

THE FLUORESCENCE AND ABSORPTION OF A MIXTURE  
OF MERCURY AND ZINC VAPORS

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## ABSTRACT

It was observed that light from the aluminum spark of wave-length below 2000A excited vapor distilling from slightly amalgamated zinc, causing the emission of the first triplet of the sharp series of zinc, but excited neither the non-distilling vapor nor that distilling from pure zinc. The same kind of mercury-zinc mixture showed a continuous absorption from 2050 to <1850A in distilling but not in stagnant vapor. The stagnant vapor and pure zinc vapor show in addition to the absorption lines of zinc three new absorption bands. Two of these correspond to absorption bands in cadmium. The absorption spectrum of mercury alone is also studied and shown to be different from that of zinc amalgam. The fluorescence excited by the aluminum spark is emitted by  $2^3S$  zinc atoms which may have been produced either through absorption by HgZn molecules and dissociation into excited zinc and normal mercury atoms or through collisions of the second kind between normal zinc atoms and excited HgZn molecules.

**E**XPERIMENTS by Franck, Cario, and others have shown that mixtures of gases illuminated by light which only one gas will absorb may emit a fluorescence light, the spectrum of which shows lines characteristic of both gases. In mixtures of monatomic gases, atoms of one gas absorb energy from the incident radiation and excite the atoms of the other gas through collisions of the second kind. The gas mixture then contains excited atoms of both gases and these atoms emit the fluorescence light. Such experiments are known for mixtures of mercury vapor with thallium, silver, cadmium, lead, bismuth, indium, sodium,<sup>1</sup> and zinc<sup>2</sup> vapors.

In a mixture of mercury and zinc, the sharp triplet of zinc ( $2^3P_{2,1,0} - 2^3S$ ) was excited by light from an aluminum spark which did not coincide in wave-length with absorption lines in either mercury or zinc. It was assumed that at the pressures used the 1849 absorption line of mercury was sufficiently broad to include the 1854 line of aluminum but later experiments on absorption spectra in similar mercury-zinc mixtures have shown that the 1849 line does not extend to 1854. The fluorescence excited by the aluminum spark can not then be explained by the simple process which holds for monatomic gas mixtures. To ascertain the processes involved a study has been made of the fluorescence in a mercury-zinc mixture and in pure zinc, and of the

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<sup>1</sup> J. Franck and P. Jordan, *Anregung von Quantensprungen durch Stösse* p. 210-232.

<sup>2</sup> J. G. Winans, *Phys. Rev.* **30**, 1 (1927).

absorption spectrum in a mercury-zinc mixture, zinc, mercury, and a mercury-cadmium mixture.

### 1. FLUORESCENCE OF A MERCURY-ZINC MIXTURE

The fluorescence tube is shown in Fig. 1. A condensed spark between electrodes of aluminum, iron, nickel, cadmium, or copper served as the source. In preparation, the fluorescence tube was evacuated to less than  $10^{-6}$  mm and baked out at  $650^{\circ}\text{C}$  for over ten hours. Some zinc was then distilled in, a slight amount of mercury vapor was allowed to enter, and the tube was sealed off at a temperature near  $650^{\circ}\text{C}$ . The correct amount of mercury was obtained by heating a small reservoir of mercury, attached to the vacuum system 12 cm from the tube, over boiling water for five minutes before sealing off.

With the condensed aluminum spark as source and part *B* slightly hotter than part *A*, fluorescence was observed at temperatures over  $450^{\circ}\text{C}$ . The

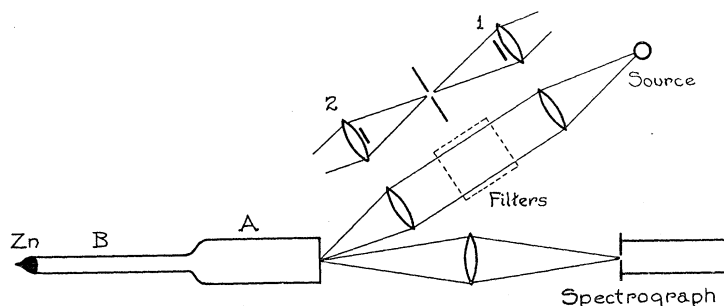


Fig. 1. Diagram of apparatus showing the arrangement for filtering the light. When desired, the lenses could also be arranged as shown at 1 and 2 with a system of diaphragms for the focal isolation of certain wave-lengths.

spectrum showed the sharp triplet of zinc ( $2^3P_{2,1,0} - 2^3S$ ) 4810, 4722, 4680 and much scattered light. The scattered light was eliminated when the lenses were arranged for focal isolation with diaphragms as in Fig. 1, 1 and 2, and focussed so that the exciting light contained only wave-lengths below  $2000\text{\AA}$ . The fluorescence excited by this light showed also only the sharp triplet of zinc. When only one lens was used in the path of the exciting light, the fluorescence was sufficiently intense to be observed visually through a Hilger D1 glass spectrograph. The following observations were made.

1. The sharp triplet was excited with about the same intensity by light from condensed sparks of iron, cadmium, nickel, and aluminum when the temperature of *B* was greater than that of *A* and over  $500^{\circ}\text{C}$ . Light from the copper spark gave only very faint fluorescence.

2. When the window was heated by a blow torch, the fluorescence disappeared but reappeared as soon as the window had cooled slightly.

3. When the temperature of *A* was greater than that of *B*, no fluorescence resulted.

Of the sources tried, only those sparks which had strong lines below 1860 excited strong fluorescence and then only when there was an opportunity for evaporation of vapor near the window. In the first observation, distilling vapor resulted from the evaporation of small drops of metal which had condensed on or near the window. Heating the window for observation 2 prevented this condensation and evaporation, and only stagnant vapor was present.

## 2. ABSORPTION SPECTRUM OF A MERCURY-ZINC MIXTURE

A quartz absorption cell 18.7 cms long was prepared with a mixture of mercury and zinc in the same way as the fluorescence tube, and mounted in a furnace as shown in Fig. 2. Nitrogen was passed continuously through the furnace and spectrograph during exposure to sweep out the air, and so eliminate the absorption due to oxygen. A condensed spark between aluminum electrodes gave a good continuous spectrum extending from 1840–7000A (see Fig. 3, No. 1). The spark gap had electrodes 0.4 cm in diameter

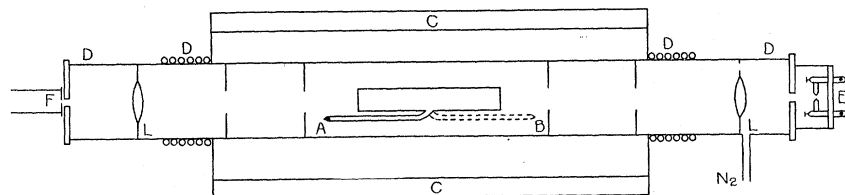


Fig. 2. *E*, aluminum spark; *C*, furnace; *F*, spectrograph; *D*, water cooling.

0.2 cm apart and was operated from a 1 KW., 17000 volt transformer connected in parallel with a 1 mfd condenser. A small E31 Hilger quartz spectrograph focussed for the region from 1850–2300 was used with Schumann plates.

With the absorption cell as in Fig. 2 *A* so that one window was cooled by the nitrogen stream, an absorption band appeared at temperatures greater than 160°C when the temperature was rising. This band extends continuously from  $\lambda$ 2050 to wave-lengths less than 1850 and is especially strong for wave-lengths below 1860. The band limits are shown at *a-b* Fig. 3, Nos. 2 and 3. As the temperature and vapor pressure of the zinc increased, the limits of this band remained the same. The absorption line 2138( $1^1S-2^1P$ ) broadened symmetrically with pressure to a width of over 100A at 4.0 cms. The breadth of this line roughly indicated the pressure.

When the temperature of the furnace was falling or when the absorption cell was arranged as in Fig. 2 *B*, the absorption band from 2050–<1850 was no longer observed. Fig. 3, No. 3 *a-b* shows the absorption band observed

with increasing temperature and No. 4 shows the absorption with falling temperature. The vapor absorbs the aluminum spark lines 1854 and 1862 when the temperature is rising, but transmits these lines when the temperature is falling; the pressure as indicated by the width of 2138 at *e* was nearly the same in both cases. The temperature changed at the rate of about three degrees per minute.

The effect of the nitrogen stream in the arrangement of Fig. 2 *A* was to make the body of the cell cooler than the stem in which the zinc was contained. Zinc then condensed on the walls of the cell and later re-evaporated with further heating to give distilling vapor in the light path. On cooling or with the arrangement of Fig. 2 *B* only stagnant vapor was present. The

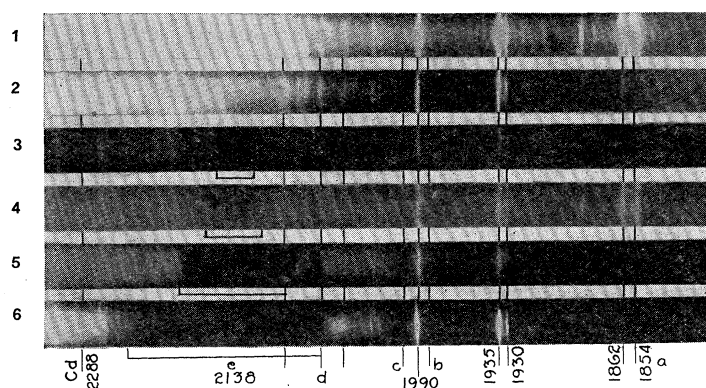


Fig. 3. (1) Aluminum spark (2) Absorption spectrum of distilling zinc amalgam vapor at 160°C (3) Absorption spectrum of distilling zinc amalgam vapor at 570°C. (4) Absorption in stagnant zinc amalgam vapor at 600°C. (5) Absorption in zinc at 670°C. (6) Absorption in zinc at about 720°C.

conclusion is that vapor distilling from the metal in a mercury-zinc mixture shows a continuous band absorption from 2050–<1850 which is not observed in stagnant vapor. The resolving power was not sufficient to detect any fine structure.

### 3. ABSORPTION SPECTRUM OF ZINC

The absorption cell was prepared as in the previous cases except that no mercury was introduced. The absorption spectrum of zinc with no mercury was the same in distilling and stagnant vapor, and was identical with that observed in stagnant vapor over zinc amalgam, except that the absorption lines 1849 and 2536 of mercury were absent. The band from 2050–<1850 was not observed.

Three absorption bands appear at pressures over 9 mm (590°C). At 35.6 mm (667°C) one band extends from about 1900 to wave-lengths below 1850, one from 1997 to 2006, and the other from a sharp edge at 2064.2 to a diffuse edge at 2072. Edges were measured at the position at which the

background intensity was estimated to have been reduced by one-half. With increased pressure the band at 1900 broadened slightly toward longer wave-lengths, the 1997–2006 band broadened a little in both directions and the 2064 band broadened only toward longer wave-lengths. With increased pressure the 2138 line broadened symmetrically until it overlapped the 2064 band on its short wave-length side, after which it broadened only toward longer wave-lengths. Fig. 3, Nos. 5 and 6 show the absorption of pure zinc at two pressures. Bands appear at *a*, *c*, *d*, and *e* (2138 line). At the higher pressure *d* and *e* are overlapped but have retained a sharp edge at *d*. The band at 1900 is similar in appearance to that found in distilling zinc amalgam. These are, however, two distinct bands, for the one at 1900 appears both in distilling and stagnant vapor, but only at pressures over 9 mm (590°C); the zinc amalgam band 2050–<1850 appears only in distilling vapor at temperatures over 160°C.

#### 4. ABSORPTION SPECTRUM OF MERCURY

The same cell, 18.7 cms long, was prepared in the same way with mercury. For some of the observations on mercury and cadmium a hydrogen discharge tube similar to that described by Lambrey and Chalonge<sup>3</sup> was used as a source and photographs were taken with a medium size (E2) Hilger quartz spectrograph on Cramer contrast plates.

The absorption spectrum of mercury was the same in distilling and stagnant vapor. With increasing pressure of mercury, the 1849 line appeared at 1.2 mm (130°C) and widened into a band extending toward longer wave-lengths. At 4.2 mm (160°C) the band at 2540 appeared as a narrow line and broadened toward longer wave-lengths with increasing pressure. At 96.3 mm (260°C) the band at 2345 appeared and broadened only toward shorter wave-lengths until at 1400 mm (393°C)\* it met the 1849 band at a wave-length of 2277. The three sets of flutings associated with the 2345 and 2540 bands observed by Rayleigh<sup>4</sup> in distilling vapor were observed in this experiment in stagnant vapor.

#### 5. ABSORPTION SPECTRUM OF A MERCURY-CADMIUM MIXTURE

The absorption cell was prepared as in 1 with a mixture of cadmium and mercury. In the only case tried, too much mercury was admitted so that the 1849 absorption band of mercury overlapped the region in which the band analogous to that observed in the mercury-zinc mixture should lie. The cadmium bands corresponding to two of the bands found in pure zinc were, however, observed. At 83 mm (600.2°C) the band corresponding to the one from 1997–2006 in zinc extends from  $\lambda$ 2120 to 2130 and the other correspond-

<sup>3</sup> M. Lambrey and D. Chalonge *Comptes rendus* **184**, 1057 (1927).

<sup>4</sup> Rayleigh, *Proc. Roy. Soc.* **A116**, 702 (1927).

\* Vapor pressures from International Critical Tables v3 p. 205–6 and Landolt and Börnstein *Physikalische Chemische Tabellen* 5th ed. p. 1338.

ing to the 2064.2 band in zinc extends from 2208.7 to longer wave-lengths. With increasing pressure, this latter band appears first at 2211 and broadens toward longer wave-lengths till it overlaps the 2288 line. The 2288 line broadens nearly symmetrically with pressure until it meets the 2211 band at about  $\lambda 2225$ , after which it broadens only toward longer wave-lengths. At 186 mm (654°C) the band formed from the union of 2288 and 2211 extends from 2207.1 to about 2530 terminating in a series of flutings on the long wave-length side. At 186 mm the other cadmium band limits are 2118-2130A. The flutings and the band at 2211 were first observed by Mohler and Moore<sup>5</sup> and the one from 2120-2130 was found by Jablonski.<sup>6</sup>

## 6. DISCUSSION

*Absorption and fluorescence of a mercury-zinc mixture.* The appearance of an absorption band in vapor distilling from slightly amalgamated zinc and its failure to appear in stagnant vapor shows that distilling vapor contains some molecules which are not present in stagnant vapor. Since this absorption band was not observed in either zinc or mercury alone, it must be attributed to a compound of the two. It will be assumed to be HgZn. These HgZn molecules must distill out of the metal and later be dissociated by thermal impacts. This would require that the energy of dissociation be very low.

The appearance of fluorescence in a mercury-zinc mixture in distilling vapor but not in stagnant vapor indicates that the fluorescence is associated with the absorption of light by HgZn molecules. This view is strengthened by the fact that the  $2^3S$  zinc atoms which emit the fluorescence possess an energy corresponding to a wave-length of 1862 and the HgZn absorption band showed especially strong absorption in this region.

To produce these  $2^3S$  zinc atoms, HgZn molecules may absorb light of wave-length below 1862 receiving enough energy to dissociate into  $2^3S$  zinc atoms and normal mercury atoms or the molecules may reach a fairly stable excited state through absorption of light near 1860 and later transfer their energy to normal zinc atoms through collisions of the second kind. The experiments described here offer no means of determining what percentage of the fluorescence is due to each process.

Many observers have found that the visible band-fluorescence of mercury can be excited only when the mercury is distilling. Wood and Voss<sup>7</sup> have recently shown that this is due to the sweeping away of impurities such as water and hydrogen by the vapor stream. In stagnant vapor the impurities are assumed to destroy the excited mercury molecules through collisions of the second kind so that no fluorescence results.

<sup>5</sup> F. L. Mohler and H. R. Moore J.O.S.A. **15**, 74 (1927).

<sup>6</sup> A. Jablonski, Zeits. f. Physik **45**, 878 (1927).

<sup>7</sup> R. W. Wood and V. Voss, Jour. Frank. Inst. **205**, 486 (1928).

This explanation can not be applied to the fluorescence in a mercury-zinc mixture for both the fluorescence and the corresponding absorption band were observed in distilling but not in stagnant vapor. One would not expect purification by distillation to introduce a new absorption band but if distilling vapor contained molecules which did not exist in stagnant vapor, such a band should appear.

*Absorption and fluorescence of cadmium.* Kapuscinski<sup>8</sup> found that greater pressures were required to obtain the sharp triplet ( $2^3P_{2,1,0} - 2^3S$   $\lambda\lambda 5086, 4800, 4678$ ) in fluorescence in pure cadmium than when a trace of mercury was present and Power<sup>9</sup> observed that the sharp triplet of cadmium was excited in fluorescence only when the vapor was distilling. Both used spark sources of light. The conditions of Power's experiment were such that the tube probably contained a slight amount of mercury. The fluorescence of the sharp triplet in these experiments is very likely due to unstable HgCd molecules which exist only in distilling vapor. The process of excitation would be the same as that described above for a mercury-zinc mixture. The existence of unstable HgCd molecules in distilling vapor was suggested also by MacNair<sup>10</sup> to explain the emission of the mercury line 2536 in vapor distilling from a mixture of mercury and cadmium illuminated by light of wave-length 2288.

Jablonski<sup>6</sup> has associated the fluorescence of the sharp triplet of cadmium with absorption of light in the cadmium band 2120–2130. He makes the hypothesis that two cadmium atoms at the instant of collision absorb light of wave-length 2120–2130 and separate as one excited and one normal atom. The kinetic energy of the colliding atoms is added to the energy of the light to produce the excited atom. This process should occur equally well in pure cadmium or cadmium with a trace of mercury, and in distilling or stagnant vapor but the fluorescence in these cases is markedly different. This process, however, may account for the fluorescence in pure cadmium at high pressure and temperatures.

*Conclusions.* These experiments lead to the conclusion that fluorescence in gas mixtures may occur in several ways. In a mixture of zinc and mercury illuminated by light from a spark or arc the zinc atoms may be excited through collisions of the second kind with excited mercury atoms, or with excited HgZn molecules, or may result from the absorption and dissociation of HgZn molecules into excited zinc and normal mercury atoms. These processes will also account for the emission in fluorescence of the cadmium lines 5086, 4800, 4678 by a mixture of cadmium and mercury.

Wood and Kinsey<sup>11</sup> have assumed the same processes to account for the

<sup>8</sup> W. Kapuscinski, *Nature* **116**, 863 (1925) *Zeits. f. Physik* **41**, 214 (1927).

<sup>9</sup> A. D. Power, *Phys. Rev.* **26**, 761 (1925).

<sup>10</sup> W. A. MacNair, *Phys. Rev.* **29**, 677 (1927).

<sup>11</sup> R. W. Wood and E. L. Kinsey, *Phys. Rev.* **31**, 793 (1928).

excitation of the *D* lines in mixtures of hydrogen, nitrogen, or air with sodium by light of wave-length 5100–5250A.

Compounds like HgZn may exist in other gas mixtures and should be considered in the explanation of their fluorescence. Wood and Guthrie<sup>12</sup> and later Waring<sup>13</sup> have found absorption bands in mixtures of mercury and thallium which were not observed in either mercury or thallium alone.

In conclusion I wish to express my thanks to Dr. K. T. Compton for permission to carry out this work in Palmer Physical Laboratory. I also wish to thank Professors K. T. Compton and L. A. Turner for their helpful suggestions.

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*Note added in proof:* The absorption spectrum of pure cadmium has been found to be the same as that described above for a mercury-cadmium mixture. The asymmetrical broadening with pressure, over 60 mm, of the 2288 line from a constant short wave-length edge near 2208, must be attributed to cadmium and not to HgCd molecules. No absorption lines or bands were observed in cadmium between 2120 and 1860, at pressures less than 60 mm in a 32 cm absorption cell.

<sup>12</sup> R. W. Wood and D. V. Guthrie, *Astrophys. J.* **26**, 41 (1907).

<sup>13</sup> R. K. Waring, *Nature* **121**, 675 (1928).



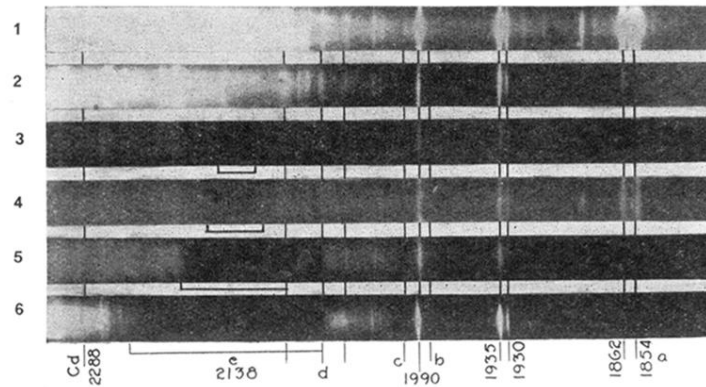


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