ABSORPTION AND EMISSION SPECTRA OF THE GEISSLER DISCHARGE IN MERCURY VAPOR AND IN MIXTURES OF MERCURY AND HYDROGEN

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Abstract

In a quartz tube 4 cm in diameter, mercury vapor was maintained at about 3 cm pressure and a current of .5 amp. was sent from a tungsten filament cathode to a nickel anode 18 cm away. The absorption of light from a quartz Hg arc lamp on passing transversely through the discharge tube was determined with a small Hilger quartz spectrograph. (1) *Absorption by the continuous positive column.* Several lines of the diffuse and subordinate triplet series were absorbed by atoms in the $2p$ states, $2p-2s$ lines very strongly, $2p-3s$ lines less strongly, $2p-3d$ lines strongly, $2p-4d$ lines less strongly, $2p-5d$ lines weakly. No trace of absorption of combination lines by $2p$ atoms or of absorption by other excited atoms was observed. An unidentified faint line 4279 showed absorption. These results confirm and extend those reported by Metcalfe and Venkatesachar. The absorption by atoms in the $2p_1$ state is greatest but of the same order of magnitude as that by atoms in the $2p_2$ and $2p_3$ states. This is hard to reconcile with the extremely short life of the $2p_2$ state. (2) *Absorption by the striated positive column*, obtained by adding hydrogen. The bright region of the striation showed greater absorption of the $2p-2s$ lines than did the dark regions. (3) *Emission spectra of various parts of the discharge.* The negative glow emitted the arc spectrum and the spark line 2848. All these lines appeared with diminishing intensity through the Faraday dark space. The continuous positive column emitted the arc spectrum. The striated positive column emitted the arc spectrum and HgH bands. The intensity of emission attained its maximum for different lines at different regions in the striations in a manner apparently connected with the excitation energies for the lines.

In connection with a study of the glow discharge in Hg vapor, the results of which have already been published,[1] many observations of the emission and absorption spectra under different conditions were made. A few of these gave results which had a bearing on the theory of the discharge and were discussed in that connection, but other interesting results were obtained which have not been reported. It seemed advisable to collect all these spectroscopic observations and publish them together.

The apparatus used for the greater part of this work was a tube made of fused quartz, 4 cm in diameter. The electrodes were sealed in through glass tubes attached to the quartz by graded seals. The cathode was a tungsten filament and the anode was a nickel plate placed 18 cm from

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[1] K. T. Compton, Louis A. Turner, and W. G. McCurdy, Phys. Rev. **24**, 597 (1924)

the cathode. A pressure of about 0.3 cm of Hg was maintained in the tube by means of two side arms which contained Hg and were immersed in boiling water. One of these was attached to the closed end of the tube and the other to the outlet connection to the pump. The tube and connections between the two Hg cells were kept at a temperature of 160° by a furnace. Some observations were made visually with a Hilger constant deviation spectroscope. The photographs were made with a small Hilger quartz spectrograph. The source of light for the absorption experiments was a small quartz Hg arc lamp cooled by being half immersed in a pail of running water.

McCurdy[2] found that the presence of a slight amount of impurity was necessary to obtain the striated discharge. He used hydrogen for that purpose and we did the same. By visual observation we found that the light of the three lines of the sharp subordinate series of wave-lengths 5461, 4358, and 4047 was more strongly absorbed in the bright parts of the striations than in the dark spaces between them. This indicates a higher concentration of excited atoms in the $2p$ states in the bright parts of the striations, excited atoms in these states being the absorbers for these lines. The significance of these observations has been discussed fully elsewhere.[1]

When the impurities were pumped out the positive column became uniform and the current through the tube increased greatly. We found by photography that this positive column was a strong absorber for many lines of the sharp and diffuse subordinate series. Inasmuch as the glow itself emitted the whole arc spectrum it was necessary to have a source which would give light of much greater intensity than that emitted by the glow in order to observe the absorption. The cooled mercury arc, with its light concentrated by a suitable lens arrangement, fulfilled this requirement. The exposures were taken in sets of three. The first was a superposition of successive exposures (1a) to the light of the arc alone passing through the tube when the glow was not running and (1b) to the glow alone, both for the same length of time. The second was an exposure to the light of the arc while the glow was running for this same length of time, and the third was taken with the glow alone, also for the same length of time. The absorption of light of any wave-length manifested itself as a diminution in the density of the line in question in the second spectrum as compared with that line in the first spectrum. The third spectrum of the glow alone enabled us to make an estimate of the relative intensity of the total light coming to the spectro-

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[2] W. G. McCurdy, Phil. Mag. **48**, 898 (1924)

graph to that from the glow alone. Plate IA shows several such sets of exposures with time of exposure increasing from top to bottom. Weak absorption is apparent only in the exposures where the line concerned is very weak so that probably the reproduction will show the absorption only for the first lines of the series, for which it is the greatest.

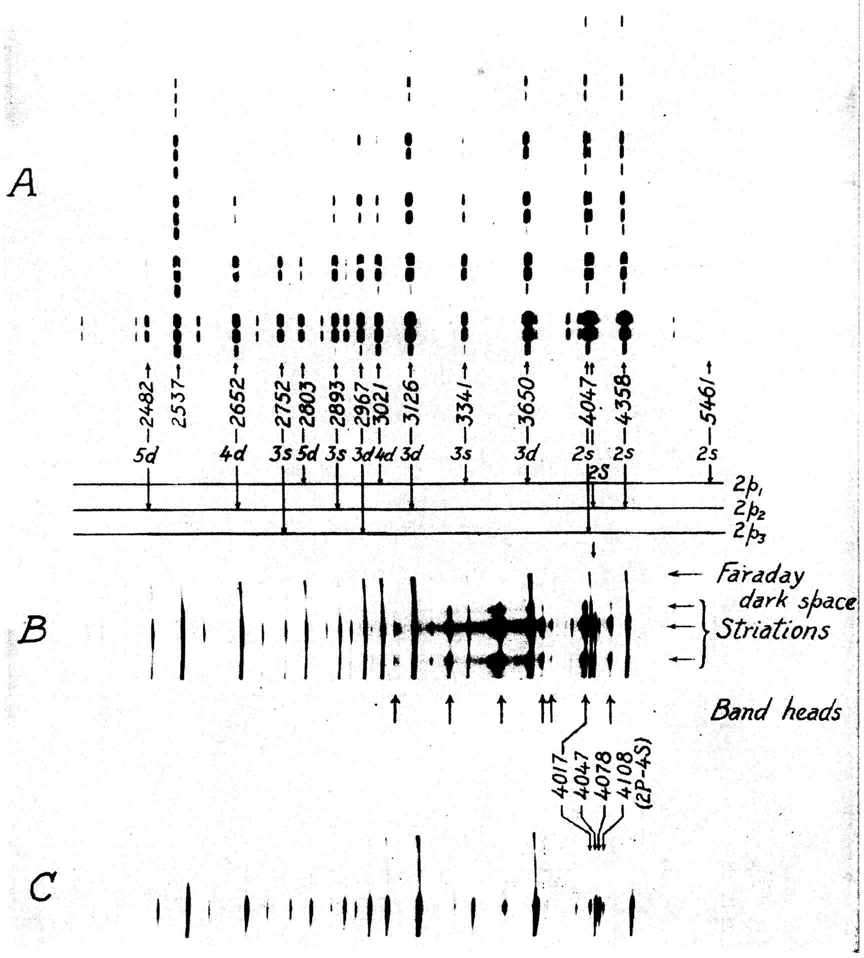

Plate I.

A. Sets of exposures with increasing time, showing absorption by the positive column.
B. Spectrogram showing relative intensities in various parts of positive column.
D. Spectrogram showing variation in length of different lines in a striation.

Table I gives a list of the lines which were absorbed and an estimate of the degree of the absorption of each. Lines which are close together and which were not resolved by the small spectrograph are bracketed together.

TABLE I

Wave-length	Series	Absorption
3663	$2p_1-3d_3$	strong
3655	$2p_1-3d_2$	"
3650	$2p_1-3d_1$	"
3132	$2p_2-3d_3$	"
3126	$2p_2-3d_2$	"
2967	$2p_3-3d_3$	"
3025 3023 3021	$2p_1-4d_{3,2,1}$	"
2654 2652	$2p_2-4d_{3,2}$	medium
2535	$2p_3-4d_3$	?*
2805 2804 2803	$2p_1-5d_{3,2,1}$	weak
2483 2482	$2p_2-5d_{3,2}$	"
5461	$2p_1-2s$	very strong
4358	$2p_2-2s$	strong
4047	$2p_3-2s$	"
3341	$2p_1-3s$	medium
2893	$2p_2-3s$	very slight
2752	$2p_3-3s$	" "

* Too close to 2537 to observe

It will be observed that all of these lines are ones absorbed by atoms in the $2p_{1,2,3}$ states. No absorption of any lines by atoms in the $2P$ or any other state was observed. This is not surprising, for the number of atoms in the $2p$ states was undoubtedly much greater than the number in any other excited state, since an electron which has fallen through a potential drop sufficient to excite a $2p$ state would, in the conditions of our experiments, make an average of more than 1000 collisions before it would acquire sufficient additional energy to excite the $2P$ state. The chance of exciting this state in any other manner than by further excitation of an atom already in the $2p$ state, is therefore negligible. There was no trace of absorption of the combination lines $2p_2-2S$ and $2p_2-3S$ of wave-lengths 4078 and 2857. The combination lines of the $2p-mD$

series are too close to the $2p-md_3$ lines to be separated. In addition, an unidentified faint line of approximate wave-length 4279 showed some absorption.

These results are a slight extension of those obtained by Metcalfe and Venkatesachar[3] with a somewhat different apparatus. They used an arc between two pools of Hg and observed the absorption in a column of glowing vapor 52 cm long, excited by a subsidiary anode. Apparently our arrangement is more efficient in producing excited atoms for we observed greater absorption of light passing transversely through our tube 4 cm in diameter than they did with their long tube, the current density in our tube being 40 milliamp. per cm^2 as compared with 10 milliamp. per cm^2 in their experiment. One would expect the concentration of excited atoms to be proportional to the current density, other things being equal. Differences in vapor pressure of the Hg may account for the different results. The value of the pressure in their experiment is uncertain but was presumably less than in ours. Of the above lines they observed absorption of only the $2p_{1,2,3}-3d$, the $2p_{1,2,3}-2s$, and the $2p_1-3s$ lines. Our plates do not show the lines 5289, 5295, and 5308 which they found to be slightly absorbed.

The relative intensities of absorption by the atoms in the $2p_1$, $2p_2$, and $2p_3$ states is a matter of interest. The fact that the absorption by these three varieties of excited atoms is of the same order of magnitude is hard to account for. The p_1 and p_3 atoms are metastable and of relatively long life,[4] so that it is easy to see how a considerable concentration of them could be built up, but several independent methods[5] of estimating the life of the atom in the $2p_2$ state agree that it is approximately 10^{-7} second, so that considerable concentrations of atoms in that state would be attained only by high rates of excitation. Zernicke[6] observed that vapor diffusing from the discharge into a space shielded electrically from it, showed absorption by the $2p_1$ and $2p_3$ atoms but not by the $2p_2$ atoms. Our result indicates that either the atomic absorption coefficients for the $2p_2$ atoms is very great or that the rate of production of such excited atoms is much greater than that for the other two varieties. Perhaps there is some sort of an equilibrium established among the three states

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[3] Metcalfe and Venkatesachar, Proc. Roy. Soc. A **100**, 149 (1921)

[4] Milton Marshall, Astrophys. Jour. **60**, 243 (1924)

[5] W. Wien, Ann. der Phys. **73**, 483 (1924);
Richard C. Tolman, Phys. Rev. **23**, 693 (1924);
Louis A. Turner, Phys. Rev. **23**, 464 (1924);
John A. Eldridge, Phys. Rev. **24**, 234 (1924).

[6] K. T. Compton and F. L. Mohler, Bull. Nat. Res. Coun. **9**, No. 48, p. 91.

by collisions of the first and second kind. Undoubtedly, the "imprisonment"[7] of the 2537 resonance radiation plays a part by increasing the length of time that the excitation energy remains in the vapor, an effect equivalent to a longer life of the atom in the $2p_2$ state. We observed a somewhat greater absorption of lines by the atoms in the $2p_1$ state than of the corresponding lines for the $2p_2$ or $2p_3$ states. Whether this depends upon a greater concentration of atoms in the $2p_1$ state or upon a greater atomic absorption coefficient cannot be said. It is of interest in this connection to note that Marshall[4] found that the life of the $2p_1$ excited atoms was eight times that of the $2p_3$ excited atoms. We hope that the future may offer the opportunity to make an accurate quantitative investigation of this absorption.

Photographs of the emission spectrum from the tube were taken by focusing an image of the tube on the slit of the spectrograph with the axis of the tube parallel to the slit, the striations being perpendicular to it. The negative glow shows, in emission, all the lines of the arc spectrum, the prominent spark line of wave-length 2848, and the strong raies ultimes of the W spectrum of wave-lengths 4295 and 4009. These lines are emitted with diminishing intensity through the Faraday dark space, showing no discontinuity until the edge of the continuous positive column or of the first striation, as the case may be, is reached. The first striation is usually closer to the second than the fairly uniform spacing of the others and appears to the eye to be less intense than any of the others. The second one appears to be the most intense. These differences show themselves with the spectrograph, the intensity changes apparently being the same for all the lines of the arc spectrum. The continuous positive column shows simply a uniform emission of the lines of the arc spectrum throughout its length. When there is much hydrogen present in the tube the HgH bands[8] appear with considerable intensity in the positive column, but not in the other regions of the discharge. They are of more nearly uniform intensity in all the striations than are the lines (Plate IB). Their intensity is roughly proportional to the amount of hydrogen present.

Different lines appear to be of different length, in the second striation in particular. That is, it appears as if the maximum intensity of emission of the different lines occurred in different parts of the striation. This is particularly noticeable in the group of three lines of wave-lengths 4047, 4078, and 4108 (Plate IC). It so happens that the order of

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[7] K. T. Compton, Phil. Mag. **45**, 450 (1923)

[8] K. T. Compton and Louis A. Turner, Phil. Mag. **48**, 360 (1924)

length of these three lines is the same as the order of intensity. One set of exposures of different lengths of time taken from the same striations shows that it is not an intensity effect, however, for the apparent lengths of the lines stay the same in all the exposures even though the stronger one in a short exposure is of about the same density as the weaker one in a long exposure. It also happens that the lengths are in inverse order to the excitation energies of the upper stationary states involved in their emission and the differences in length are roughly proportional to the differences between the energies of these upper states. The ultraviolet lines were not in good enough focus on the slit to enable us to extend these observations to them. A refined investigation of this effect, might, however, give valuable information concerning the mechanism of the discharge in the striated positive column.

These experiments were performed in the Palmer Physical Laboratory of Princeton University.

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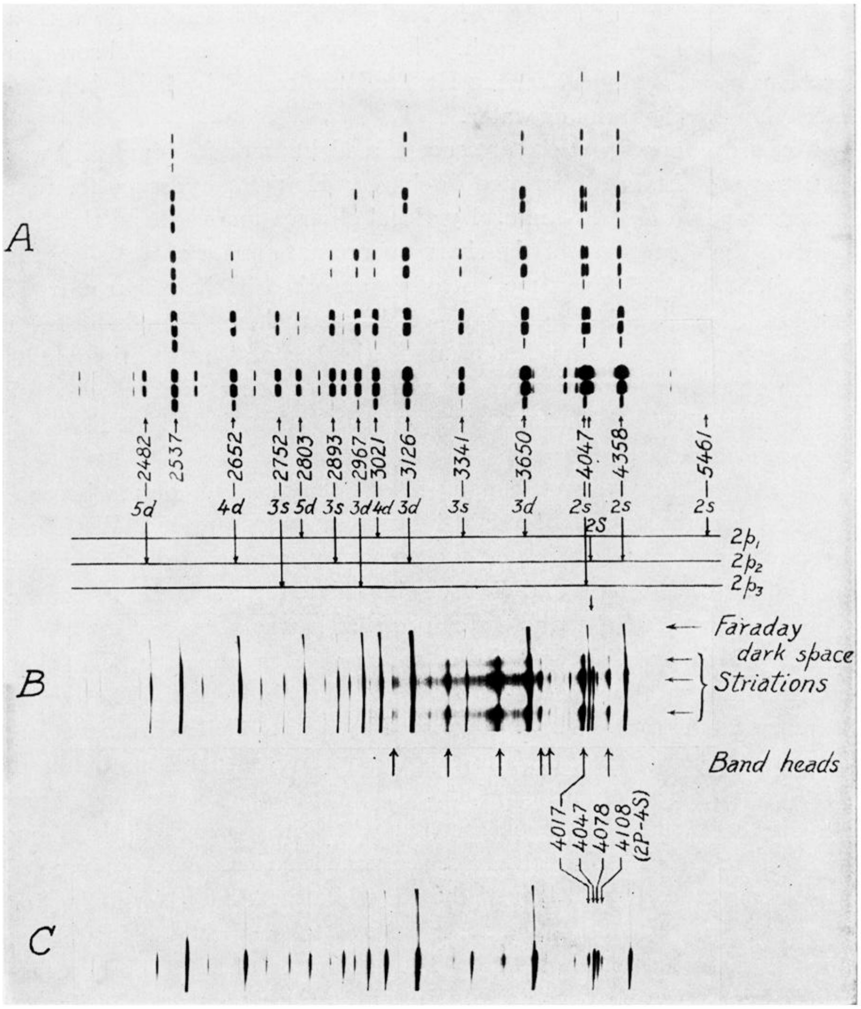

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