Fluorescent Excitation of Mercury by the Resonance Frequency and by Lower Frequencies. Further Studies.

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[Plates 16, 17.]

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§ 1. Introduction.

In a previous paper on this subject* I examined in some detail the fluorescence excited by the atomic resonance line 2537, and by frequencies lower than this, which act by absorption in the region of longer wave-length than 2537. The fact that this absorption-region is immediately juxtaposed to the atomic line, and that the absorption is (at any rate on a rough view) stronger the nearer we go to the line, makes the distinction between the two cases difficult; and it must be admitted that the phenomena themselves are not at first sight so distinctive as might be expected, if we take the obvious view that in one case absorption is by atoms and in the other by molecules. This has led some writers to the opinion that atomic absorption does not act at all in giving rise to band-fluorescence.† It was shown, however, in the communication mentioned that a discontinuity of intensity in the fluorescence can be observed as the exciting beam traverses the vapour, and is robbed of its more absorbable component. The initial fluorescence due to the core of the resonance line is referred to as

† Pringsheim and Terenin, 'Z. Physik,' vol. 47, p. 330 (1928); Pienkowski, 'Z. Physik,' vol. 50, p. 791 (1928); Mrozowski, 'Z. Physik,' vol. 60, p. 412 (1930); Niewodniczanski, 'Z. Physik,' vol. 55, p. 676, has argued against this view from the influence of a magnetic field in putting the vapour "out of tune" with the source (Zeeman effect). Mrozowski, loc. cit., has attempted to answer this, but I find it difficult to appreciate the exact force of his arguments.
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the "core effect," and the much weaker fluorescence distinguishable after the core effect has died out is called the "wing effect," because it is excited by the wing, or outer region, of the line. With dense vapour, however, excitation can be observed more than 1000 A. to the long wave side of the line, and the term "wing effect" is extended to the whole of this region, because no reason has been found for restricting it.

It was found (loc. cit., p. 9) that the core effect is cut out by a supplementary absorption cell of mercury vapour producing a reversal of the line only 0·1 A. in breadth. I wish now to emphasise that this reversal agrees exactly in position with the narrow atomic emission line from a cold source within less than this amount.

The hair-like lines necessary to show this coincidence to the best advantage do not lend themselves well to reproduction; but a stronger exposure, No. 1, Plate 16, will give some idea. The top and bottom photographs taken independently are placed in register by means of the line 2534·77 (faint in the upper photograph). This line does not otherwise enter into the question. The reversal in the lower photograph represents the radiation necessary to produce the core effect. It has been urged that this coincidence is not really conclusive and that the absorption concerned is molecular, the strongest molecular absorption coinciding with the atomic line. It may be admitted that strong molecular absorption does, in fact, occur in this neighbourhood, as evidenced, for example, by the molecular band 2540. We may take the position of this band as a general illustration of the degree of accuracy of coincidence between the molecular and atomic absorption phenomena. In the experiment in question we know that the whole fluorescent effect which I call the core effect is cut out. There must, therefore, be a complete reversal of that part of the spectrum which excites it. The only reversal of this kind which we find to occur coincides with the atomic line within 0·05 A. The band at 2540 is, say, 70 times further off. It would seem that an exact coincidence between atomic and molecular phenomena is not likely and that the exact coincidence of the fluorescence-absorption in this case with the atomic line is strong evidence that it is in fact atomic absorption.

The conclusion will, however, be strengthened still further if it can be shown that there are important differences of behaviour between the wing effect and the core effect, other than the power of penetrating into the vapour. In the present paper a variety of definite evidence of this kind will be offered.
§ 2. *Selective Extinction by Hydrogen.*

According to the results of Pringsheim and Terenin* very minute additions of hydrogen to mercury vapour are able to quench the fluorescence. Thus they found that using saturated mercury vapour at $185^\circ$ C, $10^{-4}$ mm. of hydrogen was enough.

This has, I believe, generally been regarded as indicating that the energy absorbed by the mercury vapour, instead of being radiated, is got rid of in collision with hydrogen molecules, which are dissociated into neutral atoms in the process.

The energy of dissociation of hydrogen is now well established to be 4.465 volts.† I found, however, that the green fluorescence could be excited by a wave-length as long as 3450, corresponding to 3.51 volts, which is much less than what is required for dissociation. It was of interest, therefore, to re-examine the effect of hydrogen on the fluorescence, using long wave excitation. The experiments which will be described have reference to the visual fluorescence only.‡

In preliminary experiments an arrangement was used similar to that of Pringsheim and Terenin, with a barometric column to cut off the fluorescence-vessel from the pump, after the addition of gas. This arrangement proved troublesome for various reasons and was abandoned. The results seemed to be complicated by gaseous impurities which came out from between the mercury column and the walls of the tube, as heat penetrated downwards. This part of the investigation was limited to examining the effect of added hydrogen, and I found it best to seal the silica fluorescence vessel on to the pump, to exhaust it thoroughly, boiling the contained mercury for an hour or more, then after cooling to admit the desired pressure of hydrogen and seal off.

A rectangular vessel made from silica sheet, and measuring $3 \times 3 \times 5$ cm. was used in many of the experiments, but a 25-c.c. flask does nearly as well. It is advantageous to make a dimple in one side of the flask, where the exciting beam enters, after the fashion of fig. 1 (which, however, refers to another series of experiments). In this way it becomes much easier to look for fluorescence in the immediate neighbourhood of the entrance wall. The vessel was contained in an electrically heated oven, and a thermometer was placed against it.

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The luminous source was focussed on the vessel with a quartz lens. Visual light was filtered out with a combination of a silica cell 7.5 cm. thick containing bromine vapour, nearly saturated, and a plate of blue-purple "corex" glass. This combination transmits the ultra-violet pretty freely from 3600 to below the resonance line 2537.*

The source used in many of the experiments was a mercury vapour lamp, which could be cooled with a fan so as to give a narrow resonance line, suitable for the core effect, or allowed to warm up, so that the line became broadened and partially reversed. A magnet was used in the usual way to squeeze out the reversing layer. In other cases the iron or nickel arc was used as source. These last two sources can give the wing effect only, since they do not contain any component near enough to the centre of the atomic line to excite the core effect. The mercury lamp partially cooled (terminal voltage, say, 25 or 30 volts) is suitable to excite both effects.†

The vessel was first thoroughly exhausted and well boiled out, without addition of hydrogen. The mercury lamp was run at 25 volts. The core effect was then very bright at 220° C., and the wing effect was visible at this temperature. When the vessel was sealed off after admission of 1 mm. of hydrogen, the wing effect from the mercury arc running at 25 volts was seen at 200° C., but no trace of the core effect could be detected at this or at higher temperatures. The core effect, if present, would be concentrated near the entrance window, and would therefore have to compete with the fluorescence of the silica wall. This difficulty introduces some uncertainty as to the minimum amount of hydrogen necessary to extinguish the core effect. On cooling the mercury lamp with a more vigorous air blast, so that it ran at only 18 volts, the wing effect disappeared also, and there was then no observable fluorescence.

Observations were also made with the mercury arc at 30 volts. The wing effect stretching right across the bulb was seen at 200° C., and was strong at 240°. The core effect was not seen at all.

Similar experiments were made with 1 cm. and 10 cm. of hydrogen pressure. Finally, 30 cm. of hydrogen was admitted and the vessel sealed off. With the iron arc, the fluorescence (wing effect) was visible at 170° C. At a rather higher temperature it was bright enough for the green colour to be definite. At 250° C. it was very bright, and could still be detected when a sheet of "vita" glass cutting at about λ 2850, was interposed in the exciting beam;

* The corex filter seems to lose much of its transparency to these short waves after hours of exposure to strong radiation.
and at 320° C. it was seen when a filter of ordinary glass 2 mm. thick, was interposed, cutting the exciting spectrum at about \( \lambda 3200 \).

At the higher temperatures used with either kind of excitation, iron arc or mercury arc, the partial pressure of admixed hydrogen is of the order of 1 atmosphere. It was contemplated to try still more, and the vessel was opened for that purpose. On applying the blowpipe, the vessel was broken by the explosion of the contained hydrogen, which had not been given enough time to diffuse away. There was at any rate no doubt of a large amount of hydrogen having really been present when the fluorescence was observed.

A few casual experiments were made on the behaviour of other added gases. So far as was determined, air added in the small amount required to destroy the core effect destroyed the wing effect also. The addition of considerable amounts of nitrogen did not destroy either effect. The sealed bulb method of working is not well adapted to experiments with traces of air or oxygen, since oxygen is removed by oxidation of the mercury while the experiment is in progress.

Another form of experiment may be mentioned, though it scarcely calls for detailed description. Mercury was kept boiling in a fluorescence-vessel with reflux condensation, a pressure of a few centimetres of nitrogen being maintained in the condenser. A nozzle near the entry of the light admitted either hydrogen or air at pleasure. By admitting the former, the core effect could be selectively extinguished, leaving the wing effect. This was tried on and off very often. When the same experiment was tried with air admission, extinction of the core effect was accompanied by extinction of the wing effect.

To sum up, the reality of the distinction between core and wing effects is confirmed by the fact that the former is extinguished by a trace of hydrogen, while the latter can tolerate any amount of it.

The wing effect extends to great distances away from the atomic line, and all would agree that it is due to molecular or quasi-molecular absorption. The core effect which reacts so differently towards added hydrogen must differ in some essential respect. It is associated with absorption exactly at the atomic line, and therefore it is natural to connect it with atomic absorption, which further provides a natural explanation of the distinction between the two effects.

We shall see later on in this paper that the fluorescent spectrum associated with the core effect shows features which are not present in the wing effect.

Notwithstanding the large number of investigations that have been made, our knowledge of the fluorescence spectrum of mercury is still incomplete. In particular we know little of the region from 2540 to about 3000, where the continuous stretch culminating at 3300 begins. When the molecular spectrum is excited by electric discharge a series of bands appears in this region.† It seemed important to determine whether these could be observed in fluorescence, when the conditions of excitation are much more under control. This problem unexpectedly led to the discovery of characteristic differences of spectrum between the wing and the core effect in fluorescence.

The arrangement used is shown in fig. 1 (one-third actual scale). The fluorescence vessel is a silica bulb A of 25 c.c. capacity, with a dimple sucked in as shown, to allow a clear view near where the exciting light enters.

B is a reflux condenser. The space above it can be filled with nitrogen at any desired pressure, the nitrogen pressure serving to measure the pressure of saturated mercury vapour. Further, the arrangement acts as its own thermostat, and we can heat the bulb direct over a burner which allows free access. This is practically much more convenient than an electrically-heated oven.

The jet C and the flame from it shown in fig. 1, were not in use for the first experiments, and may for the moment be disregarded. Excitation was by a mercury lamp of ordinary commercial pattern, kept cold by an electric fan, and a small electromagnet to press the discharge forward as before. The radiant was limited by a diaphragm, and

* A preliminary notice was given in 'Nature,' vol. 127, p. 854 (1931).
the light from this was rendered parallel by a quartz lens, of 8 cm. diameter and about 10 cm. focus. Then followed a filtering layer of chlorine 46 cm. thick, which, while fairly transparent to the resonance line, is nearly opaque for wave-lengths from about $\lambda 2625$ to the middle of the visual spectrum. In this way stray light from the mercury line spectrum was very much reduced and the field left clear for observing fluorescence which is weak in the region under investigation. The mercury lines came through faintly, and were convenient as wave-length standards. A second lens similar to the one already mentioned focussed the beam on the bulb.

A small Hilger quartz spectrograph was used, and the fluorescent light was focussed on the slit by a quartz-fluorite achromat. It was found convenient to adjust the mercury pressure to 5 mm. The fluorescence (core effect) then extended several millimetres from the wall of the vessel, and at the same time was not too much diluted by expansion. Under the conditions it only showed slight signs of passing upwards with the vapour stream (Phillips effect). The position of the image of the bulb on the slit plate was as shown at fig. 1, D (inset). The slit is shown by a dotted line.

With these arrangements a 13-hour exposure was given, and showed a series of bands in the region 2750 to 3100. These bands are of very poor contrast however, and are difficult objects for measurement without a microphotometer. In the absence of such an instrument, I succeeded best as follows. A second 13-hour exposure was taken and superposed on the first, film to film. This was enlarged on to paper, to a large enough scale to allow further magnification to be dispensed with and the enlarged print was measured with an ivory scale, setting the zero of the scale on each band in succession, and reading the position of a fiducial mercury line used as a standard. Only a moderate range of the spectrum, comprising about 10 bands, was readily measurable, owing to lack of contrast. The measurements are given in the first column of Table I. For comparison the spectrum measured in excited vapour rising from a special form of low current discharge* is given in column 3. Considering the difficulty of measuring these faint and diffuse bands, the agreement is satisfactory, and allows us to identify the two spectra.

The comparison is seen in No. III, Plate 16. The upper spectrum is that of the excited vapour rising from the special type of discharge. The lower spectrum is the fluorescence (core effect). The specially broad band at $\lambda 2913$ apparently breaking the regularity of the series is seen in both, and comparison of the original photographs is convincing apart from the measurements. It is

hoped that the reproduction will come out well enough for independent verification. The two spectra were not made on the same instrument, which accounts for the imperfect fit of the mercury lines.

### Table I.

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* Obscured by mercury line. † Anomalous broad band.

The earlier spectrogram with electrically excited vapour gives the bands most clearly for measurement. Moreover, it was taken with a more dispersive instrument. The measurements extended over a much larger range, a part only being quoted in Table I, column 3.‡


The series of bands, Table I, is excited by the core of the resonance line. It was important to investigate whether the same bands would occur when excitation was away from the core of the line (wing effect). The iron arc afforded a convenient bright source, the peculiarities of spectral distribution apparently not affecting the result. The incident light was filtered by 46 cm. of chlorine and also (in many experiments) 7·5 cm. bromine vapour, of good density, but not saturated. These filters combined, cut out all photographically active rays of greater wave-length than λ 2625 leaving the region between this and the resonance line to give excitation. The fluorescence vessel was as before, but it was found that the intensity was very much enhanced by superheating. This will be discussed further in the next section.

A series of bands was obtained in this case also. It was necessary to work


|| A preliminary notice of the results of this section was given in 'Nature,' vol. 127, p. 662 (1931).
at much higher pressures than before, since the absorption and also the fluorescence are too weak at the low pressures used in the previous experiments. A pressure of 32 cm. was often used, but the results are the same at atmospheric pressure or at lower pressures down to 4 cm. At a pressure of 1 cm. they were not obtained in 1 hour, but in all probability a longer exposure would reveal them.

In the above experiments the excitation was by the iron lines comprised between $\lambda 2537$ and $\lambda 2625$. Of these the lines nearest $\lambda 2537$ are the more easily absorbed, and the more effective in producing fluorescence. It was important to verify that iron lines some considerable distance away from the resonance lines are also effective in exciting the bands. For this purpose the fluorescence vessel was turned round as shown in fig. 2, and the fluorescence observed near the dimple, the exciting beam being then filtered through 31 mm. of mercury vapour saturated at atmospheric pressure. This cut out everything within 20 A. from the resonance line, the range of excitation being now from $\lambda 2557$ to $\lambda 2625$. The bands were still obtained in 1 hour’s exposure.

I was at first inclined to take for granted that these bands were the same as those found with core excitation (cooled mercury lamp). The negatives were not bold enough for easy direct comparison, owing to lack of contrast in the bands. Measurements were made by the same method as before, on a paper enlargement from two superposed negatives. The results are given in column 1 of Table II. In column 2 of the same table are given the absorption bands which I formerly measured in this part of the spectrum, in long columns of unexcited mercury vapour at pressures of the order of the atmospheric.*

The differences are in column 3, and it is evident that the two spectra are identical. The strongest proof of this is in the fact that there is no tendency for such discrepancy as appears to accumulate as we pass along the series (vernier effect).

Fluorescent Excitation of Mercury.

Table II.

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* Anomalous broad band.

The same criterion shows very definitely the non-identity of this series with the series obtained by core excitation (cooled mercury lamp). The latter series is given in the fourth column, and it is seen that over the same spectral range there are three bands less in this series. The non-identity of the two series was fully emphasised in the former paper (loc. cit.). I then distinguished them as the absorption series and the emission series of the less refrangible region. Since both are now obtained in emission, these names are discarded, and I call them the wing series and the core series respectively in accordance with their mode of excitation in fluorescence.†

The wing series in emission is shown in Plate 16, No. II, upper photograph, and the same reversed, in absorption, in the lower photograph. In comparing these photographs it is to be remembered that the bright regions in the upper should coincide with the dark regions in the lower. The mercury line comparison spectrum was superposed across the upper photograph. It has been strengthened by hand retouching outside the strip of band spectrum, as it was originally rather too faint to reproduce well. The emission bands are less distinct than the absorption bands, but it is hoped that they will come out in reproduction. They have not, of course, been retouched in any way.

† These names are provisional. It is quite probable that the wing series is present along with the core series in core excitation, though masked by the greater intensity of the core series.
§ 5. General Discussion of the Spectra. Effect of Superheat on Emission of Wing Series.

We have seen that one series of bands occurs with core excitation and another with wing excitation. I shall next consider the spectra more generally, bringing the other features into relation with these band series and with the conditions of excitation.

The discussion will refer chiefly to the part of the spectrum from $\lambda 2625$ upwards, which is largely protected from false light from the source. The part nearer the resonance line includes important features, but it will be necessary to improve the technique before these can be adequately examined.

The photographs V and VI, Plate 17, show the fluorescence at 16 cm. pressure, using iron arc excitation. V was taken with the vapour at boiling temperature under 16 cm. pressure. In VI the vapour is superheated by bringing a small jet of burning hydrogen to bear on the concave external surface of the dimple in the silica vessel, which heats the silica wall to dull redness (see fig. 1). The merit of this arrangement is its simplicity and convenience. Naturally it does not allow of any precise control over the temperature conditions. It will be noticed that in V the broad visual maximum at 4580 is far more conspicuous than the ultra-violet maximum at 3300. In VI with superheat these intensities are inverted. It is to be noted that V and VI were taken under identical conditions, as to exposure and illumination, the only difference being the application of superheat in VI. The absolute intensity of 4850 is enormously diminished, and the absolute intensity of 3300 enormously increased by superheating.*

At the same time that 3300 is enhanced by superheat, the bands of the wing series are enhanced along with it. These bands are not discernible on the print of VI, but they can be seen on the negative, occupying the region from 2750 to 2950.† They do not appear on the negative of V, but can be brought up by longer exposure under the same conditions. In some comparison exposures at 16 cm. pressure it was found that 15 times as long an exposure was required to bring up the bands without superheat as with it.

In these emission spectra the wing series of bands seems to behave as if it

* The differential effect of superheat on these maxima was first shown in 'Proc. Roy. Soc.,' A, vol. 114, p. 632 (1927). Subsequent observations have been made by Wood, Niewodniczanski and Mrozowski.

† A considerable enlargement and special photographic technique (duplication of negatives, use of contrast paper and contrast developer) is needed to make these bands conspicuous enough for reproduction as in II, Plate 16.
were one unit with the continuous maximum 3300. This nexus is suggested by examining even a single photograph on which the bands appear, such as the original of VI. The bands of the series become broader and of poorer contrast as we proceed towards long waves. At the same time the general luminosity of the spectrum increases, and at about \( \lambda 2950 \) the bands become imperceptible, and pass into the continuous region. The latter comes to a maximum at \( \lambda 3300 \) and then diminishes in intensity.

The same point of view is strengthened by comparing photographs taken under various conditions. We may use superheat or no superheat, high pressure or low pressure; we may excite nearer or further from the resonance line, short of going right up to it; but if we get the maximum 3300 of a certain photographic intensity, as in VI, the wing series appears with it, and failing this, as for instance in photograph V, the wing series does not appear.

These statements apply only to the case of wing excitation, not to core excitation (when, possibly, the wing series is obscured by the core series overlying it) nor to absorption, of which more later.

On the short wave side the wing series converges and becomes less distinct, merging into an apparently continuous spectrum. However, in the former absorption experiments* the series was measured as far as \( \lambda 2613 \cdot 9 \), thus beyond the point where the iron lines cover the fluorescence spectrum in VI.

In VI the visual maximum 4850, though much reduced, is not altogether extinguished. This is due to the comparatively high vapour pressure 16 cm., and the less rapid diffusion of high temperature from the heated wall into the vapour. At lower densities we get a completely dark space near the wall. No. IV, Plate 16, shows this very clearly. This spectrogram is taken at 4 cm. pressure with the slit of the instrument horizontal, and dispersion vertical, and the left-hand vertical edge is only just inside the wall of the vessel. The position of the image on the slit plate is indicated in the inset E, fig. 1. If a straight-edge is applied to the left-hand edge of IV, it will be noticed that the band 4850 is altogether wanting at the edge. The intensity only becomes appreciable 2 mm. to the right of the edge, and reaches a maximum at 6 mm. \( \lambda 3300 \), on the other hand, has its greatest intensity at the left edge, and becomes insensible at the right edge, when 4850 is still conspicuous. The band 2540,† which may be distinguished by its greater intensity from the surrounding iron

† The photograph IV is on rather a small scale, and moreover the iron lines are confusing. But it was shown formerly (‘Proc. Roy. Soc.,’ A, vol. 125, p. 7 (1929)) that at a pressure of 4 cm. the iron arc excites 2540 without the resonance line 2537.
lines, passes from left to right, i.e., away from the heated wall with sensibly uniform intensity, thus falling into a third category very different from either 3300 or 4850. In IV the horizontal distances are about 0.7 of actual scale.

Photographs taken in this way with longer exposure show the wing series limited to near the left edge where 3300 is strongest, and photographs at lower pressure (2 cm. or less) show the resonance line behaving in the same way as 2540.

Another remarkable feature of VI is the appearance of the mercury lines 4359 and 4047 (marked with arrows). These do not appear on V and superheat is clearly the condition of their appearance. But it remains uncertain whether this is merely due to the weakening of the unfavourable background of the continuous band culminating at 4850, or whether the actual intensity of the blue mercury lines is enhanced by the heat. Special exposures on an orthochromatic plate showed that the green mercury line 5461 is present as well, thus we have all three components of the triplet $1^3S_1 - 1^3P_{012}$. No other mercury line was detected, except that the resonance line itself appears at low pressures.

These mercury triplet lines are not present in the iron arc source and it is quite clear that they are generated somehow in the mercury vapour.

The most obvious suggestion was that as in the well-known experiments of Fuchtbauer* and of R. W. Wood,† atoms in the $1^3P_2$ state are present in the vapour, and that these are raised to $1^3S_1$ by absorption of 5461. Alternatively, $1^3S_1$ may be reached by absorption of 4359 by $1^3P_0$ atoms, or of 4047 by $1^3P_1$ atoms.

It is doubtful whether any lines in the iron arc source are close enough to the mercury wave-lengths in question to serve the purpose. But, be this as it may, the explanation is excluded by a special experiment. A bromine cell combined with blue corex glass completely stops all the three wave-lengths in question, yet the mercury lines were obtained as usual in fluorescence when superheated vapour at 32 cm. pressure was excited by the iron arc through these filters.

We are left without any obvious explanation of the presence of the triplet $1^3S_1 - 1^3P_{012}$. This requires much higher excitation than any that can be directly provided by the exciting light; the shortest wave-length that gets through the corex filter is $\lambda 2380$, corresponding to 5.2 volts, while excitation to $1^3S_1$ requires 7.7 volts.

* 'Phys. Z.,' vol. 21, p. 635 (1920).
† 'Phil. Mag.,' vol. 50, p. 774 (1925).
We have now to consider the general relations in the spectrum with core excitation. The complete spectrum from which the illustration of the core series in III, Plate 16, is enlarged may be seen in IX, Plate 17. This it may be repeated, is taken at 5 mm. pressure, without superheat, and two negatives are superposed to gain intensity. The only filter in use was the 46 cm. chlorine tube. Mercury lines appear in IX, but in view of the brightness of the source and the long exposure it was believed that these could be ascribed to false light which had penetrated the chlorine filter. Considering the appearance of mercury lines in VI (iron excitation and superheat) further investigation should be made on this point.

Closely associated with the bands of the core series in IX is the apparently continuous maximum at about 2650 to which Houtermans has drawn attention.* There is no doubt about the reality of this association: 2650 is conspicuously lacking in V and VI (wing excitation). Indeed, I am doubtful whether it is really to be distinguished from the series itself. In the early measurements the bands of this series were traced and measured as far as 2659-5, which is close to the intensity maximum.

In the immediate neighbourhood of the resonance line the chlorine filter affords no protection, and false light is dominant.

The pair of photographs, VII and VIII, show the result of superheat on core excitation at 5 mm. pressure. VII is without superheat, and VIII is a comparable exposure with superheat; as in all other cases the maximum 3300 gains in intensity, while the maximum 4800 loses. The remarkable point is, however, that the region 2600–2900 which contains the core series (though these particular photographs are not sufficiently exposed and intensified to show it resolved into bands) is not increased in intensity at all. This is in sharp contrast with what we see in comparing V and VI (wing excitation) in the same region. Here we have a striking distinction between the wing series and the core series, which would confirm the general result of the wave-length measurements if such confirmation were needed. The superficial similarity of the two series breaks down completely under either test.

The broad maxima 4850 and 3300 in IX are not of very different intensity. In VI, 4850 is much the stronger. This difference, however, is not characteristic of the mode of excitation (wing effect or core effect) but of the pressure. The point was specially investigated in a series of photographs which it has not been thought necessary to reproduce. Using core excitation (cooled mercury lamp) the pressure was varied over wide limits. Since at the higher pressures

* 'Z. Physik,' vol. 41, p. 146 (1927).
the fluorescence only occurs very near the wall of the vessel, the slit was placed horizontal, so that the image of the luminous layer, viewed edgewise, cut across it, giving a narrow spectrum. In this way all difficulty of adjustment was avoided, and the small breadth of the spectrum was no practical disadvantage.

Similar experiments were made with iron arc (wing) excitation.

The results were as follows:—

<table>
<thead>
<tr>
<th>Pressure (mm.)</th>
<th>Core excitation (cooled mercury lamp)</th>
<th>Wing excitation (Iron arc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>4850 much strongest</td>
<td>4850 much strongest</td>
</tr>
<tr>
<td>22</td>
<td>4850 much strongest</td>
<td>4850 much strongest</td>
</tr>
<tr>
<td>8</td>
<td>Maxima about equal</td>
<td>Maxima about equal</td>
</tr>
<tr>
<td>4.5</td>
<td>3300 strongest</td>
<td>3300 rather strongest</td>
</tr>
<tr>
<td>2.0</td>
<td>3300 much strongest</td>
<td>Nothing to be seen (too faint)</td>
</tr>
</tbody>
</table>

It appears then that with either source the relative intensity of 4850 gains very much with increase of pressure, equality to 3300 being attained at about 8 mm. At 22 mm. 4850 has become much the stronger. It will be remembered that high temperature (superheat) favours 3300. This effect is accordingly to be attributed to the greater density of vapour, and not to the accompanying rise of temperature, which, for what it is worth, acts in the opposite sense.

Results similar to these have been obtained by Mrozouski* using short wave (spark) excitation.

§ 6. Absorption Experiments.

The remarkable effect of superheat in intensifying the wing series in emission naturally suggests the question of whether it would be similarly intensified in absorption. This was examined in a column of mercury vapour 46 cm. long. The liquid boiled in a small vessel under one atmosphere pressure of nitrogen. The vapour passed through the absorption tube, which could either be made red hot, or maintained at the boiling temperature of mercury (357° C.). The source of continuous spectrum was a hydrogen discharge tube, unfortunately not quite free from hydrocarbon contamination. The two photographs were practically identical. Absorption was complete from the position of the resonance line to about \( \lambda 2700 \), and from that point the wing series appeared in absorption, in about the same intensity in each photograph. No indication whatever of 3300 in absorption could be seen, thus the apparent nexus between this

* 'Z. Physik,' vol. 55, p. 338 (1929).
feature and the wing series which is observed in emission is not maintained in absorption. This will be apparent from X which reproduces the absorption spectrum at red heat. The wing series can be seen in the print of X, but the scale of enlargement and photographic intensification are hardly enough to satisfactorily reproduce it. The photograph is chiefly reproduced to emphasise the absence of 3300 in absorption.

Incidentally, these absorption experiments afford evidence on the question raised by Walter and Barratt* who considered the presence of small traces of oxygen necessary to develop the wing series in the absorption spectrum. In my own original observation of this series the mercury was condensing in contact with air, although the conditions were such as (in my opinion) excluded the presence of air in the optical absorption tube itself. In the present work an atmosphere of nitrogen purified from oxygen by phosphorus was used instead of air; but this made no difference to the appearance or intensity of the wing series absorption band. The same applies to the numerous experiments which have been here described above on the wing series in emission. The mercury was always boiling under an atmosphere of nitrogen purified by phosphorus and dried. The apparatus was absolutely tight, all joints being sealed, with the exception of an accurate cemented cone fitting which united the silica to the glass work. So far as my own experience goes, there is nothing to suggest that oxygen is necessary to develop the wing series, either in absorption or in emission.

§ 7. Summary of Chief Points.

The paper is mainly concerned with fluorescence of mercury vapour when it is excited by—

(a) light of the frequency of the core of the resonance line 2537 (core excitation);

(b) light of less frequency, absorbed in the band which begins at the resonance line. I call this wing excitation because it begins, and is strongest, in the wing of the resonance line; but the term is applied to excitation anywhere in the absorption band mentioned, which stretches 1000 A. or more towards long waves.

The fluorescence with core excitation is extinguished by adding a trace of hydrogen.

With wing excitation, it survives very large additions of hydrogen.

Fluorescent Excitation of Mercury.

In the region from $\lambda$ 2650 to $\lambda$ 3000, a series of diffuse bands is found in core excitation (core series). In the same region another series of bands is found in wing excitation (wing series).

The two series have only a superficial resemblance, and the wing series alone appears in absorption by the unexcited vapour.

The wing series in emission is enormously increased in intensity by superheating. In this, it goes with the continuous maximum 3300, though the latter, unlike the wing series, does not appear in absorption.

The core series is not increased in intensity by superheating.

It is considered probable that core excitation is a process of excitation by collision with excited mercury atoms. Such atoms, as is known, lose their energy by collision with hydrogen molecules, dissociating the latter. Hence the extinction of the core effect by hydrogen.

Wing excitation on the other hand, is directly due to molecular absorption of light, though the subsequent processes are complex. The excited molecules produced are indifferent to hydrogen.

It is clear that these two processes of molecular excitation are not equivalent, since the core series of bands is only obtained by the former process.

DESCRIPTION OF PLATES 16, 17.

I.—*Top*: Atomic emission line 2536.52. *Bottom*: The same line in absorption, using a broadened source, and a mercury absorption cell just sufficient to cut out the core effect. The photographs are put in register by the line 2534.77. Note that the absorption which cuts out the core effect agrees very exactly with the atomic emission line.

II.—*Top*: Emission bands of mercury vapour at 32 cm. pressure, iron arc excitation ("wing series"). *Bottom*: The same bands produced by absorption in a long column of unexcited mercury vapour of atmospheric density.

III.—*Bottom*: Mercury bands 0.5 cm. pressure, excitation by cooled mercury lamp ("core series"). *Top*: The same bands emitted by the vapours rising away from a hot cathode discharge of low current density.

IV.—"Wing effect" fluorescence. Iron arc excitation 4 cm. pressure. Entrance wall of the vessel (to left) heated. Fluorescent light focussed on horizontal slit of spectrograph. The maximum 3300 is intensified near the hot wall: 4850 extinguished near the wall (test by a straight-edge placed along left edge of photo), 2540 unaffected by hot wall.

V.—Iron arc excitation (wing effect) 16 cm. pressure.

VI.—Identical conditions with V, except that the vapour is superheated. Note the enhancement of 3300 and the weakening of 4850. Note also enhancement of the region 2600 to 2900 containing the wing series bands (not discernible in reproduction on this scale). Note the mercury lines 4047 and 4359, which are not present in the exciting source (marked with arrows).

VII.—Core effect, without superheat. Excitation by cooled mercury lamp.
VIII.—The same with superheat. Note extinction of 4850 and enhancement of 3300. Note also that the region 2600 to 2900 containing the core series is not enhanced by superheat. Contrast with VI.

IX.—Intensified spectrum similar to VII. Shows the wing series and the maximum 2650, which only appears with it.

X.—Absorption by 46 cm. of mercury vapour, red hot at atmospheric pressure. The wing bands appear in absorption (just visible in reproduction) but 3300 does not in this case appear with them.

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The Origin of the $\gamma$-Rays.

By Lord Rutherford, O.M., F.R.S., and C. D. Ellis, F.R.S.

(Received July 4, 1931.)

§ 1. Introduction.

In a recent paper, Rutherford, Ward and Lewis* have described the results of their measurements on the long-range $\alpha$-particles emitted by radium C. They were able to identify nine groups of $\alpha$-particles of different energies in addition to the group characterising the normal mode of disintegration. It was pointed out how the modern theories of $\alpha$-particle disintegration based on the wave mechanics make it possible to infer from these results the existence of a corresponding number of excited states of the radium C' nucleus. The excess of the energies of these stationary states over that of the ground state responsible for the normal $\alpha$-particle are shown in Table I.

Table I.

<table>
<thead>
<tr>
<th>Number of state.</th>
<th>Energies of excited states of radium C' nucleus in excess of ground state volts $\times 10^{-3}$.</th>
<th>Number of long-range $\alpha$-particles per normal disintegration $\times 10^5$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.3</td>
<td>0.49</td>
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<tr>
<td>2</td>
<td>14.6</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>17.6</td>
<td>0.53</td>
</tr>
<tr>
<td>4</td>
<td>19.4</td>
<td>0.53</td>
</tr>
<tr>
<td>5</td>
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<td>0.56</td>
</tr>
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<td>7</td>
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</tr>
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<td>8</td>
<td>28.4</td>
<td>0.67</td>
</tr>
<tr>
<td>9</td>
<td>30.2</td>
<td>0.21</td>
</tr>
</tbody>
</table>