On the Bands at λ 2536 and λ 2540 of Mercury

By

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ABSTRACT.

Two bands at λλ 2536 and 2540 which are generally accepted as responsible for the molecules of mercury (Hg_2) have been investigated under various physical conditions.

1. The ordinary non-luminous vapor of mercury shows a strong absorption band at λ 2536 shaded towards the red and a very much weaker one at λ 2540 shaded in the opposite direction.

2. The luminous vapor, which is isolated from the negative arc of mercury in the air with a small horse-shoe magnet, shows the strong bands at λ 2540 and λ 2536 in absorption and the band at λ 2536 in emission.

3. The luminous vapor highly excited in the positive column of a vacuum tube emits the band at λ 2540 without the noticeable band at λ 2536.

It is concluded that the band at λ 2536 might be of the arc type, responsible for the neutral moleclue (Hg_2), and the band at λ 2540 might be of the spark type and responsible for the ionized one (Hg_2^+).

The band spectra of mercury were first studied by Wood and Guthrie[1] and subsequently by Stark and Wendt,[2] McLennan and Edwards,[3] Nagaoka,[4] and many other investigators.

In the band spectrum of mercury two different types of bands are easily noticed. The bands of the first kind are generally located in the less refrangible part of the spectrum the strongest of which are of wavelengths 4219, 4017 and 3728. At a moderate dispersion the component

1 Astro. J., **29**, 211 (1909).
2 Phys. Zeits., **14**, 562, 567 (1910).
3 Phil. Mag., **30**, 695 (1915).
4 Jap. J. Phys., **1**, 1 (1922—24).

lines of these bands are fairly resolved. Series of investigations have been recently carried out upon these bands by Compton and others[1,2,3,4,5] with the conclusion that the carriers of these bands might probably be ascribed to the excited mercury hydrides (H_gH). Quite recently Hulthén[6] has analysed the same bands and came also to the conclusion that the emitters of this band spectrum must be molecules composed of a mercury atom and atoms of an element of low atomic weight, since the wide spacing of the band lines indicates a small moment of inertia of the molecule.

In the second kind of bands, on the other hand, the bands at λ 2536, λ 2540 and also these located at the more refrangible part of the spectrum, all with apparently unresolvable structures might be included.

Now, the possibility of the existence of the diatomic mercury molecule Hg_2 has been suggested by Frank and Grotrian.[7] The expected value of the order of the magnitude of the distance between the successive band lines is but 10^{-3} A for the green light, and it is thought quite appropriate to ascribe the apparently continuous bands of the second kind to the diatomic molecule Hg_2. Tate's[8] recent experiment has also shown that the band at λ 2540 might be responsible for the molecule Hg_2.

In the course of an investigation upon the arc spectrum of mercury in the air the present writer has found a remarkablly strong development of an absorption band at λ 2540 as well as the band at λ 2536 near the mercury cathode of a vertical arc, the anode being a coreless carbon rod. On sending the current in the reverse direction in this vertical arc, these bands practically disappeared, a strong reversal of the resonance line over the entire length of the arc only remaining. In the present paper these two bands at $\lambda\lambda$ 2536 and 2540 have been examined under different excitations and various physical conditions, and some discussions have been offered under the hypothesis that both bands are responsible for the diatomic mercury molecules.

Results.

A coreless carbon rod of 1 cm. in diameter was pierced at one end. The hole was filled with mercury and this was utilized as one of the electrodes in our vertical arc, the other electrode being a coreless carbon

1 Phys. Rev., **23**, 768 (1924).
2 Phys. Rev., **24**, 597 (1924).
3 Phil. Mag., **48**, 898 (1924).
4 Phys. Rev., **25**, 606 (1925).
5 Phil. Mag., **49**, 360 (1925).
6 Zeits. f. Phys., **32**, 110 (1925).
7 Zeits. f. Phys., **4**, 89 (1921).
8 Phys. Rev., **25**, 110 (1925).

of the same size. The applied voltage was varied from 110 to 440V and the current was regulated from 2 to 5 A with high resistance nickel-chrome wires arranged in series.

A small and a medium quatz Hilger spectrographs were used and the image of the arc was focussed upon the slits of these spectrographs with a quartz fluorite achromatic combination.

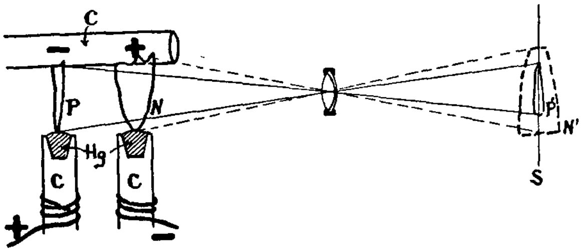
In general appearance, the form of the positive mercury arc is quite different from the negative one. Magnified images of the positive and negative arcs are given in Eigs. 1 and 2, Pl. I. In both arcs the applied voltage was 220V and the current traversed was 3·1A for the positive arc and 2·6A for the negative one. The positive arc is quite stable, but in this case owing to the rapid vaporization of the mercury, the cup must be filled with mercury at an every exposure. In the negative arc, however, though the arc is unstable, the vaporization of the mercury is fairly small, and the arc can be maintained without charging the mercury to secure several photographs.

For the spectroscopic examination of these arcs an entire image of the arc was focussed upon the slit of the spectrograph, and the distribution of the spectral lines over the whole length of the arc was examined. With a mercury anode and a carbon cathode the lines due to mercury are generally strong near the mercury electrode, and gradually lose their intensities as they proceed towards the cathode. Though the spark lines such as at λ 2848 and λ 2248 are faint, they however show their appearances extended further up to the carbon electrodes. Besides this, the reversal of the resonance line is remarkable. Next, with a mercury cathode and a carbon anode the line distribution in its spectrum is almost the same as that of the former one. The spark lines mentioned above are, however, strong at the cathode surface showing a larger concentration of the ionized mercury atoms in this region than at the anode surface of mercury. In addition to this, I found a remarkable development of the dark bands at λλ 2536 and 2540 in the spectrum of the light from the neighbourhood of the cathode surface where the spark lines are emitted most strongly. These bands are utterly absent in the spectrum of the positive arc. This is clearly visible in the photographs given in Figs. 3 and 4, Pl. I, and also in the enlarged ones (Figs. 5 and 6, Pl. I).

The continuous background due to the broadening of the line at λ 2536 emitted at the central core of the arc was absorbed at λ 2536 and λ 2540 by the luminous outer layer near the cathode surface of the arc. The development of the band at λ 2540 is quite remarkable, its intensity being nearly equal to that of the band at λ 2536.

Next, a fine image P′ of the positive arc P(source) was formed upon the slit S of our spectrograph through the luminous vapor layer of the negative arc N(absorber), N′ being the out-focussed image of the negative arc N as indicated in the following diagram (Fig. 1) and the absorption of the latter arc was examined.

Fig. 1.



The continuous background due to the broadening of λ 2536 in the spectrum of the former (positive arc) was absorbed at λλ 2540 and 2536 by the latter (negative arc) as may be seen in the spectrum given in Fig. 8, Pl. I, the upper one (Fig. 7, Pl. I) being that of the source alone. With a positive arc absorber no such absorption bands were obtained.

The luminous vapor capable of producing the absorption band at λ 2540 has an ionized character, and this is easily deflected or isolated from the arc in any desired direction with a small horse-shoe magnet. If we deflect the luminous excited vapor towards the slit or along the line of sight (i. e. increasing the thickness of the absorbing layer), the development of the absorption band at λ 2540 is remarkablly strong, its intensity being several times stronger than that at λ 2536. Next, if we deflect the excited vapor outside the line of sight no trace of the band at λ 2540 is obtained in the spectrum. The spectrum of this isolatable luminous vapor was taken and it was found that in this spectrum there was no trace of the band at λ 2540 observed in emission nor in absorption, and the band at λ 2536, on the other hand, appeared as an emission, being sharply defined at wave-legth shortor side and shaded towards the red. This is shown in Fig. 11, Pl. I, the upper ones (Figs. 9 and 10, Pl. I) of this spectrum are those of the light from a quartz mercury lamp. The lower is the spectrum under the weak, and the upper under the heavy, current excitations, showing the symmetrical broadening of the line at λ 2536.

On a closer examination upon the light of the positive arc of mercury a fainter bluish fluorescent light has been observed just above the boiling mercury anode with a comparatively non-luminous space about 0·5 mm. thick between. The intensity of this fluorescent glow becomes tolerably stronger as it proceeds towards the luminous arc. This is seen in the photogragh of the positive arc (Fig. 1, Pl. I), but a greater part of the image of this luminous glow is disappeared in this reproduction, a trace at the right side of the arc and near to the mercury surface only remaining. In the spectrum of this fluorescent glow, as already been observed by wood and others, the resonance line λ 2536 is predominant, and in addition we have a band in the extreme violet and another band in the green, the latter accounting for the visible luminousity of the fluorescence.

The vapor was next excited in a vacuum tube by an induction coil of a medium size. At a certain vapor pressure the vapor came to emit the band at λ 2540 only with no noticeable trace of the band at λ 2536. One of the photographs thus obtained is given in Fig. 13, Pl. I and a

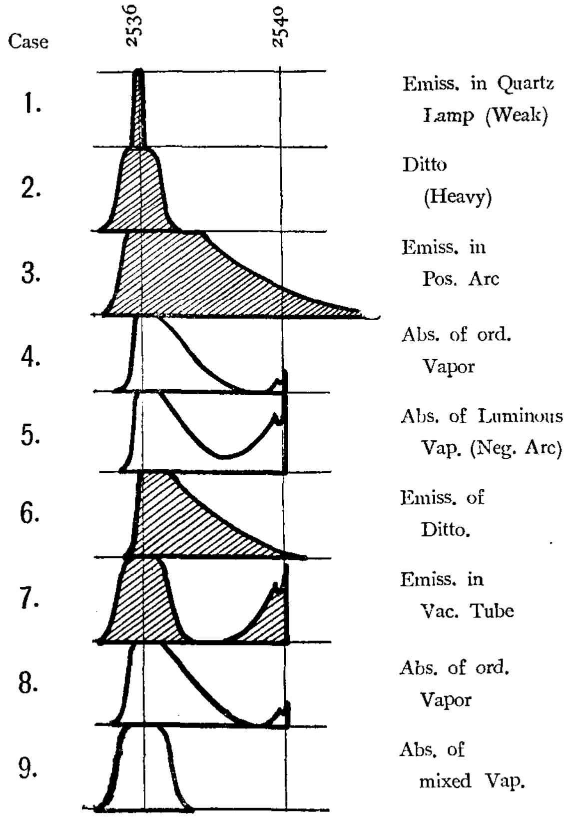


Fig. 2.

negative arc spectrum is also given in the upper one for comparison sake.

The diagrammatical representation of the intensity curves of these bands obtained in the spectra under various conditions are also given in

Table I.

Case	Discription of Source and Absorber in Fig. 2.	Analysis.
1	Emission in quartz lamp under weak current excitation.	Sharp line at λ 2536 in emission.
2	Ditto under heavy current excitation.	Broadening of the line at λ 2536 in emission.
3	Emission of the positive arc in the air.	Broadened line and band shaded towards the red at λ 2536 both in emission.
4 and 8	Absorption of non-luminous ordinary vapour.	Broadened line and band at λ 2536 and weak band at λ 2540 all in absorption,
5	Absorption of luminous vapor in the cathode arc.	Broadened line and band at λ 2536 and storong band at λ 2540 all in absorption.
6	Emission of luminous vapour isotated from the cathode arc.	Line and band at λ 2536 both in emission.
7	Emission in the positive column of a vacuum tube.	Broadened line at λ 2536 and strong band at λ 2540 in emission.
9	Absorption of ordinary vapor mixed with foreign gases.	Broadened line at λ 2536 in absorption.

the annexed sketch (Fig. 2). The manifoldness in the modifications of the spectral region between λ 2536 and λ 2540 is remarkable. This is, however, plainly explained by a simple hypothsis as given in the above table.

The peculiar modification, found by Wood,[1] in the appearance and the position of the band at λ 2536 (corresponding to 8 and 9 in Fig. 2 and also in Table I.) which resulted from the presence of the foreign gas, is completely explained by the above view, the reason of which might be as follows: — With pure mercury vapor the excited atoms which are brought forth by the absorption of the resonance radiation will partly re-emit the line on returning to the normal state and partly combine in their excited states with the normal atoms forming the diatomic molecules Hg_2 which show the characteristic asymmetrical absorption band shaded towards the red. With an admixture, on the other hand, though the

1 Astro. J., **27**, 41 (1907).

activated atoms are also produced at the expense of the resonance radiation, they will combine with the mixed gas molecules and therefore the band at λ 2536, responsible for the diatomic molecules of mercury, practically disappear, the strong reversal of the resonance line alone remaining.

The present experiment indicate that the more heavier the vapor is excited the more strongly the band at λ 2540 is enhanced. With normal non-luminous vapor the absorption band at λ 2536 is prevailing and only a trace of the band at λ 2540 appears. Next, with excited luminous vapor which is positively charged and produced at the cathode surface, both absorption bands come out in nearly equal intensities. Lastly, on the degree of excitation being still further raised, the vapor is caused to emit the band at λ 2540 without the sensible band at λ 2536.

Now, in the negative arc of mercury, large numbers of the ionized atoms are produced near the mercury cathode which is readily seen to be the case by the strong enhancement of the spark lines in this region. These ionized atoms will partly emit the spark lines, and then the arc lines in combination with the neighboring electrons, and partly combine in their ionized state with the normal mercury atoms forming the ionized molecules Hg_2^+. These ionized molecules thus produced will show, on being animated further, the characteristic absorption bands. Besides these ionized molecules, there might exist in the excited luminous mercury vapor numbers of excited molecules without ionization as was already conjectured by Frank and Grotrian.[1] Among the bands corresponding to the two kinds of molecules in different states of activity, it is quite natural to consider that the former bands (spark type) should become pronounced as the vapor is excited more heavily in comparison with the latter ones (arc type) as is the case with the spark and arc lines in atomic radiation. From this point of view it might be quite appropriate to conclude that the band at λ 2540 is responsible for the ionized molecules Hg_2^+ and the band at λ 2536 for the neutral molecules Hg_2.

Steubing[2] has already observed an electrical conductivity of the mercury vapor illuminated by ultra-violet lights such as a spark or a mercury lamp, showing that the vapor is ionized by the ultra-violet lights. Moreover, it was found in the present experiment that the band at λ 2540 was remarkablly developed in the positively charged vapor in absorption. These two facts will be quite in harmony with our conclusion that the band at λ 2540 might be one of the spark bands of the mercury molecules.

Again, it may be imagined that the main constituents of the posi

1 Loc. cit.

2 Phys. Zeits., **10**, 787 (1909).

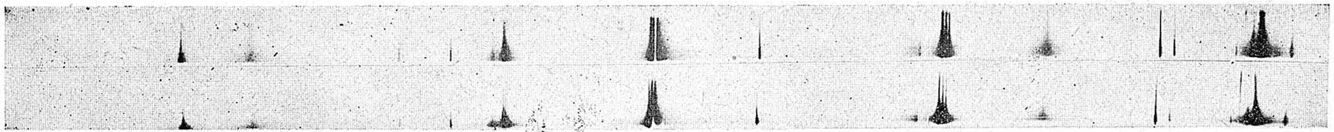
tively charged vapour, freshly liberated from the negative arc and deflected by the magnet, might be ionized molecules at an energy level ready for the band absorption at λ 2540 in their ionized states, and for the band emission at λ 2536 on catching the neighbouring electrons and returning to their neutral state.

Lastly, the possible reason for the absence of the band at λ 2540 in the positive arc might be the too small concentration of the ionized molecules to produce the sensible absorption owing to the rapid diffusion of these ionized molecules towards the cathode by the action of the electric force acting between the electrodes of this arc.

In conclusion, the writer wiches to express his hearty thanks to Prof. M. Kimura, who gave valuable advice in the present investigation and took much interest there-in

Fig. 3. Positive Arc.

Fig. 4. Negative Arc.



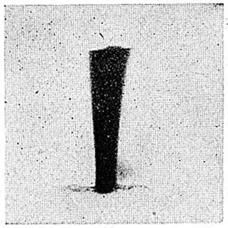


Fig. 1. Positive Arc

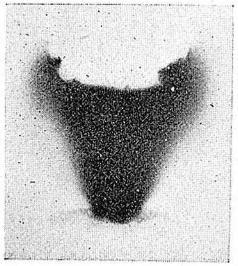


Fig. 2. Negative Arc

Fig. 5.

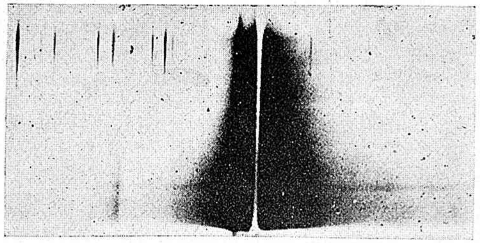


Fig. 6.

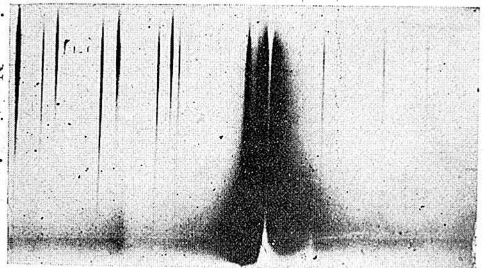


Fig. 7.

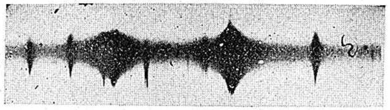


Fig. 8.

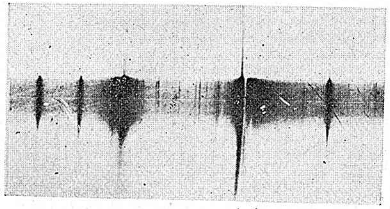


Fig. 9. Fig. 10. Fig. 11.

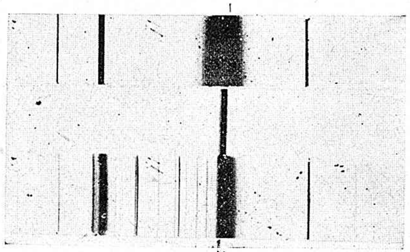


Fig. 12. Fig. 13.