

ON THE BAND SYSTEMS OF MERCURY.

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THE band spectrum of mercury has been the subject of a number of investigations. A resumé of the results so far obtained has been given by Finkelnburg in the *Physikalische Zeitschrift*.¹ Although many of the features of these bands have been qualitatively accounted for, quantitative results are few and conflicting. The present communication is concerned with an analysis of five of the band systems. As preliminary to a discussion of the new analysis, a brief statement of the present state of knowledge in regard to the band spectra of mercury is given below.

The band system of mercury consists of the following bands and continua :

- (1) A continuum between 4000 Å and 5300 Å with a maximum at 4850 Å. This appears only in emission.
- (2) A system of bands discovered by Volkringer between 3685 Å and 4024 Å. The interval between successive bands falls from 262 cm.⁻¹ at the red end to 92 cm.⁻¹ at the violet end.
- (3) Another continuum between 3000 Å and 3700 Å having a maximum at 3300 Å and appearing only in emission.
- (4) The series of bands between 3143 Å and 3337 Å observed by Hamada in a hollow cathode discharge. In these the intensity alternates at every fifth band. $\delta\nu$ is nearly constant being about 50 cm.⁻¹
- (5) The series of bands between 2660 Å and 3098 Å appearing only in emission. $\delta\nu$ falls from 250 cm.⁻¹ to 50 cm.⁻¹ This is the 'Core Series' of Lord Rayleigh.
- (6) A series of bands between 2614 Å and 2943 Å appearing in absorption and emission. $\delta\nu$ falls from 148 cm.⁻¹ to 47cm.⁻¹. This is Lord Rayleigh's 'Wing Series.'
- (7) A weak continuum at 2650 Å appearing only in emission.
- (8) A continuum with a sharp head at 2540 Å appearing in emission and absorption.

(9) Eight sharp bands between 2450 Å and 2494 Å appearing only in emission.

(10) A group of weak sharp bands closely spaced between 2341 Å and 2297 Å, appearing in emission and absorption. These bands show heads. Measurements of Lord Rayleigh and Kuhn give a nearly constant $\delta\nu$ of 18 cm^{-1} whereas Hamada gives a coarser structure with $\delta\nu$ varying from 126 cm^{-1} to 52 cm^{-1} .

(11) A group of bands between 2322 Å and 2064 Å which vary with the kind of excitation. They are known as Steubing's bands. $\delta\nu$ varies from 500 cm^{-1} to 100 cm^{-1} , as observed by Mrozowski. In the measurements of Kremenewski between 2150 Å and 2000 Å $\delta\nu$ falls from 117 cm^{-1} to 70 cm^{-1} . Hamada's measures between 2167 Å and 2044 Å give $\delta\nu$'s falling from 227 cm^{-1} to 126 cm^{-1} .

(12) A continuous band with short wave limit at 1850 Å, appearing in emission and absorption, accompanied by a band at 1807 Å which occurs only in absorption.

(13) A continuous band at 1690 Å appearing in emission and absorption.

(14) A continuous band at 1403 Å observed only in absorption.

According to current views Nos. (2), (5) and (6) with which we are chiefly concerned in the present paper, are considered to be each an unbroken series of fluctuations due to vibrational levels corresponding to a single electronic state. Extrapolation based on this view leads to the assignment of electronic levels to each of these series. The following is a summary of the current theoretical views on the subject.

Diatomic mercury molecules may be formed by the union of two atoms in the 1S_0 ground state or by that of one atom in the 1S_0 state and another excited atom. The molecule made up of two 1S_0 atoms is supposed to be loosely bound and its heat of dissociation is assumed to be very small. Koernicke² found the heat of dissociation into two unexcited neutral atoms to be 1.4 kilogramme calories per mol., while Mrozowski³ found a value of 17 K cal./mol. by one method and nearly zero by another method. Winans⁵ estimates it at 3.5 K cal./mol., while Kuhn and Freudenburg¹⁰ confirm Koernicke's value. Mrozowski³ says that Koernicke used a wrong formula, but Kuhn and Freudenburg use the same formula. The potential curve corresponding to two 1S_0 atoms is, however, represented nowadays as one of continuous repulsion with only a very slight minimum. Of the potential curves corresponding to ($^1S_0 + 2\ ^3P_0$), ($^1S_0 + 2\ ^3P_1$), ($^1S_0 + 2\ ^3P_2$) and ($^1S_0 + 2\ ^1P_1$) molecules, the first has only one branch while the others have each two

branches—one branch having a minimum and the other corresponding to repulsion and thus possessing only a slight minimum if at all. The vibrational levels are situated in the hollows corresponding to the minima, while a transition from the minimum itself to the portion of the ($^1S_0 + ^1S_0$) curve lying vertically below gives rise to a continuum. Though a transition from the 2^3P_0 and 2^3P_2 states to the 1S_0 state is forbidden in the atom, transitions from the ($^1S_0 + 2^3P_0$) and ($^1S_0 + 2^3P_2$) molecular states to the ($^1S_0 + ^1S_0$) state are allowed and the probability of transition is the greater the larger the difference between the energies of the atomic and molecular terms.

The various bands and continua are assigned to transitions from excited molecular states to the ($^1S_0 + ^1S_0$) ground state as follows :

The continuum (3) and the 'wing' bands (6) are assigned by all authors to transitions from the ground state to the ($^1S_0 + ^3P_1$) state. The continuum (1) is similarly attributed to transition to the ($^1S_0 + ^3P_0$) state. In his latest paper Mrozowski has assigned Volkringer's bands (2) to ($^1S_0 + ^3P_0$) as the upper state. The 'core' series (5) has been assigned by Kuhn⁴ to transition from ($^1S_0 + ^3P_0$) to ($^1S_0 + ^1S_0$), but ascribed to transitions from ($^1S_0 + ^3P_1$) by Mrozowski. Nos. (11) and (12) are similarly ascribed to the ($^1S_0 + ^1P_1$) \rightarrow ($^1S_0 + ^1S_0$) transition, while (13) and (14) are transitions from ($^1S_0 + 2^1S_0$) and ($^1S_0 + 3^1P_1$) to ($^1S_0 + ^1S_0$). According to Winans¹ (9) is due to Hg_2^+ molecules. From transitions from near the flat portions of the two branches of each curve arise continua or closely spaced bands. Transitions from ($^1S_0 + 2^3P_0$), ($^1S_0 + 2^3P_0$) and ($^1S_0 + 2^3P_2$) thus give rise to Nos. (7), (8) and (10) respectively. The bands observed by Hamada⁶ (4) have not explicitly received any explanation. Only, Hamada conjectured that they were an extension of the 'wing series' towards longer wavelengths. It is assumed that a band series, similar to the 'core' and 'wing' bands and arising from the ($^1S_0 + 2^3P_2$) state may exist but has not been observed. In order to obviate the necessity of ascribing two band series to one state, Volkringer's bands were assumed not to form a separate system but to be a continuation of the 'core' series. The great distance between the 'core' bands and Volkringer's bands which have approximately the same $\delta\nu$ makes this explanation untenable and so Mrozowski ascribes Volkringer's bands to ($^1S_0 + ^3P_0$) and the 'core' bands to ($^1S_0 + 2^3P_1$). According to his view, however, there would be two band systems — the 'core' and 'wing' series — arising from ($^1S_0 + 2^3P_1$). The explanation offered by him for such a phenomenon is not satisfactory; besides it fails to explain the observed differences in the conditions of excitation and the behaviour of these bands under different conditions. There is also a further difficulty in assuming that the 'core' and 'wing' series are fluctuations arising from vertical

transitions from vibrational levels attached only to the upper state. To explain the large distance between the continuum at 3300 and the corresponding 'wing' series, the potential curve of the ($^1S_0 + ^1S_0$) ground state is supposed to rise very steeply in the region corresponding to small distances between the nuclei. This being the case, the wavenumbers of two vertical transitions from two neighbouring vibration levels of the upper state should differ by a quantity not merely equal to the interval between these levels, but depending also upon the difference in level between the points where the verticals cut the lower ($^1S_0 + ^1S_0$) curve. In such a case extrapolation from the first differences between the wavenumbers of the successive bands of the series treated as a single whole cannot lead to any correct result. Yet it is in this way that extrapolation from the 'core' series is made to prove that it arises from the ($^1S_0 + 2\ ^3P_0$) state. Before taking up the above difficulties we shall briefly describe the experimental facts intended to be covered by these explanations.

The 'wing' series is emitted when mercury vapour is made fluorescent by the outer portions or 'wings' of the resonance line 2537, as also by its central part or 'core'. The 'core' series comes out only by 'core' excitation. The 'wing' series is observed also in absorption while the 'core' series is not found in absorption. The 'core' fluorescence is limited to the place where the exciting light is incident, while the 'wing' fluorescence penetrates into the vapour. Addition of hydrogen quenches the 'core' series but not the 'wing' series. Superheating increases the intensity of the 'wing' series while the 'core' series is not so affected. Lord Rayleigh⁷ to whom the above observations are due concludes that the excitation of the 'core' bands and of the 4850 Å continuum is an indirect process involving excitation of the atoms and not of the molecule as a whole, while the excitation of the 3300 Å continuum and the 'wing' series is due to direct molecular absorption. The behaviour under superheat shows that the 3300 Å continuum and the 'wing' bands are directly connected, except that the 3300 Å continuum does not occur in absorption. In the visual luminosity due to 'core' excitation, both 3P_0 and 3P_2 atoms are shown to be present by actual experiment. Wood's bands (10) are associated with the forbidden line 2270 ($^1S_0 - ^3P_2$) and both occur in 'core' excitation. No connection between the 'core' series and the 4850 Å continuum has been mentioned such as that found in the case of the 'wing' series and the 3300 Å continuum. Lord Rayleigh has also shown that "starting with Wood's 'resonance radiation' at atmospheric temperatures in vacuo, and raising the temperature of the mercury, we can pass continuously to the phenomenon of the moving ultraviolet 'core' effect."

The ascription of electronic levels to the various bands and continua discussed previously is made to yield an explanation of the experimental results in the following manner. The non-occurrence of the 3300 Å continuum in absorption in spite of the fact that the other systems arising from the ($^1S_0 + 2\ ^3P_1$) state, *viz.*, Nos. (6) and (8) do appear in absorption, is explained by the fact that its lower state lies high above the dissociation energy of the ground state. The spectra attributed to the 3P_0 and 3P_2 states appear with small intensity because transitions from them to 1S_0 are forbidden in the atom though not in the molecule. The difference in behaviour between the 'wing' and 'core' series and that between the 3300 and 4850 continua is explained by the indirect nature of the excitation required to produce the 3P_0 state supposed to be involved in the emission of the 'core' series and the 4850 continuum. Their non-appearance in absorption and insensitiveness to temperature are explained by the fact that 3P_0 atoms must first be produced from 3P_1 atoms and the formation of the $^1S_0 + ^3P_0$ molecule follows as a secondary process. Wood's observation that there is a time interval between the absorption of the incident light and the emission of the visible green fluorescence is also explained by the same facts. But nothing in the explanation distinguishes between the two metastable states 3P_0 and 3P_2 , and since Lord Rayleigh has experimentally proved the existence of both 3P_0 and 3P_2 atoms in the visual fluorescence, the 'core' series may be attributed to ($1\ ^1S_0 + 2\ ^3P_2$) molecules in better accordance with experimental facts than if ascribed to ($^1S_0 + ^3P_0$) molecules. For, Lord Rayleigh has shown that the visible and ultraviolet 'core' effects behave differently in a stream of moving vapour and that the two can be separated in space. If it is correct to ascribe the 'wing' series and the 3300 continuum to ($^1S_0 + ^3P_1$) molecules, the experimental facts require that the 'core' series and the 4850 continuum be attributed to a different molecular state involving metastable electronic levels. Finkelburg's objection against associating the 'core' series and the 4850 continuum both with the same state, *viz.*, ($^1S_0 + ^3P_0$), on the ground that the distance between the two is too large, must be upheld. We will presently show reasons to attribute the 4850 continuum and Volkringer's bands (which are sufficiently near to this) to the ($^1S_0 + ^3P_0$) state and the 'core' series to the ($^1S_0 + ^3P_2$) state. We thus get a satisfactory explanation not only of Volkringer's bands but also do away with the puzzling absence of a band system associated with the lower potential curve of the ($^1S_0 + ^3P_2$) state.

Since all the band systems have the ($^1S_0 + ^1S_0$) ground state involved in their emission or absorption and since the potential curve of this state should rise steeply, it appeared unsatisfactory that the characteristics of the

common level could not be recognised in all of them. Especially when no explanation is forthcoming in the case of Hamada's bands except a vague surmise that they form an extension of the 'wing' series, and the appearance of a smaller $\delta\nu$ in the case of Hamada's bands is contrary to the expectation that they form members due to lower vibrational quantum states of the same level as the one which gives rise to the 'wing' series, the unsatisfactory nature of our knowledge becomes evident. The smaller $\delta\nu$ has been ascribed to the vibration levels of the ground state; but since in order to explain the system (10) the ground state is assumed to have a $\delta\nu$ of 36 cm.^{-1} while the $\delta\nu$ in Hamada's bands is nearly 50 cm.^{-1} , both explanations cannot be correct. The assumption that all the vibration levels are attached to the upper electronic states and that the steep course of the potential curve of the ground state produces no appreciable difference at least in the 'core' series was thought improbable and so an attempt was made to arrive at a vibrational analysis of the several bands. The results are set forth in the tables. It will be seen that Volkringer's bands, Hamada's bands, the 'wing' bands, the 'core' bands and Steubing's bands (measurements of Hamada have been chosen in this case because Mrozowski's values seem to be irregular), all show common differences characteristic of the common ground state, in spite of the apparently different $\delta\nu$'s of the various bands. Because of the difficulty of accurate measurements in the case of these weak and diffuse bands and because of the absence of recognisable band heads, the ΔF^v 's show variations which are larger than in the case of better developed band systems. However, the irregularities have at least a parallel in all spectra, since, even when measurements are certainly more accurate, the ΔF^v 's are not constant to within the error of measurement. With regard to the $\Delta^2 F$'s the irregularities are within the errors of measurement; moreover such variations are quite common when the binding does not correspond to a small anharmonic term. The ΔF 's of the ground state also show a peculiarity so far observed in three other diatomic spectra, *viz.*, LiH, NaH and H₂,⁸ in that they first increase and then decrease, assuming the same values as those that occurred during the increase. Because we do not know how the potential curve is to be drawn in such a case we shall not attempt to draw the other potential curves also. (Rydberg⁹ leaves out the cases of LiH and NaH when deducing an expression for the potential energy.) But the experimental facts are well explained by the vibrational quantum numbers themselves. Corresponding to the discovery of the 'wing' series at first only in absorption, the vibrational levels of the ground state here start from $v'' = 0$, whereas in the 'core' bands they start with $v'' = 4$. In spite of their smaller $\delta\nu$ Hamada's bands fit in well

TABLE I.
"Wing" Bands of Lord Rayleigh.

| $(^1S_0 + ^1S_0)$ $V'' =$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------------|--------------|--------------|--------------|--------------|------------------|-------------|---------------|--------------|
| $(^1S_0 + 2^3P_1)$ $V' = 0$ | 36300 689 | 36200 699 | 35905 | | | | | |
| 1 | 36989 605 | 36899 629 | | 36114 628 | 35384 625 | 849 625 | 34535 625 | |
| 2 | 37594 555 | 37528 559 | 37243 553 | 36742 569 | 733 558 | 1048 554 | 34112 554 | |
| 3 | 38149 | 38087 | 37796 | 37311 485 | 744 522 | 1048 486 | 34666 494 | |
| 4 | | | | 37796 450 | 707? (37089?) | 1040 457 | 35160 462 | 33964 426 |
| 5 | | | | 38246 | 718 (37528) | 1035 | 35622 387? | 34390 399 |
| 6 | | | | | 37918 | | 36009* | 34789 371 |
| 7 | | | | | | 999 | 36390 341 | 35160 350 |
| 8 | | | | | | 988 | 36742 302 | 35510 311 |
| 9 | | | | | | | 38032 | 35821 |

* Used twice.

TABLE I.—(Contd.)
Hamada's Bands.

| $(^1S_0 + ^1S_0)$ $V'' =$ | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|--------------------------------|-----------------|------|--------------|--------------|-------|--------------|-----|--------|
| $(^1S_0 + 2^3P_1)$ $V' = 0$ | | | | | | | | |
| 1 | 30891 | | | | | | | |
| 2 | (29961) 496? | | | | | | | |
| 3 | 30457 | | | | | | | |
| 4 | 525 | | | | | | | |
| | 30982 | | | | | | | |
| 5 | | | | | | | | |
| 6 | 31810 | 1067 | 30743 337 | 735 353 | 30008 | | | |
| 7 | | | 31080 | 719 336 | 30361 | | | |
| 8 | | | | 30697 335 | 483 | 30214 | | |
| 9 | | | 31760 | 728 | 479 | 30553 287 | 288 | 30265 |
| 10 | | | | | | 30840 | 287 | 30457* |
| 11 | | | | | | 31080* | 287 | 30413 |
| 12 | | | | | | | 288 | 30649 |
| 13 | | | | | | | 288 | 30697* |
| 14 | | | | | | | 288 | 30840 |
| 15 | | | | | | | 288 | 30891* |
| | | | | | | | 288 | 30982* |
| | | | | | | | 288 | 31032* |
| | | | | | | | 288 | 31131 |
| | | | | | | | 288 | 31182 |
| | | | | | | | 288 | 31131* |

* Used twice.

TABLE II.
Steubing's Bands measured by Hamada.

| $(^1S_0 + ^1S_0)$ $V'' =$ | 1 | 2 | 3 | 4 | 5 |
|------------------------------|--------------|--------------|--------------|--------------|---------------|
| $(^1S_0 + ^1P_1)$ $V' =$ | | | 47373 183 | 801? | 46572 214 |
| | | 48035 162 | 479 177 | 47556 177 | 770? 213 |
| | | 48197 161 | 464 148 | 47733 148 | 734 182 |
| | 48650 188 | 292 146 | 48358 146 | 477 154 | 47881 154 |
| | 48788 126 | 284 146 | 48504 146 | 469 | 48035* |
| | 48914 | 264 | 48650 | 700 | 47181 |
| | | | | 857 | 46142 227? |
| | | | | 812 | 46369 |

* Used twice.

TABLE III.
"Core" Bands of Lord Rayleigh.

| $(^1S_0 + ^1S_0)$ $V'' =$ | 4 | 5 | 6 | 7 | 8 | 9 | |
|--------------------------------|--------------|------------|--------------|-------------|---------------|-------------|-----------------------|
| $(^1S_0 + 2^3P_2)$ $V' = 0$ | 36647 343 | 851 344 | 35796 344 | 983 314 | 34813 314 | 1222 350 | 33591 350 |
| 1 | 66990 301 | 850 317 | 36140 317 | 1013 317 | 35127 317 | 1186 317 | 33941 317 |
| 2 | 37291 | 834 | 36457 360 | | | | |
| 3 | | | 36817 333 | 1021 333 | 35796* 344 | | 33166 |
| 4 | | | 37150 330 | 1010 330 | 36140* 317 | 1195 314 | 34945 314 |
| 5 | | | 37480 | 1023 | 36457* 278 | 1198 259 | 35259 259 |
| 6 | | | | | 36735 255 | 1217 278 | 35518 278 |
| 7 | | | | | 36990* 234 | 1194 235 | 35796* 235 |
| 8 | | | | | 37224 201 | 1193 204 | 36031 204 |
| 9 | | | | | 37425 | 1190 | 36235 |
| 10 | | | | | | | 33166* 220 |
| 11 | | | | | | | 33386 205 |
| 12 | | | | | | | 33591* 181 |
| 13 | | | | | | | 33772 169 |
| 14 | | | | | | | 33941* 182 |
| 15 | | | | | | | 34123 194 |
| 16 | | | | | | | 34317 193 |
| 17 | | | | | | | 34510 153 34663 |

* Used twice.

TABLE IV.
Volkringer's Bands.

| $(^1S_0 + ^1S_0)$ $V'' =$ | 3 | 4 | 5 | 6 | | | |
|-------------------------------|-------|-----|--------|------|--------|------|-------|
| $(^1S_0 + ^3P_0)$ $V' = 0$ | 26680 | | | | | | |
| | 230 | | | | | | |
| 1 | 26910 | 746 | 26164 | 829 | 25335 | | |
| | 219 | | 228 | | 233 | | |
| 2 | 27129 | 737 | 26392 | 824 | 25568 | | |
| | | | 196 | | 171 | | |
| 3 | | | 26588 | 849 | 25739 | | |
| | | | 200? | | 147 | | |
| 4 | | | 26788? | 902? | 25886 | 1042 | 24844 |
| | | | | | 142 | | |
| 5 | | | | | 26028 | | |
| | | | | | 136 | | |
| 6 | | | 27027 | 863 | 26164* | 1058 | 25106 |
| | | | 102 | | 131 | | |
| 7 | | | 27129* | 834 | 26295 | | |

* Used twice.

into higher vibrational levels of both the states involved, so that we have also an explanation for the difficulty which attends the production of these bands. A comparison of the corresponding quantum transitions of the 'wing' and 'core' series shows that the members of the latter are of shorter wavelength than those of the former; this and the slower rate of convergence of the vibrational levels of the upper state of the 'core' bands show without doubt that the limit of the upper state of this series is far higher than that of the $(^1S_0 + ^3P_1)$ state. This is our justification for attributing the 'core' series to the $(^1S_0 + ^3P_2)$ lower potential curve. Because of the peculiar behaviour of the levels of the ground state, it has not been possible to deduce the heat of dissociation for this state, but the conflicting results obtained by Mrozowski by two different methods—by varying the temperature and pressure he obtained 17 K cal. per mol. and nearly 0 by varying the temperature without altering the pressure—seem to be due to this peculiarity. The fine structure obtained by Lord Rayleigh and Kuhn in the case of Wood's bands is at present not fully explained. The common differences of the ground state (88 cm.^{-1} and 288 cm.^{-1}) can be obtained in this case also, and probably the value of $\delta\nu = 16 \text{ cm.}^{-1}$ is the ΔF^v of the upper potential curve of the $(^1S_0 + ^3P_2)$ state, but this point of view is only tentative. The heat of dissociation of the $(^1S_0 + 2 \ ^3P_1)$ state, however, can be easily found from the analysis of the 'wing' bands completed by Hamada's bands. On calculation I find this to be 0.64 volt, while

Kuhn and Freudenburg¹⁰ have estimated it to be 0.84 volt. From the difference ($^1S_0 - ^3P_1$) known from the atomic spectrum and the limit of the ($^1S_0 + ^3P_1$) state thus found we find that the electronic level corresponding to the ($^1S_0 + ^1S_0$) state is 0.25 volt above $v'' = 0$ of this state. This corresponds to a level where $\Delta F^v = 700$. If we take this as about the normal vibration quantum of the ground state—a hypothesis supported by the decreasing portion of the ΔF^v values beginning with $\Delta F^v = 700$ —the presence chiefly of the diagonal terms in the 'wing' series becomes intelligible. Some other facts relating to the conditions of excitation and fluorescence can also be explained from the new view-point. Thus, a few of the bands included in Lord Rayleigh's list of core-bands do not find a place in this analysis. It is interesting to find that these very bands are among those which are identical in the 'core' and 'wing' series and that they find a place in the analysis of the 'wing' bands. Similarly, most of those bands of the 'wing' series which did not fit into the analysis of this series have been included in the 'core' series. A few bands from Hamada's list also do not fit in among the 'wing' series but seem to find a place in the 'core' series. Since the 'wing' series are also known to appear weakly in emission with core excitation, it is not astonishing that some of them fall into the positions where there are no real 'core' bands and thus produce the impression that the 'core' series is an unbroken system. The occurrence of a few bands of the 'core' series amidst the 'wing' bands lends support to Kuhn's assumption that the 'core' series also occurs in absorption but is overshadowed by the more intense 'wing' series. The partial identity of the two series which was thought to be such a puzzling feature by Lord Rayleigh is thus seen not to be an identity but a confusion of members of one series with those of another. The fact that the long wave members of the 'wing' series occur only at high pressures will not be easily intelligible on the old view that they are transitions to the lower vibrational quantum number states of the ($^1S_0 + ^3P_1$) level. On the new view, however, this can be explained if the vibrational levels discovered in the ground state as lying above the level of dissociation are assumed to represent only favoured states for the formation of quasi-molecules, for then, the atoms can approach nearer at high pressure and quasi-molecules in the higher vibrational states can be formed and the long wave members due to transitions from these states can then be absorbed. The assumption of such favoured states for the formation of quasi-molecules will also explain why even when mercury vapour is excited by light of wavelength 3360 Å, the 3300 Å continuum occurs in fluorescence, although it does not appear in absorption. For if the point of the ($^1S_0 + ^1S_0$) curve vertically below the minimum of the ($^1S_0 + ^3P_1$) state does not correspond to such a favoured

position for the formation of a quasi-molecule the 3300 Å continuum will not appear in absorption. But 3360 can be absorbed from favoured states lying above that corresponding to 3300, resulting in a ($^1S_0 + ^3P_1$) molecule in a state above the minimum of its potential curve, and the subsequent emission of the 3300 continuum from the minimum can then follow as a result of impacts. These views about quasi-molecules are suggested by the present analysis and the experimental facts. Whether the mercury molecule in its ground state is really in the ($^1S_0 + ^1S_0$) state and whether the vibrational levels now discovered as belonging to the common ground state of the several band systems are really vibrational levels or are only favoured states lying above the level of dissociation in which the formation of a quasi-molecule is more probable than in other positions is an open question. That the absorption in Hg vapour is due to quasi-molecules is shown by the work of Kuhn and Freudenburg.¹⁰ The view here adopted is tentative and is put forward as being suggested by the experimental facts. So little is known at present about molecules kept together by van der Waals forces that no definite conclusion can be reached. The present work seeks to remove the difficulties associated with the 'core' bands and the curves of the ($^1S_0 + ^3P_2$) state, while in the other cases the previous explanation is in its general aspect unaltered but quantitative results are added. An investigation of the nature of the potential curve corresponding to the peculiar behaviour exhibited by the ground state may be expected to lead to a better understanding of the band spectra of mercury; it will also show whether the value 0.25 volt deduced here is really the heat of dissociation of the ground state of the mercury molecule.

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