INTENSITY VARIATIONS OF MERCURY MOLECULAR SPECTRA AND THE ORIGIN OF THE BANDS AT 2482 A.U.†

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Abstract

The origin of the system of bands around 2482 A.U. observed in a mercury lamp has been given evidence as due to mercury molecular ion. Quantitative determination of the intensity variations as a function of pressure and current of the 2482 bands and other band of neutral molecules, shows marked difference between 2482 bands and other bands. All the differences can only be explained on the basis of an ionic origin of the 2482 bands. The excited state of the molecular ion that emits 2482 bands is given evidence as that state resulted from a combination of a normal atomic ion and a neutral atom at the $^3P_1$ excited state.

Introduction

Among the many systems of band spectra of mercury vapor,[1] there is a system around 2482 A.U. whose nature has not been fully studied. Works of Winans[2] and others[3] seemed to indicate that the 2482 A.U. bands are emitted by ionized mercury molecule instead of neutral ones. The arguments in favor of this view were (1) the absence of the spectrum in absorption and flurescence of cooled mercury vapor, (2) the relative enhancement of the bands under high excita-

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[1] W. Finkelnburg, Phys. Zeits. Juli 1933, S. 529.

[2] J. Gibson Winans, Phys. Rev., Vol. 42, p. 800 (1932).

[3] Rayleigh, Proc. Roy. Soc. A, Vol. 137, p. 101 (1930).

tion condition as compared with the neutral molecular bands at 2345 A. U., and (3) the successful interpretation of the structure of the 2482 bands as a sequence of bands seems to disfavor the possibility of a transition between two excited states. Argument one is not conclusive, argument three depends much on the interpretation of the structure and argument two was good but much involved by the complicated nature of a high-frequency electrodeless discharge. Therefore it is very desirable to seek means of a more definite and quantitative kind to study further the problem of the emitter of these bands. With the ionic or neutral nature of the emitter settled, we can then attempt to answer the question as to what are the dissociate products of the emitter.

Method and Experimental

We choose to vary the intensities of the bands concerned by varying the discharge conditions in a controllable way. Radiations emitted by ionic emitter would depend more on the electron and ion concentrations than that of a neutral emitter. And pressure would have a direct and larger effect on the number of neutral mercury excited molecules than on the number of ionic mercury excited molecules. A comparison of the intensity variations of the 2482 bands and any other known bands of neutral mercury molecules could supply data for a semi-quantitative interpretation on the basis of an ionic or neutral emitter hypothesis.

A suitable light source was found to be a hot cathode high pressure mercury arc. In the pressure range of a few millimeter to a few centimeter one can run a discharge with tube current from a few milliamperes to a hundred milliamperes without great change of character of the discharge. Under these conditions the 2482 bands are quite strong. And meantime three systems of bands due to neutral mercury molecules are also present. The two systems of continuous bands at 3300 A. U. and 2540 A. U. associated to the excited state[1] $Hg+Hg'(3P_1)$ have considerable intensity. The system at 2345 A.U. has medium intensity. It is interesting to notice that the continum at 4850 A. U. associated to the $Hg+Hg'$ $(^3P_0)$ excited state[1] is absent. It will come out however by running the discharge at higher pressure, say >180°C saturated vapor, and smaller current. The rest on the plate is entirely the Hg I lines which is significant in showing that the mean electron energy is low and the probability of an atomic ion being excited is small.

Intensities of the different bands are measured simultaneously as a function of tube current and pressure. Intensity marks are put on the same plate by means of a step-diaphragm in front of the slit and a continuous spectrum from hydrogen discharge. Eastman polychrome plates are used to ensure the applicability of this method of intensity measurement.[4] Uni-

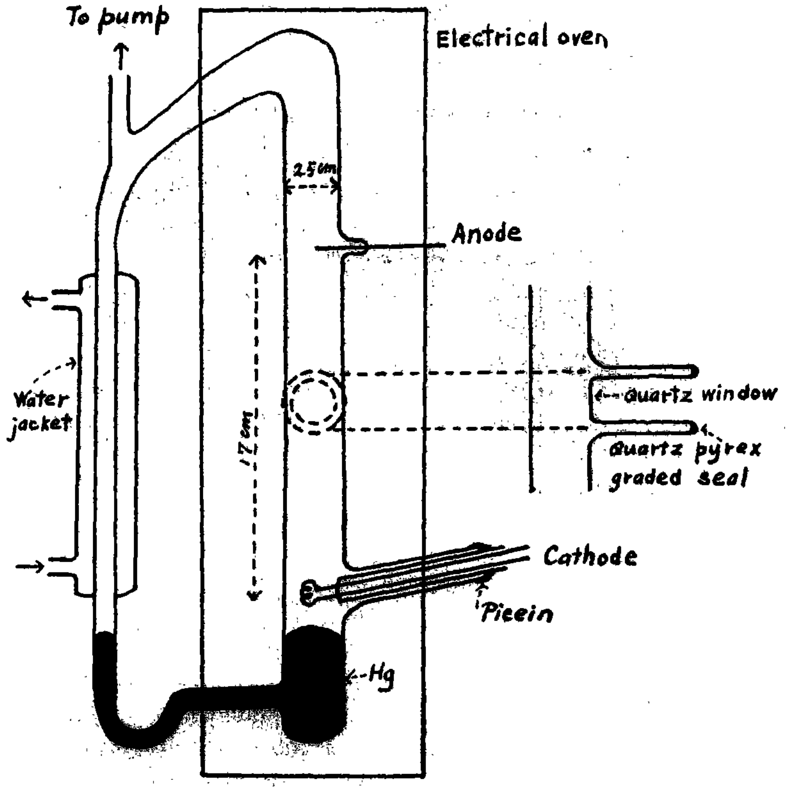

Fig. 1. High pressure Hg discharge tube

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[4] K. B. Thomson and O. S. Duffendack, J. O. S. A. vol. 23, p. 101 (1933).

formity of illumination at the slit is tested to be good by a photograph taken at the slit.

The construction of the discharge tube is self-explanatory in fig. 1. It was developed along with experimenting with a view to obtain a steady discharge in pure mercury. For instance the oven must be built high enough to enclose the upper bending part of the tube in order to avoid minute drops of mercury from falling back into the discharge which will cause flickers in the discharge. Such a small disturbance will cause difficulty in reproducing the intensity measurements. Temperature in the oven is kept as uniform as possible. A thermocouple is put close to the quartz window, and a thermometer is put in the opposite side of the window. During experiment there is always some mercury in the double walls of the graded seal, that serves to maintain the right vapor pressure.

Results and Interpretation

As a typical example we reproduce in fig. 2 a spectrogram with six exposures of varying currents. The relative intensities of the different bands on one plate are evaluated from microphotometer curves. Several plates are taken over a period of several weeks. The values of the relative intensities in arbitral units are given in tables I, and II. The difference in values of one plate to corresponding values on another plate is to be traced to the difference in intensities of the hydrogen spectrum source at different times. Suitable change of unit on the values of one plate or other will enable us to plot the data of all plates on one curve as in fig. III and IV. That the results are reproducible is thus evident.

An examination of the intensity curves as a function of pressure discloses that both 3300 and 2345 bands increases with pressure. This is no doubt due to an increase of molecular formation with increasing pressure. That the 2345 bands increase slower than 3300 may be interpreted as a decrease of $^3P_2$-state excitation as compared to $^3P_1$ state. This is in agreement with the general property of gas discharge that the mean

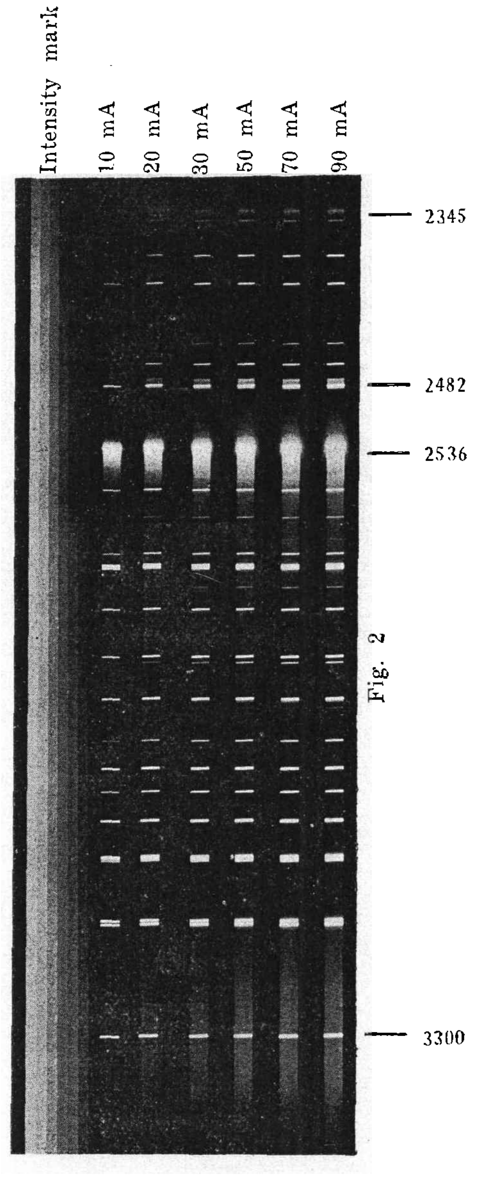
Intensity mark
10 mA
20 mA
30 mA
50 mA
70 mA
90 mA
2345
2482
2536
3300

Fig. 2

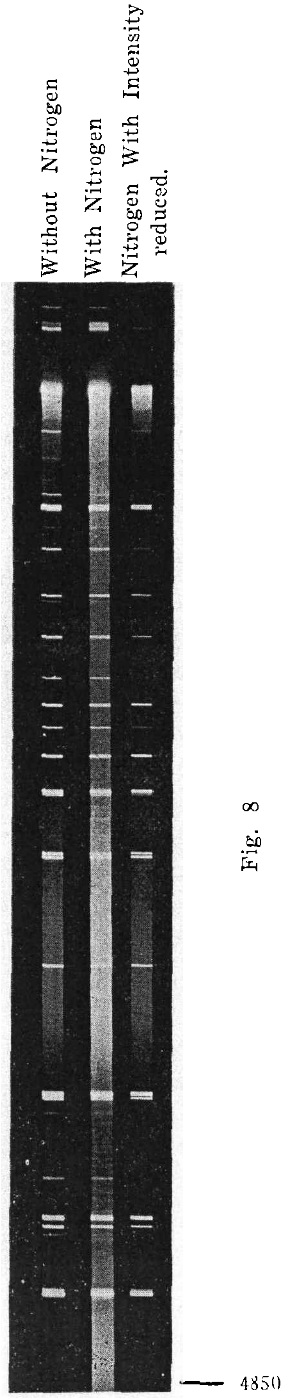
Without Nitrogen
With Nitrogen
Nitrogen With Intensity reduced.
4850

Fig. 8

kinetic energy of electrons decreases with increasing pressure.[5] On the other hand one can see the striking difference between both of these curves and that of 2482 bands. It decreases in the beginning and then remains practically constant over a considerable range of pressure. We therefore have to drop the possibility that the emitter of 2482 bands is the same as that of 3300 band or of 2345 bands. Moreover an assumption of an ionic emitter for 2482 is just suitable for the situation. The ion concentration in the tube must be fairly constant for constant tube current. And it is an observed fact that the lines

TABLE I.

Current Variation

(Temperature at 153°C)

	Plate	Current in MA								
		10	20	30	40	50	60	70	80	90
Intensity of 2482 band.	156	1.26	3.64	5.49		7.94		8.92		9.78
	157	1.27	3.43	5.19		7.08		8.04		8.61
	160	2.02	5.02	7.67		10.3		11.7		12.6
	133	.65	1.04		2.09		2.69			3.16

	Plate	Current in MA								
		10	20	30	40	50	60	70	80	90
Intensity of 3300 band.	156	.97	1.18	1.53		2.16		2.4		2.54
	157	.98	1.37	1.82		2.24		2.48		2.64
	160	.70	.99	1.35		1.82		2.07		2.19
	133	.56	.70		1.02		1.29			1.45

	Plate	Current in MA								
		10	20	30	40	50	60	70	80	90
Intensity of 2345 band.	133	.69	.832		1.04		1.22			1.4
	156	1.2	1.76	2.4		3.17		3.55		3.93
	140	2.58	3.24		4.27		4.79			5.5

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[5] A. v Engel und M. Steenbeck: Elektrische Gasentladungen Zweiter Band p. 86.

TABLE II.

Pressure Variation

For plate 134, temperature varies from 117°C to 201°C. n is the concentration of atoms in arbitral units.

Intensity of 2482 band

n	Plate 134	n	Plate 142	n	Plate 158	n	Plate 159
1.2	3.2	1.3	2.43	1.53	6.03	1.52	9.12
4.8	3.0	3.9	2.29	4.84	7.76	4.84	10.1
9.7	2.5	8.8	2.2	9.69	6.61	9.45	10.0
13.2	2.3	15.2	2.04	16.1	5.96	16.9	9.12
24.4	2.3	24.4	2.04	26.1	5.96	26.1	8.92
39.6	2.3	39.6	2.03	38.7	6.03	38.7	8.92

Intensity of 3300 band

n	Plate 134	n	Plate 142	n	Plate 158	n	Plate 159
1.2	.71	1.3	1.16	1.53	.83	1.53	.78
4.8	1.29	3.9	1.97	4.84	1.52	4.84	1.23
9.7	2.14	8.8	2.88	9.69	2.26	9.45	1.91
13.2	2.51	15.2	4.73	16.1	3.09	16.9	2.66
24.4	3.55	24.4	5.28	26.1	3.81	26.1	3.39
38.6	5.62	39.6	7.76	38.7	4.27	38.7	4.27

Intensity of 2345 band

n	Plate 134	n	Plate 142
1.2	.74	1.3	1.26
4.8	.94	3.9	1.78
9.7	1.13	8.8	2.29
13.2	1.33	15.2	2.54
24.2	1.51	24.4	2.88
39.6	1.8	39.6	3.15

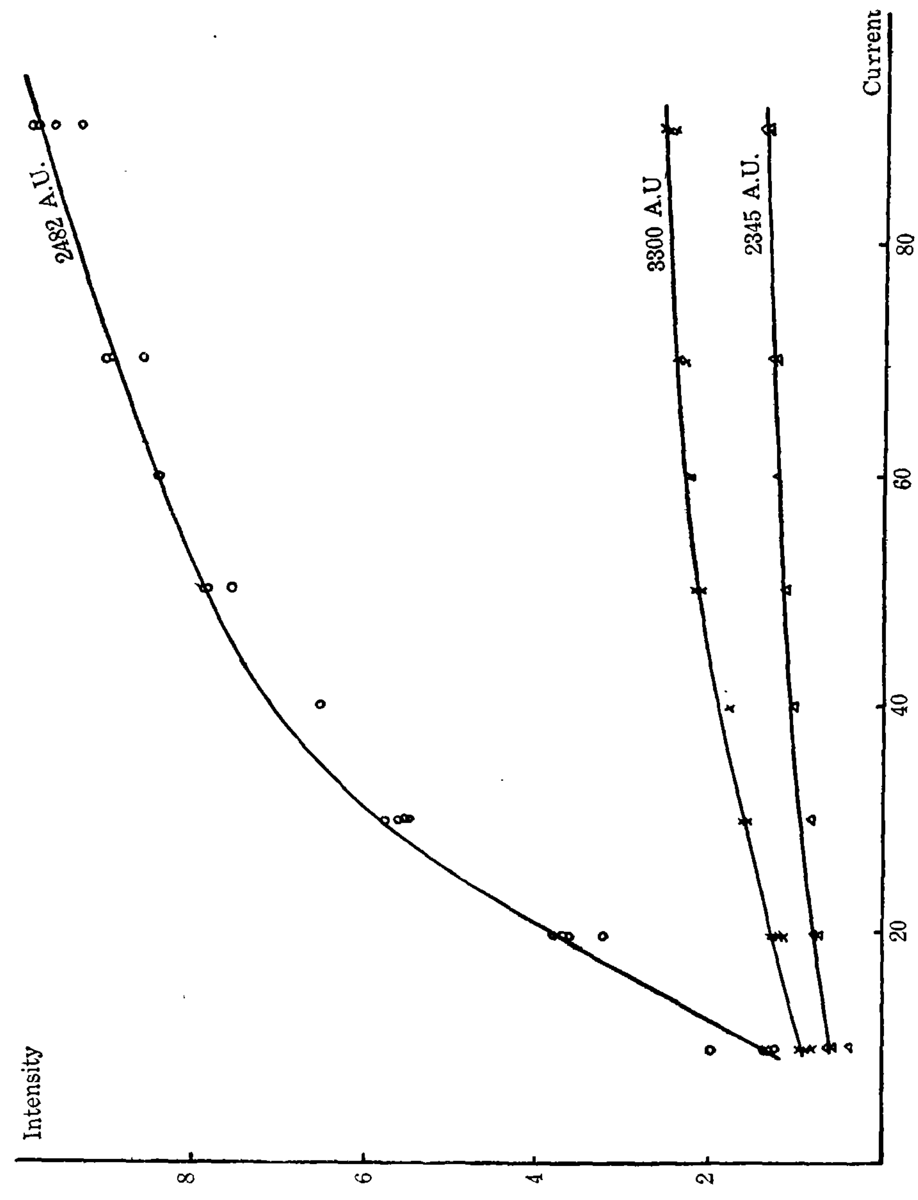

Fig. 3. Intensity current variation curves at temperature 153°C

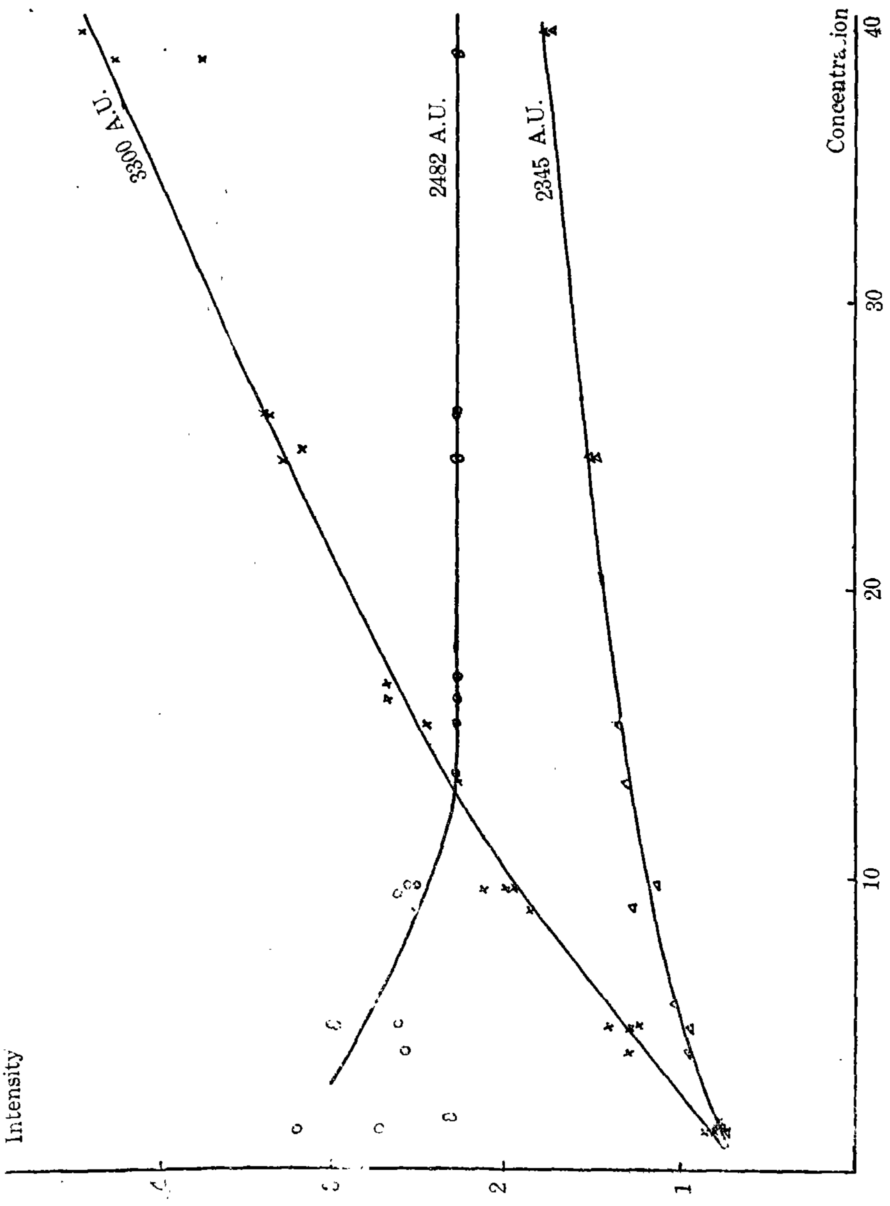

Fig. 4. Intensity concentration variation curves at current 40 ma.

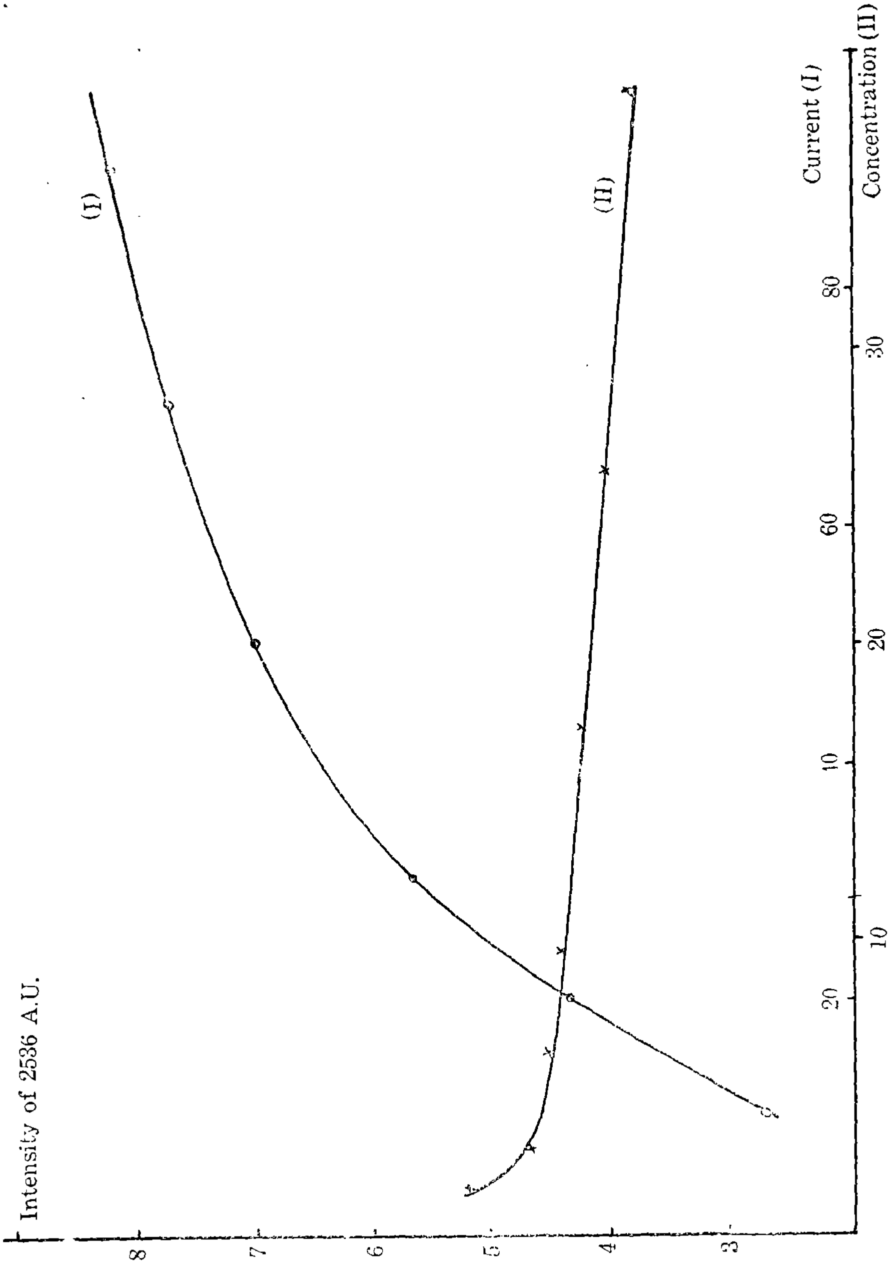

Fig. 5. Variation of Intensity of resonance line

have a general decrease in intensity with increasing pressure which indicates that the number of excited atoms decrease slightly with increasing pressure. An estimate of the decrease of resonance line at 2536 A.U. is shown in figure 5. The intensity curve of 2482 band could therefore be made intelligible on the hypothesis that the excited state of the emitter is a state by uniting an atomic ion and some excited atom, probably the $^3P_1$ state.

The data of the intensity relation with current also support this view. The intensities of both 3300 and 2345 bands have an increase of two to three-fold for current increase of nine-fold. This is of the order of the increase of line intensities. Evidence is given by an estimate of the intensity relation of 2536 line with current as shown in figure 5. The increase of intensity of the 2482 bands amounts to more than eight-fold for the same current increase. This can hardly be explained on the hypothesis of an excited neutral molecule. For the ratio of two excited states will vary from one condition to another only when their effective temperature, which is related to the effective temperature of electron, changes. An increase of the effective temperature would enhance the relative number of states of higher energy and a decrease of effective temperature enhance the relative number of states of lower energy. Our data can neither be explained by an increase nor by a decrease of effective temperature. The 2345 bands requires more energy of excitation than that of 2482 band. But the former is not enhanced relative to 3300 while the latter is very much enhanced. Therefore we have to introduce a new factor to explain the rapid increase of 2482 bands. The union of an ion with an excited atom for the excited state of the 2482 bands seems to be a reasonable choice.

Another possibility that one can think of is neutral molecule excited cumulatively to still higher level with the lower level in one of the excited triplet states. Such a mechanism could account for the rapid increase of intensity with increasing current. But we also find evidence that this is not possible. In an experiment, whose main bearing on our work will be discussed later, we add a few millimeter of pressure of nitrogen to the discharge. The intensity of both 3300 and 2482 are increased. And 3300 is increased more than 2482. This is in strong contrast to the change of intensity by increasing the pressure of mercury itself. In the former case 3300 is enhanced and 2482 weakened. In this case both are increased. And the number of atoms at $^3P_1$ state is found without any change. Since the concentration of the mercury atoms is not changed the increase of intensities of the 3300 and 2345 A.U. bands must be due to an increase of excitation by excited nitrogen molecules. Should the 2482 bands be emitted by a level cumulatively excited, one would expect a much larger increase of intensity for 2482 bands than 3300. That we find it otherwise leads us to discard this possibility. Therefore we are left with the only possible choice of an molecular ion as the emitter.

Nature of the Excited State

Having had so much evidence for the ionic nature of the emitter one naturally asks as to what are the two electronic states between which transitions occur for the production of the bands at 2485 A.U. Take the lower state as the state associated to the union of a neutral atom and an ionized atom both at the ground state (Hg^+ Hg). Then the upper state must have its dissociate products either $Hg'+Hg^+$ or $Hg+Hg^{+\prime}$, where Hg′ and $Hg^{+\prime}$ represent an excited atom and an excited ion respectively. The absence of spark lines on the plate disfavor the second possibility. Moreover the energy difference of the dissociate products of the upper and lower electronic states shall not be much different from 2482 A.U. according to Winans' interpretation of the sequence structure of the 2482 bands. But none of the lowest few excited states of Hg^+ has an energy difference from ground state that is close to 2482 A.U. On the other hand the $^3P_{0,1,2}$ states of Hg are all rather close to the 2482 A.U. energy. This adds support to the view that the dissociate products of the upper state are: Hg and Hg′ (any of the ^3P states). The following calculation will show that $^3P_1$ state is most probable the state of the dissociate atom. And we find some experimental confirmation also.

Referring to fig. 6 we want to calculate X. The following quantities are known from Brozowska's measurements[6] and Winan's designation.[2]

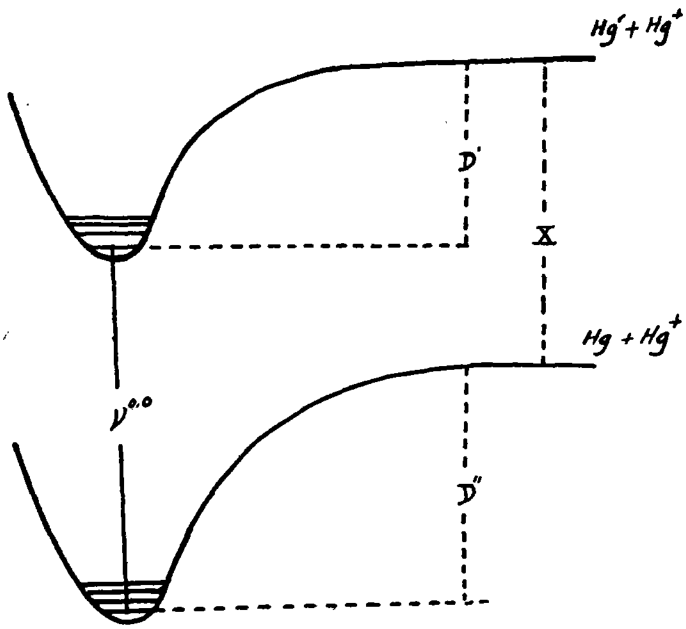

Fig. 6. Potential energy curves

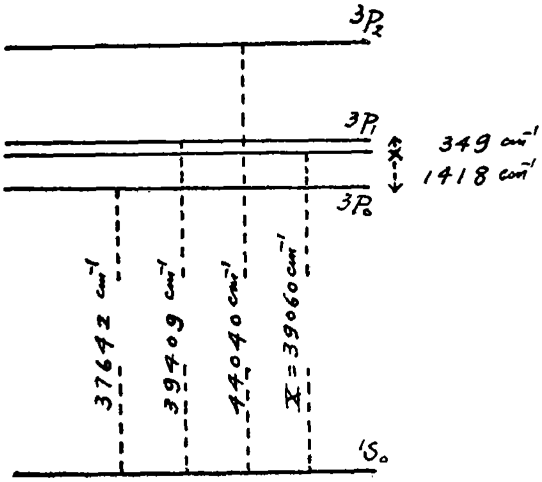

Fig. 7. Energy levels

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[6] J. Brozowska, Zeits. f. physik Vol. 63, p. 577 (1930).

$$\nu^{v'=0\ v''=0}=\nu^{0'0}=40283.92\ \text{cm}^{-1}$$
$$\nu^{1'1}=40292.03\ \text{cm}^{-1}$$
$$\nu^{2'2}=40299.75\ \text{cm}^{-1}$$
$$\nu^{3'0}=40671\quad \text{cm}^{-1}$$

Take the vibrational energy expression to the xw-term we have:

$$\nu^{v'v''}=\nu_e+\left[w'(v'+\tfrac{1}{4})-x'w'\,(v'+\tfrac{1}{2})\right]-\left[w''\,(v''+\tfrac{1}{2})-x'w''(v''+\tfrac{1}{2})\right]$$

So

$$\nu^{1'1}-\nu^{0'0}=w'-w''-2\,(x'w'-x''w'')=8.11\ \text{cm}^{-1} \tag{1}$$
$$\nu^{2'2}-\nu^{1'1}=w'-w''-4\,(x'w'-x''w'')=7.22\ \text{cm}^{-1} \tag{2}$$
$$\nu^{3'0}-\nu^{0'0}=3\,(w'-4x'w')=387\ \text{cm}^{-1} \tag{3}$$

These relations should be rather accurate inspite of the neglect of terms of higher powers of $(v+\frac{1}{2})$ because of the small values of vibrational quantum numbers involved. Solving (1) and (2) we have

$$w'-w''=8.5 \tag{4}$$
$$x'x'-x''w''=.195 \tag{5}$$
$$w'-4\,x'w'=129 \tag{6}$$

We have further the value of D″ calculated in the following way

$$Hg+10.4\ \text{volt}=Hg^{+}$$
$$Hg\,Hg+.07\ \text{volt}[7]=Hg+Hg$$
$$Hg\,Hg+.07+9.5\ \text{volt}[8]=Hg\,Hg^{+}$$
$$Hg\,Hg^{+}+D''=Hg+Hg^{+},$$

Add up these energy equations and cancel out equal things on the two sides we obtain:

$$D''=10.4-9.57+0.7=.9\ \textit{volt or}\ 7295.4\ \text{cm}^{-1}$$

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[7] Heinrich Kuhn, Zeits. f. Physik Vol. 72, p. 462 (1931).

[8] F. G. Houtermans, Zeits. f. Physik Vol. 41, p. 619 (1927).
F. L. Arnotand J. C. Milligan, Proc. Roy. Soc. A, Vol. 153, p. 359 (1936).

But $$D_e'' = \frac{w''^2}{4x'' w''}, \therefore 7295.4 = \frac{w''}{4x''} \qquad (7)$$

Substituting (4) and (5) into (6), we get

$$8.5 + w'' - 4(.195 + x'' w'') = 129$$

$$w'' - 4x'' w'' = 121.3 \qquad (8)$$

Solving (7) and (8) we have

$$x'' w'' = .521$$

$$w'' = 123.4 \text{ cm}^{-1}.$$

$$x' w' = .716$$

$$w' = 131.9 \text{ cm}^{-1}$$

The dissociation energy of the upper state is $D'_e = \frac{w'}{4x'}$

$$\therefore \; D_e^1 = 6075 \text{ cm}^{-1}.$$

The energy difference between the upper and lower electronic state at maximum V is equal to

$$40284 - 7295 + 6075 - 4 = 39060 \text{cm}^{-1}.$$

The energy differences between $^3P_1$ and $^3P_0$ and the ground state are 39409 and 37642 cm^{-1} respectively. The calculated value lies between them and is nearer to $^3P_1$ as shown in fig. 7. This favors $^3P_1$ as a dissociate product of the upper state of the 2482 bands.

This calculation is subject to an error due to the neglect of terms of higher powers of $(v + \frac{1}{2})$ than the second in the vibrational energy expression. Consequently the expression $D_e^1 = \frac{w^2}{4xw}$ may not be accurate. However it is fair to assume that the mercury molecule being a homopolar molecule will have a finite value for v_{max}. And the error in *De* calculated in this way may very well be within twenty per cent. Having allowed this amount of uncertainty we can still conclude that the excited atom of the dissociate products of the upper state is certainly not the $^3P_2$ state.

To decide between $^3P_1$ and $^3P_0$ we did the following experiment. With the tube current and mercury vapor pressure maintained constant we take two exposures one with an addition of a few millimeter of nitrogen and one without. The two spectrograms do not have any difference in the line spectrum. There is however a general change of intensity for all the band spectra. The 4850 A.U. continum increases in intensity from nothing on the plate to a strong blackening. This is what one expects since the effect of nitrogen is to bring molecules and atom at $^3P_1$ state to $^3P_0$ state. All other bands at 3300, 2540, 2482 and 2345 A.U. increase their intensities only moderately. One can get a better impression by taking a third exposure (see fig. 8) under exactly the same condition as the second exposure but using a wire gauze screen to cut the intensities of all light to a suitable fraction. We reduce the intensity of 3300 A.U. to about the same value as that in the first exposure. The intensity of 2482 A.U. is less than the first exposure while the intensity of 4850 A.U. is still a great many times stronger than the first exposure. We can say therefore that an enormous increase of $^3P_0$ state does not have an appreciable influence on the intensity of 2482 bands besides that little increase that can be explained as a general increase due to the collisions with excited nitrogen molecules. Therefore it favors $^3P_1$ state into which one of the atom of the upper molecular state will dissociate.

Conclusions

By a study of the intensity variations the bands of mercury at 2482 A.U. is definitely concluded as of an ionic origin. Its upper state is quite probably a state formed by the union of an ion (Hg^+) at normal state and an excited atom at $^3P_1$ state.

It gives us great pleasure to express here our appreciation of the kindness of Dr. Ny Tsi-Zé of the National Peiping Academy for allowing us to use their microphotometer. And we also want to thank Dr. Yeh Chih-sun of Tsin Hua University for allowing us to use their spectrograph for some period of time.

移動,與電場所成之直線關係, $m^2S—n^2S$ 系線在 σ 偏極面之出現,及嚴翁二氏視察得Na之 $3\,^2S—n\,^2D$ 線之分爲n—2線等現象,從量子力學之微擾理論,加以討論及解釋。

水銀分子光譜的光強和在2482 A.U.的光帶之成因

周同慶　趙廣增

水銀分子在2482 A.U.左右有組光帶,是水銀分子伊洪的還是水銀分子的這問題,我們用光譜强度的測量法解决了。將供作光源的通電管內的電流或水銀氣壓依次的改變,我們發現2482 A.U.光帶的强度的改變和旁的已知的分子光帶絕然不同。那些不同之點只要引用『分子伊洪是2482光帶的原主』這說法,就都明白了我們更進一步問放出2482光帶的是那個高能力階位理論和實驗的結果指示出一個在最低能力階位的原子伊洪 (Hg^+) 和一個在 $3P_1$ 能力階位的原子所結合成的分子伊洪是能放2482光帶的高能力階位。

H^- 之吸收係數

任之恭

本文根據波動力學計算 H^- 之吸收係數若 H^- 吸收較短於 $\lambda=17254$ Å光線時,吾人應得一極寬連續光譜。依本文極簡單計算,其係數大都在 10^{-17} cm² 附近。

單個較差脈壓所發之脈流

陳茂康

代表過渡現象之算式,有一式可名曰單變函數,本