ABSORPTION OF A LINE OF THE PRINCIPAL SERIES OF SINGLY IONIZED ATOMIC MERCURY

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Abstract

Evidence as to series relations of the mercury lines 1942, 2225 and 2848.— Light from an electrodeless discharge in Hg vapor was passed through a region of a low voltage arc in Hg vapor containing a high concentration of positive ions. The 1942 spark line showed *absorption*; the 2225 and 2848 spark lines did not show absorption. A rough determination of the *excitation potentials* showed these to be much higher for the 2225 and 2848 lines than for the 1942 line. These experiments verify J. A. Carroll's conclusion that the 1942 line is a member of the principal series, and that the other two are members of subordinate series of Hg.

THE Kossel-Sommerfeld[1] displacement law states that the first spark spectrum of any element is similar in structure to the arc spectrum of the element whose atomic number is less by one. Thus the spark spectra of the alkaline-earth metals are systems of doublets like those of the arc spectra of the alkali metals. This is also true of the spark spectra of Zn and Cd and consequently would be expected to be true of the spark spectrum of Hg which has an arc spectrum of structure very similar to that of the arc spectra of all of these elements. This expectation has recently been augmented by Thorsen's[2] arrangement of the lines of the arc spectrum of Au, the element next below Hg in the periodic table. He found a doublet system in this spectrum. Rydberg[3] suggested that perhaps the two prominent spark lines of Hg of wave-lengths 2225 and 2848 were the first pair of the principal series.

If this surmise were correct, light of these wave-lengths should be strongly absorbed in passing through a region where there is a sufficient concentration of singly charged Hg ions, i.e. a sufficient partial pressure of what is from this point of view a new substance, Hg^+. If these lines are really the first members of the principal series, light of these wave-lengths should be absorbed by positive ions in the normal state, which are atoms with one valence electron completely removed but with all the others in their normal orbits. Such is the explanation for the ap-

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[1] A. Sommerfeld, "Atombau und Spectrallinien," 3rd Ed., p. 457.

[2] Thorsen, Die Naturwissenschaften, 11, p. 500, 1923.

[3] A. Fowler, "Report on Series in Line Spectra," p. 151.

pearance of the first principal pair of the spark spectrum of Ca as the strong H and K Fraunhofer lines. Foote and Mohler[4] state, however, that hitherto no laboratory experiments of this sort have been performed.

The measurements[5] of the concentrations of positive ions in discharges in Hg vapor showed a high concentration in the neighborhood of the hot filament cathode and suggested to us that such a region might contain a sufficient concentration of these ions to show this absorption. Accordingly, we undertook experiments to test the matter.

While this work was in progress we heard of a new arrangement of the Hg^+ spectrum by J. A. Carroll, as yet unpublished. We are greatly indebted to him for his kind permission to refer to his results in this article. According to Carroll the first pair of the principal series consists of the lines of wave-lengths 1649.8 and 1942.5. The wave-length of the first of these is too short for us to observe it with our spectroscopic equipment, but we were able to photograph the latter with a small quartz spectrograph. We found no indications of an absorption of the lines 2225 and 2848 but found a decided absorption of 1942, thus verifying Carroll's arrangement.

Apparatus and Results

For the experiment we needed an intense source of ultraviolet light and an absorbing tube which would give a maximum concentration of positive ions in the normal state with a minimum amount of emission of the spark lines. We adopted, for the source, an electrodeless ring discharge in Hg vapor contained in a small fused quartz bulb. It could be adjusted, by regulation of the vapor pressure of Hg, to give radiation of great intensity in the spark lines in which we were particularly interested. For the absorber we used a low-voltage arc discharge in Hg vapor from which the emission of the spark lines was weak. In such a discharge ionization is presumably produced by cumulative[6] effects so that there are very few electrons present having sufficient velocity to excite the spark lines. Fig. 1 is a diagram of the apparatus. The cathode was a fifteen mil (.4 mm) tungsten filament. The anode was a liquid Hg surface of adjustable height. A double set of windows made of fluorite plates was used. The inner ones were within the furnace and at the temperature of the liquid Hg so that no condensation on them occurred. They were pressed against the flat ground ends of the projecting side

[4] Foote and Mohler, "The Origin of Spectra," p. 103.
[5] W. G. McCurdy, Phil. Mag. **48**, 898 (1924)
[6] K. T. Compton, Phys. Rev. **20**, 283 (1922). See also Foote and Mohler, "Origin of Spectra," p. 154.

tubes and made contact sufficiently well so that practically no Hg vapor leaked out and there was no difficulty from condensation of Hg on the outer, cold, windows which were sealed on with deKhotinsky cement. The spectrograph was a small Hilger quartz instrument, of size A. We used Seed 60 plates sensitized for the short wave-lengths with Nujol.[7] The method of exposure was first to superimpose separate exposures of the same length of time (1) from the source without the discharge in the absorbing tube running, and (2) from the discharge in the absorbing tube alone, by exposing them successively. This was followed by another exposure of the same length of time taken with the two running simultaneously so that the light from the source passed through the region of the discharge in the absorbing tube. Any absorption of the light from the source showed itself as a diminution in the density of the line in the second spectrum as compared with the same line in the first spectrum.

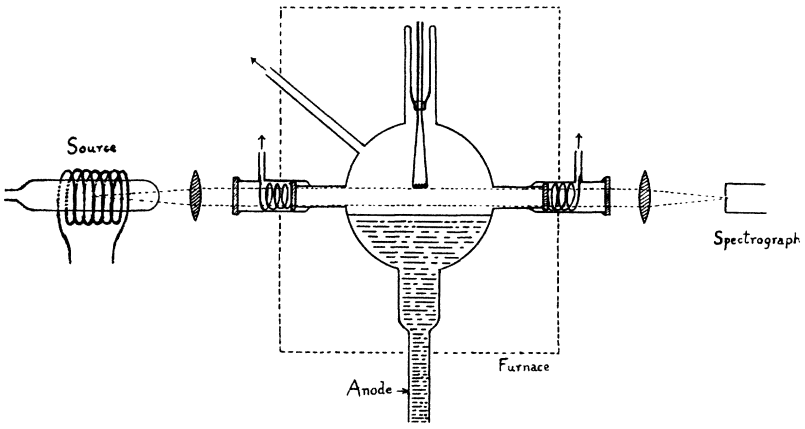

Fig. 1. Apparatus showing electrodeless source, and absorption tube in furnace.

The best results were obtained with the temperature of the absorbing tube at 135° (giving a vapor pressure of Hg of 1 mm), an applied arc voltage of 6.6 volts and an arc current of 2 amp. On the basis of other measurements in similar discharge tubes, the partial pressure of positive ions is estimated to be about 5 $(10)^{-5}$ mm of Hg. The effective length of the absorbing path was about 5 cm. The plates showed a distinct weakening of the 1942 line but no weakening of the 2225 and 2848 lines. Measurements made at Harvard with Dr. George R. Harrison's densitometer showed a marked decrease in the intensity of the 1942 line but only small variations in the densities of other spark lines of comparable intensity

[7] Ducleaux et Jeantet, Jour. de Physique **11**, 154 (1921); T. Lyman, Science, p. 48, July 20, 1921.

chosen at random. We estimate that about one fourth of the incident light was absorbed, but because of lack of sufficient data for the establishment of the characteristic curve of the photographic plate at this wavelength, this estimate may be in error by a factor of 2 one way or the other.

Fig. 2 shows a set of densitometer curves for line 1942 from one set of exposures. The original photographs of the spectra are similar to those shown in Fig. 1 of the preceding paper, and are not reproduced here.

Measurements made with other lines showed an increasing intensity from (1) to (6).

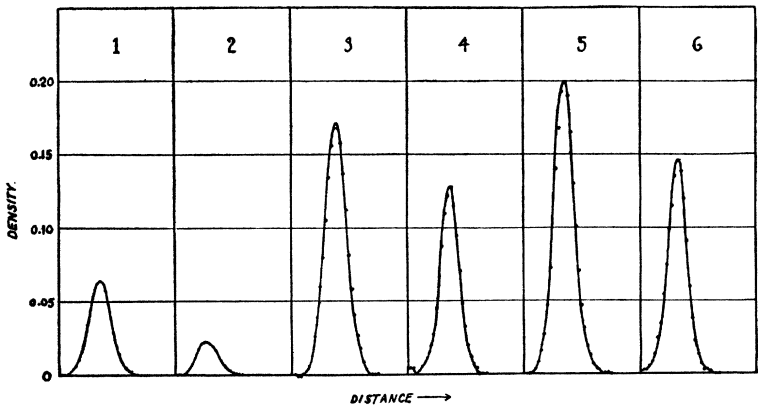

Fig. 2. Densitometer curves for line 1942. 1. Source alone. 2. Absorber alone. 3 and 5. Superposition of exposures from source and absorber. 4 and 6. Light from source through absorber.

Excitation Energies of Spark Lines

We took a set of exposures of the light emitted from the discharge tube for different anode voltages, the current through the tube being kept the same for all by regulation of the filament current. The anode voltages for these exposures were 4.5, 5.3, 6.7, 8.1, 9.4, 10.7, 12.3, 14.5, . . . The 1942 line appeared first at 6.7 volts, the 2848 line at 10.7 volts, and the 2225 line at 12.3 volts. The relative intensities after the appearance of all the lines showed that these differences were not merely the result of intensity differences. This would seem to indicate that the two lines of the Rydberg "doublet" belong to subordinate series, which is in accord with Carroll's conclusions.

As the anode voltage was lowered and the filament current was increased to keep the current in the tube constant, a condition was reached such that further reductions in the voltage could only be secured by very great increases of the filament current, the voltage dropping suddenly.

The spectrum of the light emitted after this voltage drop was very much more intense, even though the current density was the same. The spark lines were present with considerable intensity. Apparently this was the condition for the oscillating discharge[8] so that electrons of high velocity were present in the tube for a part of the time.

In conclusion we wish to thank Dr. Harrison for the use of his densitometer. These experiments were carried out in the Palmer Physical Laboratory of Princeton University.

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[8] Carl Eckart and K. T. Compton, Phys. Rev. **24**, 97 (1924)