from the observed transitions into the 6^3P_1 level from higher levels. Since 2537A was very weak relatively to the other lines in the afterglow as compared with its value in the radiation from other mercury sources of comparable pressure, the net direct excitation of this level has been assumed to be zero. The direct excitation of the 6^3P_0 and 6^3P_2 levels and higher levels of the same series have also been neglected. As will be evident later these assumptions have no effect on the conclusions to be drawn from the results. For other lines reversal was neglected, since the work of Barnes and Adams[8] has shown that, for the conditions under which the present investigation was made, only minor reversal effects for all but the resonance lines are to be expected.

Absolute intensity

The absolute intensity of each of the lines in the afterglow spectrum emitted per second by a cubic centimeter of the vapor opposite the window was calculated from the above measurements of the relative intensities of the lines and from a measurement of the absolute intensity of the group of lines 3650A–3663A, which were not individually resolved by the thermocouple. This measurement was made by first determining the sensitivity of the thermocouple-galvanometer system, with a standardized incandescent lamp. The thermocouple and galvanometer were then used with the quartz spectrograph to measure the absolute intensity of the 3650A–3663A group emitted per unit solid angle from a measured area of the controlled quartz arc. The computations involved the geometry of the arc and spectrograph combination and corrections for the transmission

[7] E. D. McAlister, Phys. Rev. **34**, 1142 (1929).

[8] B. T. Barnes and E. Q. Adams, Phys. Rev. **53**, 545–563 (1938).

of the spectrograph at these wave-lengths. The relative intensity of this group of lines in the afterglow and in the arc was then determined photographically with the magnesium carbonate block and step weakener before the slit and varying the distances to the sources until equal photographic densities were obtained. From the known absolute intensity of the arc radiation, the absolute intensity of the group of lines in the afterglow was computed.

The total energy radiated per second as 3650A–3663A from one cubic centimeter of the afterglow, computed from this value and the volume of glowing vapor from which radiation reached the carbonate block, was 5.4×10^{-4} watt. From Table II we find that the direct excitation into the 6^3D_{123} levels, measured in quanta, was 38 percent of the total of such excitation processes. This gives the result that, in the experimental tube, from each cc of vapor at the window there were emitted as the result of direct excitation at least 2.6×10^{15} quanta per second.

A repetition of this measurement of absolute intensity with a photo-cell and a quartz mercury arc, calibrated in another laboratory, gave results in good agreement with the above.

Discussion

In this investigation of the mercury afterglow, as well as that described in I, measurements were made primarily on the line spectra. The series limit continua, which involved considerably less than 1 percent of the quanta radiated under the conditions used in the present work, were of such low intensity that relatively few quantitative data were obtained in regard to their behavior. The intensity of the band spectrum was so low that it was not observed with the large tube used in the work described in this paper, although under special conditions with the tube used in I more energy was radiated in the band than in the line spectrum. The conclusions drawn below apply primarily to the atomic line radiation.

The measurements of total intensity indicate that the radiation of this line spectrum is not due to ion-electron recombination. From the work of Randall and Webb[9] and from the data reported in I, the velocity of the vapor stream in the present experiments was estimated to be somewhat less than 10^4 cm per second. Randall[10] has shown that the lifetimes of the 7^3S_1 and 6^3D_{123} levels are less than 10^{-7} second, and if we assume that the lifetimes of the states in a given series are approximately proportional to the cube of the effective total quantum numbers as in hydrogen, we find that the lifetimes of those states which contribute substantially to the afterglow are all less than 10^{-5} second. Hence in the present experiments an excited atom travelled less than 1 mm in an excited state between excitation and radiation.

The product of the vapor velocity (10^4 cm/sec.) and the concentration of ions near W, (6.7×10^{11} ions per cc) gives the maximum number of ions passing through each cc per second, 6.7×10^{15}. But the total intensity was found to involve 2.6×10^{15} radiating atoms per cc per second in this region. Therefore if the line radiation were due only to ion-electron recombination, the ionization in the vapor would have been exhausted in moving about 3 cm. This is however, contrary to the experimental observations made earlier under similar conditions that the ion concentration decreases by only about 10 percent in 3 cm. Furthermore, the total amount of energy radiated by the vapor beyond the window was estimated and the corresponding number of quanta involved was found to be at least 20 times greater than the ion concentration at the window.[11]

The conclusion that the afterglow line spectrum is not due to ion-electron recombination is apparently supported by the observations of Mohler[12] who measured by electrical means the rate of decay of the ion concentration in a mercury arc after extinction. Using approximately the same vapor pressure and electron

[9] R. H. Randall and H. W. Webb, Phys. Rev. **48**, 544 (1935).

[10] R. H. Randall, Phys. Rev. **35**, 1161 (1930).

[11] The pressure 0.37 mm, at which these intensity measurements were made was judged to be sufficiently low to avoid the possibility of any substantial error in the measurement of the ion concentration such as has been suggested. [F. L. Mohler, Nat. Bur. of Stand. Research Paper R.P.948]. As a further check on this, the measurements of absolute intensity were repeated at a pressure of 0.1 mm for which the probe measurements could not have been significantly in error, and again it was found that the number of excited atoms which were radiating was much too large to be due to ions recombining near the point of observation.

[12] F. L. Mohler, Nat. Bur. Stand. Res. Paper R.P.1045.

temperature as in the present experiments, he found that an initial ion concentration of 6.7×10^{11} per cc decayed at the rate of 1.3×10^{14} per cc per second or approximately 5 percent of the rate, 2.6×10^{15}, which was found above to be the required rate of ion disappearance, if the afterglow were the result of ion-electron recombination.

This conclusion is further supported by the results given in Table II in which it is shown that the radiating atoms have an average initial energy of about 9 electron volts (somewhat less if the assumption of negligible excitation into the principal levels is incorrect.) If ion-electron recombination produced the afterglow line spectrum directly, the difference between the ionization potential and 9 volts, or 1.4 electron volts, must on the average have been carried off in the process of exciting each atom radiating the afterglow line spectrum. But in such recombination, this could have occurred only by the radiative process since no third body was involved to carry off the 1.4 electron volts as kinetic energy. However, from the data in the third and fourth columns of the table, it is evident that this could not have occurred since the number of quanta entering the upper energy state of nearly every line of substantial intensity in the afterglow is considerably less than the number leaving by radiative transitions. For example, in the case of the 7^3S_1 state, more than four quanta leave for each quantum entering from higher states. Similarly in the case of the three 6^3D states, the ratio is greater than five and is still larger for higher states. Continua, such as are observed especially with the alkalis and interpreted as resulting from ion-electron recombination, were very weak in the mercury afterglow, being detected only for the $6P$ states where they accounted for less than one percent of the total quanta radiated. Consequently, they need not be considered in discussing the excitation of the strong lines. For example, ion-electron recombination into the 7^3S_1 state would have produced a continuum starting at 4550A and extending to shorter wave-lengths, but no series limit continua were observed except for the $6P$ series. Since then there is no evidence that radiative transitions from higher levels, discreet or continuous, account for more than a small fraction of the excitation of the more important states, we conclude that, if some type of recombination of ions and electrons is responsible for the line spectrum of the afterglow, this cannot be ion-electron recombination, but must be a much more complex process and must involve collisions with neutral atoms, in order that the excess energy can be accounted for as kinetic energy. It is concluded that neutral atoms rather than electrons carry away this energy, since the average energy of the electrons in the afterglow, as measured by the electron temperature, is usually low.

From the results described in I, it was concluded that in these experiments the ions from the arc discharge were the primary source of the energy of excitation of the afterglow. If this is correct, the measurements of the absolute intensity show that whatever process was involved was initiated at some point near the anode, since

TABLE II. *Excitation data.*

SERIES DESIGNATION	ENERGY IN ν	QUANTA LEAVING	QUANTA ENTERING	RELATIVE EXCITATION RATE
7^1S_0	20,253	2.37	2.16	0.21
8^1S_0	10,219	0.56	0.21	0.35
9^1S_0	5,964	0.14	0.01	0.13
6^1P_1	30,112	?	18.3	0?
7^1P_1	12,886	?	0.36	0?
6^1D_2	12,848	10.7	2.01	8.69
7^1D_2	7,117	3.85	0.14	3.71
8^1D_2	4,521	1.29	0.014	1.28
7^3S_1	21,830	16.1	3.74	12.4
8^3S_1	10,219	3.46	0.057	3.40
9^3S_1	5,965	1.57	0.01	1.56
10^3S_1	3,912	0.57		0.57
11^3S_1	2,765			0
6^3P_2	40,138		2.35	0?
7^3P_2	12,973	1.29	0.52	0.77
8^3P_2	7,357	0.22	0	0.22
6^3P_1	44,787	4.0	22.8	0?
7^3P_1	14,519		4.0	0?
6^3P_0	46,536	0?	5.6	0?
7^3P_0	14,664	0.20	0.23	0
8^3P_0	7,734	0.054	0.014	0.04
6^3D_3	12,750	18.4	0.575	17.8
7^3D_3	7,052	10.4	0.011	10.4
8^3D_3	4,479	5.04	0	5.04
6^3D_2	12,785	13.5	2.52	11.0
7^3D_2	7,073	5.75	0.04	5.71
8^3D_2	4,491	2.34	0	2.34
6^3D_1	12,845	11.1	1.77	9.3
7^3D_1	7,096	3.74	0.043	3.70
8^3D_1	4,503	1.58	0	1.58

only near the arc discharge was the ion concentration sufficiently large to account for the total energy radiated as afterglow throughout the tube. An approximate calculation, based on the theory of the arc developed by Tonks and Langmuir[13] showed that the ion concentration near the anode was of the same order of magnitude as the total number of quanta emitted in the afterglow throughout the tube. Hence, if the ions were the source of the excitation, in order to explain the intensity distribution observed in the tube, it must be assumed that long-lived molecular particles (mean life $\sim 10^{-3}$ second) were formed near the anode, carried several centimeters down stream and then became dissociated, thus furnishing the excited atoms which radiated the afterglow line spectrum. The results discussed in the preceding paragraph indicate that the multiple collisions necessary for the formation of such a molecule did occur. Moreover, the dependence of the rate of volume recombination of the ions on the pressure, described in I, can best be explained by assuming such recombination to have resulted from multiple impacts involving neutral atoms.

In I it was concluded that atoms in the 6^3P_{012} states were not directly involved in the excitation of the line spectra, although they are the source of the molecules which radiate the diffuse band spectra. It does not seem probable, therefore, that the molecule just postulated to explain the behavior of the afterglow can be identified with any formed from atoms in the $6P$ states. For similar reasons, it is concluded that it cannot be formed from the negative molecule ions which Nielsen[14] showed to be formed by the union of neutral atoms, electrons and metastable atoms. Other mercury molecules have been suggested, but the properties of the afterglow seem best to be explained by assuming that the molecule is that proposed by Arnot and Milligan.[15] These authors observed that mercury molecule ions can be produced by bombardment of neutral atoms with electrons of 9.5 volts energy, 0.9 volt less than the ionizing potential of the atom, and presented strong evidence that these molecule ions were formed by the process

$$Hg' + Hg \rightarrow Hg'Hg \rightarrow Hg_2^+ + \epsilon,$$

where Hg′ represents an excited mercury atom in the $7D$, or a higher atomic state and Hg′Hg an excited molecule formed by its combination with a neutral mercury atom.[16]

We assume that the first of the above reactions is easily reversible; that is, the Hg′Hg molecule can dissociate readily into an excited atom and a neutral atom. This assumption is plausible, at least for the $7D$ and higher states, because the energy differences between the excited atomic states and corresponding molecular states are small. Since there is a large energy difference between any of the molecular states and the $6D$ and $7S$ atomic states, any transitions into these states must be nearly irreversible.

The marked dependence of the intensity of the afterglow on the pressure, reported in I (see Fig. 2) implies that the concentration of Hg′Hg at W, for a fixed concentration of positive ions at this point, was approximately proportional to the pressure, p. This proportionality is also suggested by Fig. 4, which shows that, for a given concentration at W, that part of the positive ion concentration near the anode which was not lost to the walls by diffusion, and which we may take as the measure of the useful excitation at that point, was very nearly proportional to p. The form of the intensity-pressure curves (Fig. 2) suggests that a better approximation to actual conditions is obtained if we take the concentration of HgHg′ to be proportional to $p-0.1$ (mm), the latter term roughly compensating for the loss to the walls.

Since the probability, Q, that the excited molecule will reform before the excited atom radiates is given by[17]

$$Q=\frac{A\sigma^2\tau p}{A\sigma^2\tau p+1},$$

where σ^2 is the collision cross section for the above

[13] L. Tonks and I. Langmuir, Phys. Rev. **34**, 876 (1929).
[14] W. M. Nielsen, Phys. Rev. **27**, 716 (1926); Proc. Nat Acad. Sci. **16**, 721 (1930).
[15] F. L. Arnot and J. C. Milligan, Proc. Roy. Soc. **A153**, 359 (1935).
[16] A similar molecule was suggested by Franck to explain the photo-ionization of cesium by absorption of radiation of the frequency of its lower principal series lines as observed by Mohler, Foote and Chenault (Phys. Rev. **27**, 37 (1926)). F. L. Mohler and C. Boeckner subsequently gave evidence strongly supporting Franck's suggestion (Nat. Bur. Stand. Research Paper, R.P.186).
[17] L. A. Turner, Phys. Rev. **23**, 464 (1924).

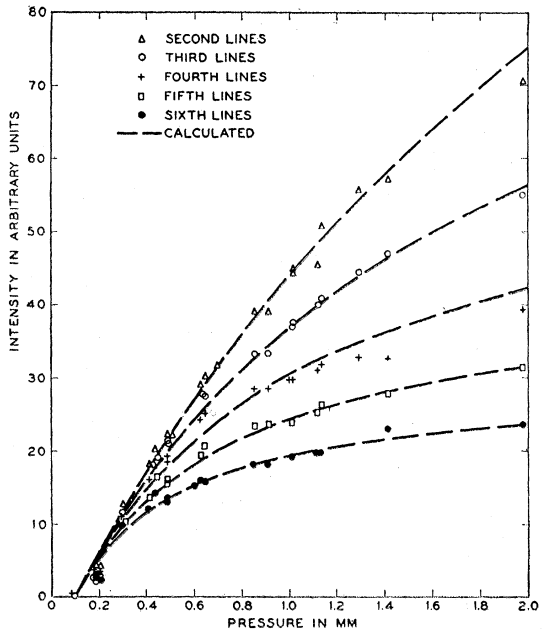

FIG. 7. Comparison of experimental and calculated forms of the intensity-pressure relationships in the mercury afterglow.

process, τ the lifetime of the atomic state in question and $p\sigma^2A$ the number of collisions per second between excited and neutral atoms. For a given ion concentration, the intensity J in the afterglow will then be proportional to the product of $1-Q$ and the concentration of the Hg′Hg molecules, or

$$J \propto \frac{p-0.1}{A\sigma^2\tau p+1}. \qquad (1)$$

Now if in this equation we use for all the excited states an average value of σ, 5×10^{-8}, which value lies in the range given by Turner[17] for similar collisions, and values of τ computed for the different states from the data of Randall[9] as in the first paragraph of this discussion, J is found to vary with p as shown by the dotted curves in Fig. 7. The experimental points shown are taken from the data plotted in Fig. 2 of I. Only the form of the curves is of interest since the intensity scale was arbitrarily chosen for each line. In view of the probability that the actual process involved is somewhat more complex than that assumed, the agreement between the calculated curve and experiment is satisfactory. To simplify the figure, curves are given only for the second to the sixth lines. The very much smaller value of σ which must be assumed because of the nearly irreversible processes producing the $6D$ and $7S$ atoms gives a linear relation between J and p for the 6^3D-6^3P and 7^3S-6^3P lines, which also agrees well with experiment. (See Fig. 2.)

The observation made by Rayleigh[18] that the afterglow is quenched by the removal of positive ions can be explained on the assumption that the second reaction postulated by Arnot and Milligan is highly probable, since the complete withdrawal of ions from the vapor stream would necessarily result in the disappearance of the excited molecules.

The quenching phenomena observed with a positively charged grid in the vapor stream are, however, not satisfactorily explained, although they are consistent with the hypothesis that fast electrons break up the molecules which carry the energy necessary to produce the afterglow. The large increase in the intensity of λ2537 accompanying the quenching suggests that the molecules are broken up into atoms in the 6^3P_{012} states, but the recovery of the glow beyond the quenched region is difficult to explain on this assumption. Adequate data are not yet available on this type of quenching.

With the methods of calculation developed by Mohler[19] the intensity distribution in the various spectral line series and the continua were examined for a possible correspondence with a Boltzmann distribution. No evidence of such a distribution was found in the line spectra. The intensity distribution in the continuum in the neighborhood of 2537A was found to correspond to a "temperature" of 1150°K as compared with the measured electron temperature of 1890°K.

The writers wish to express their thanks to Professor Harold W. Webb, who proposed this investigation, for his many suggestions and continued help throughout the work.

[18] Rayleigh, Proc. Roy. Soc. **A108**, 262 (1925).
[19] F. L. Mohler, Nat. Bur. Stand. Research Papers, R.P.901 and R.P.1036.

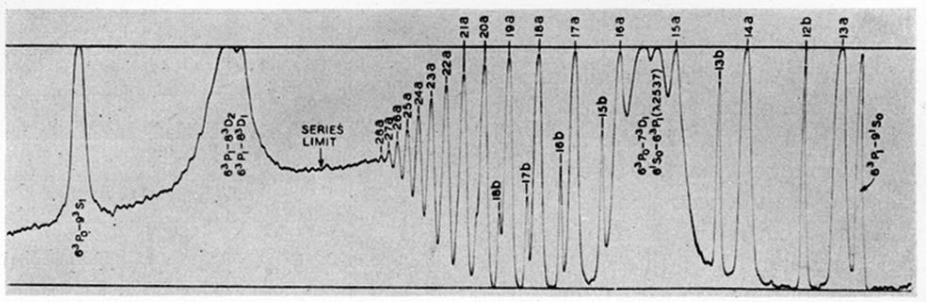

FIG. 6. Microphotometergraph showing convergence of triplet diffuse and sharp series. Series $a = 6^3P_2 - m^3D_{123}$; values of m from 13 to 28 inclusive are shown. Series $b = 6^3P_2 - m^3S_1$; values of m from 12 to 19 inclusive are shown. $6^3P_1 - 9'S_0 = 2563.88$; $6^3P_1 - 8^3D_1 = 2482.721$; $6^3P_0 - 7^3D_1 = 2534.771$; $6^3P_0 - 9^3S_1 = 2464.059$; $6^3P_1 - 8^3D_2 = 2482.008$.