The Origin of the Mercury Bands at 2480A

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The group of eight mercury bands near 2480A was photographed under varied excitation conditions with the purpose of determining their origin. The source was a discharge through mercury vapor produced in a quartz tube through external electrodes by a low-voltage Tesla coil. Five tubes containing distilled mercury and commercial mercury arc lamp showed this group of bands. These bands were weakened by heat along with known mercury bands. The origin is undoubtedly some form of mercury molecule. The most probable forms are Hg_2^+ and Hg_2. Five observations favor Hg_2^+ over Hg_2. (1) These bands have never been observed in fluorescence. (2) The 2476 band is more intense than the 2345 Hg_2 band under strong field excitation but weaker than 2345 under low field excitation. (3) No other bands with properties like those of the 2480 group have been observed in the mercury spectrum and Rayleigh has shown that these bands do not occur in absorption. (4) The bands in this group may be classified as sequences $v'-v''=0\pm1\pm2\pm3$, and a lower limit for D of 0.3 volts estimated. (5) In the $v'-v''=0$ sequence, emission is observed from state $v'=41$ indicating molecules with very high vibrational energy. This energy may be supplied by the electric field if the emitter is an ion but not if it is a neutral molecule.

INTRODUCTION

THE spectrum of a discharge through mercury vapor shows a group of eight bands near 2480A whose origin has been uncertain. These bands are shown in Fig. 1. The most intense band of the group with sharp limits at 2476 and 2482 and a fainter one between 2470 and 2476 were discovered

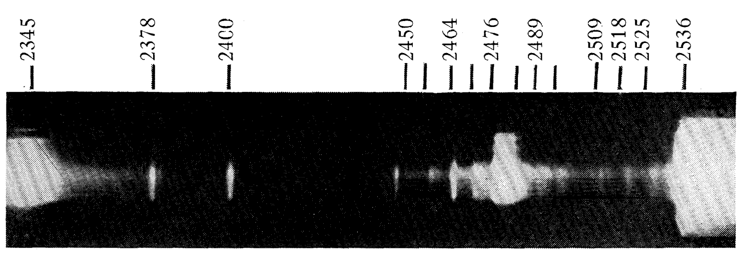


Fig. 1. Mercury bands near 2480A.

by Stark and Wendt[1] who described them as continuous. These bands were observed also by Nagaoka[2] in the light from a special type of mercury arc. Bands will be referred to by their short wave edges. Pienkowski[3] observed some flutings in the 2476 band and Rayleigh[4] showed that the flutings con-

[1] J. Stark and G. Wendt, Phys. Zeits. **14,** 562 (1913).
[2] H. Nagaoka, Japanese Jour. Phys. **1,** 1 (1922).
[3] St. Pienkowski, Bull. de. l. Acad. Pol. 171 (1928).
[4] Rayleigh, Proc. Roy. Soc. **A782,** 349 (1928).

verged toward shorter wave-lengths. Rayleigh also observed that neither 2476 nor 2470 were absorption bands and that 2470 was either continuous or had flutings much more closely spaced than 2476. Condon[5] suggested that 2476 might be a "diffraction band" of Hg_2 and showed that the frequencies of the flutings followed the law of convergence calculated for diffraction bands. The intensities, however, did not decrease exponentially as predicted. Miss Brozowska[6] obtained photographs using a spectrograph of $1A/\text{mm}$ dispersion and showed that the flutings of 2476 converged according to the equation

$$\nu = A + Cm(m + 1)$$

like the lines in the Q branch of a single band. From her photometer record, reproduced in Fig. 2, it is seen that the flutings are broad in the center and double near the long wave side. Miss Brozowska observed three bands in addition to 2476 and 2470 with short wave edges at 2458, 2450, and 2464. The short wave limit for the 2464 band was hidden by a mercury arc line. She suggested HgH as a possible emitter.

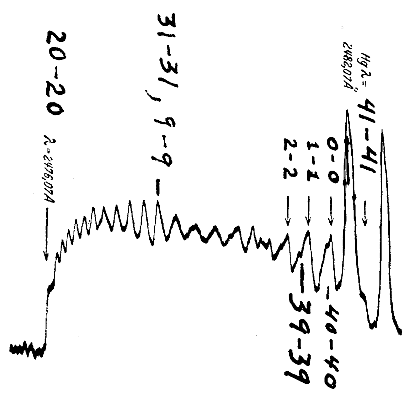


Fig. 2. Flutings of 2476.

These five bands and three new ones were observed by the writer[7] in the spectrum of an electrodeless discharge through mercury vapor. The new bands have short wave edges at 2495.6, 2489.2, and 2482. They are shown in Fig. 1. The edge of the 2482 band was covered by a mercury arc line.

The entire group of eight bands was observed independently by Hamada[8] in the spectrum emitted from the hollow cathode of a discharge tube filled with mercury vapor. He found in addition two new bands whose wave-lengths at the maxima he gives as 2504 and 2513.

In the following experiments this group of bands has been studied under varied excitation conditions with the purpose of determining their origin.

[5] E. U. Condon, Phys. Rev. **32,** 858 (1928).
[6] Miss J. Brozowska, Zeits. f. Physik **63,** 577 (1930).
[7] J. G. Winans, Phys. Rev. **38,** 583 (1931).
[8] H. Hamada, Phil. Mag. **22,** 50 (1931).

Apparatus

The apparatus for these experiments consisted simply of an evacuated quartz tube containing mercury, a low power Tesla coil, and small quartz spectrograph (Hilger E31). Wires were wrapped about each end of the quartz tube, one was grounded and the other was connected to the Tesla coil. The optimum vapor pressure for band emission was maintained by a furnace or by Bunsen burners. In all, five tubes were used, two of which had plane windows and could be viewed end on. Each tube was baked out in a vacuum, a drop of mercury was distilled into it and it was sealed off. The tubes were prepared at different times from different samples of mercury. Sufficient intensity was obtained to photograph the 2476 band in the third order of a 21 foot grating with slit width 0.03 mm and exposure of one week. Exposures with the small quartz spectrograph were made with a very small image of the discharge tube focussed for λ2480 on the slit. In this way the light from different parts of the discharge could be compared with a single exposure.

All five tubes gave the bands shown in Fig. 1 and listed in Table I. The wave-lengths agree with those given by Hamada[8] with the exception of 2518

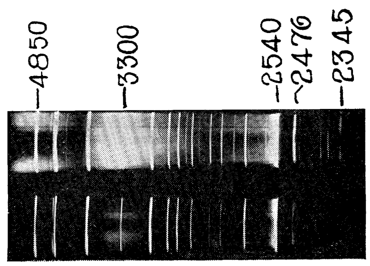


Fig. 3. Effect of heat on mercury bands.

and 2509. Hamada gives 2513 and 2504. He does not list any corresponding to 2525. The discharges also showed a continuous spectrum from 2536 to 2345 with a minimum at 2410. This may be seen in Fig. 1. Some of the tubes gave the HgH bands at 4219, 4017, and 3728 and others did not. The HgH bands when present were emitted only in the neighborhood of the electrodes.

The effect of heat without change in pressure on these bands is shown in Fig. 3 taken while a section of the discharge tube near the center was heated with a blow torch. The central part of the spectrum shows the light emitted by the heated part. Heat was found to weaken the bands at 2495, 2489, 2482, 2476, 2470, 2456 of the 2480 group in addition to the Hg_2 bands with maxima at 4850, 3300, 2650, 2540, and 2345. The others listed in Table I were too weak to be studied in this way. The effect on the 4850 and 3300 bands is the same as that observed in fluorescence.[9] This assures that the weakening is due to heat and not to a change in discharge conditions.[10]

A photometer record of the plate taken on the 21 foot grating verified the structure of 2476 observed by Miss Brozowska and shown in Fig. 2.

[9] H. Niewodniczanski, Zeits. f. Physik **49**, 59 (1928).
[10] J. G. Winans, Phys. Rev. **39**, 745 (1932).

TABLE I.

	Short wave limits A	ν cm^{-1}	$\Delta\nu$	$v'-v''$	Intensity
1	2525.4	39,586			3
			116		
2	2518.0	39,702			3
			136		
3	2509.4	39,838			2
			221		
4	2495.6	40,059		−3	3
			98		
5	2489.5	40,157		−2	4
			121		
6	2482	40,278		−1	5
			97		
7	2476.07	40,375		0	10
			107		
8	2469.5	40,482		1	5
			110		
9	2464	40,572		2	3
			99		
10	2458.0	40,671		3	3
			141		
11	2449.5	40,812			1

To observe these bands under excitation fields of different strength, one set of photographs was made with the Tesla coil disconnected from the discharge tube and operated at different distances from the tube in air. Excitation of the discharge by strong or weak fields could be obtained by changing the distance between the Tesla coil and the discharge tube. Fig. 4, No. 1 shows that for weak fields the 2345 Hg_2 band and the 2536 line are much stronger than the 2476 band. Fig. 4, No. 2 shows that for strong fields 2476 was more intense than 2345.

Fig. 4, Nos. 3 and 4 give a comparison of the spectra from an ordinary mercury arc with that from a high-frequency discharge. Fig. 4, No. 3 is the spectrum of the mercury arc. Fig. 4, No. 4 is the spectrum obtained by shutting off the arc and operating a high-frequency discharge through the arc chamber while it was cooling. No. 4 shows bands while No. 3 does not, although the vapor pressure for No. 3 was greater than that for No. 4. The exposure for No. 3 was about 0.01 that for No. 4.

DISCUSSION

The origin of the group of bands near 2480 can be definitely taken as some form of mercury molecule, since it was observed in six different tubes containing pure mercury in the present experiments and by other experimenters in previous experiments. This is indicated also by the fact that heat, which is known from the experiments of Koernicke,[11] and Kuhn and Freudenberg[12] to reduce the number of mercury molecules causes a weakening of this group of bands along with the mercury bands at 4800, 3300 and 2345. HgH is very unlikely to be the emitter since known HgH bands were found to

[11] E. Koernicke, Zeits. f. Physik **33,** 219 (1925).
[12] H. Kuhn and K. Freudenberg, Zeits f. Physik **76,** 38 (1932).

differ greatly in intensity relative to the 2476 band in different tubes and at different parts of the discharge. The most probable forms of mercury molecule are Hg_2 and ionized Hg_2 (Hg_2^+). Five observations favor Hg_2^+ over Hg_2 as the emitter.

(1) The 2476 mercury band has never been observed in fluorescence. All of the known Hg_2 bands from λ7000–2000 as well as most of the mercury arc lines have been observed in fluorescence with no trace of 2476.[13,14] This indicates that 2476 requires more energy than is available in a fluorescence tube in air, i.e., more energy than that needed for Hg_2 bands and Hg arc lines. This favors Hg_2^+ over Hg_2 as the emitter.

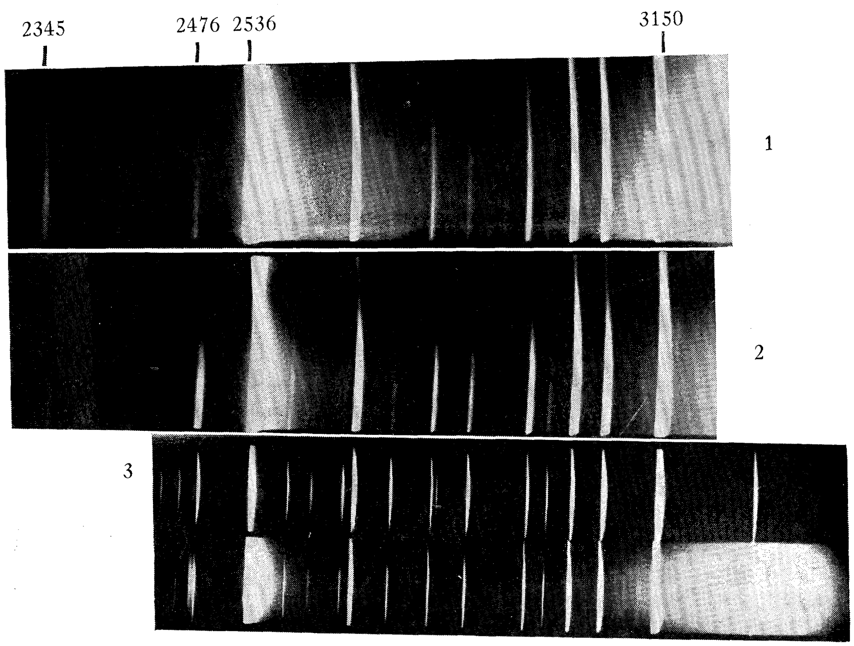


Fig. 4. No. 1 discharge under weak field, No. 2 discharge under strong field, No. 3 mercury arc, No. 4 discharge through mercury arc lamp.

(2) The comparison of intensities of the 2345 Hg_2 band and 2476 under strong and weak field excitation showed that 2476 although of longer wavelength required more energy for excitation than 2345. This also indicates Hg_2^+ instead of Hg_2 as the emitter of 2476.

(3) Rayleigh observed that 2476 is not an absorption band, and no other groups of bands similar to the 2480 group have been observed in the mercury spectrum. If 2476 were due to Hg_2 and not to Hg_2^+ it must be emitted by a transition to a final state which dissociates into one mercury atom in the normal state and one excited to 2^3P_0 or some state of greater energy. The initial molecular state for 2476 would dissociate into one 1^1S atom and an

[13] R. W. Wood and V. Voss, Proc. Roy. Soc. **A119,** 698 (1928).
[14] Rayleigh, Proc. Roy. Soc. **A137,** 101 (1932).

excited atom of 9.7 or more volts energy if D' is approximately equal to D''. The ionization potential of mercury is 10.4 volts. An atomic state of energy greater than 9.7 volts would lie near the series limit and be one of a large number of similar states. Each of these atomic states would be associated with molecular states and we should observe many bands of character like 2476 instead of only one. Since only one is observed, its origin is very unlikely to be Hg_2 or $D'' \ll D'$ for 2476.

(4) The flutings in the 2476 band are too widely spaced to be rotational lines of Hg_2 or Hg_2^+.[15] Each fluting must then represent an unresolved band and each member of the 2480 group a sequence of bands. To account for the sharp short wave edge, 2476 must be a sequence which turns back on itself forming a head of bands like those observed in sodium vapor by Loomis and Nile.[16] This point of view explains the intensity distribution, diffuseness, and doubling of flutings shown in Fig. 2. Near the head of the sequence two bands coincide to give sharp intense flutings, near the center they are separated enough to cause diffuseness, and near the long wave edge they are resolved into one strong and one weak component. If the strongest fluting is taken as band 0–0, the weakest is 41–41. If 2476 is taken as the $v'-v''=0$ sequence, the other bands in the 2480 group may be classified as the sequences $v'-v'' = \pm 1 \pm 2 \pm 3$ as shown in Table I. The narrow wave-length range of these sequences indicates that $r_e'-r_e''$ and, if Bates and Andrews relation holds,[17] $D'-D''$ are small. This strengthens the conclusion from observation (3).

Assuming this classification, a lower limit for D may be estimated. Band $v'-v''=3–0$ falls in the narrow sequence 2458 with wave number about 40670. By substracting from this, the wave number of $v'-v''=0–0$ gives the energy of the third vibration level of the excited molecule as about 380 cm^{-1}. From this $\omega_e' > 125$ cm^{-1}. If ω converges linearly with v' the average separation of vibration levels is >60 cm^{-1}. Since emission is observed from $v'=41$, D must be >2460 cm^{-1} or 0.3 volts.

(5) On the basis of the classification given above, emission by molecules in state $v'=41$ (vibration energy greater than 0.3 volts) is observed. This favors Hg_2^+ over Hg_2 as the emitter since a charged molecule may acquire high vibration energy from it's motion in the electric field. A neutral molecule will possess vibration energy more nearly corresponding to the temperature of the vapor. If $r_e'-r_e''$ is large a neutral molecule might possess high vibrational energy immediately after excitation and emit radiation from that state, but when $r_e'-r_e''$ is small as for 2476, this possibility does not exist.

Each of the five observations discussed indicates that the emitter of the 2480 group of mercury bands is Hg_2^+.

There are several other observations of interest which remain to be explained. They are (1) The 2470 band sequence has no flutings. This may mean that the flutings do not coincide sufficiently well for resolution. (2) The clas-

[15] Assume $r_e = 4A$ and the energy difference between the first two rotational states is 0.005 cm^{-1}. The smallest separation between flutings is 1.5 cm^{-1}.

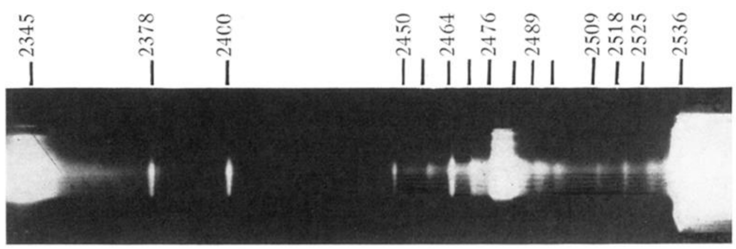
[16] F. W. Loomis and S. W. Nile, Phys. Rev. **32**, 873 (1928).

[17] J. R. Bates and D. H. Andrews, Proc. Nat. Acad. Sci. **14**, 124 (1928).

sification given above accounts for only seven of the eleven bands listed in Table I. Bands 1, 2, and 3 in Table I resemble somewhat bands 7, 8, and 9 and may be another group of sequences of Hg_2^+. (3) There is a continuous spectrum between 2536 and 2345 with a minimum near 2410. The regions between 2536 and 2410 and between 2400 and 2345 fall just beyond the limits for the 2^3P_2 and 2^3P_1 sharp and diffuse series of Hg. The continuous spectrum is probably the recombination spectra associated with these series. (4) The high-frequency discharge gave greater intensity of bands relative to lines than the mercury arc operated at greater pressure. A possible explanation is that collisions with high-velocity ions destroyed Hg_2 molecules in the arc more than in the discharge because of the greater concentration of ions in the arc.

The explanations suggested here for these last four observations need verification by further experiments.

The writer wishes to thank Professor R. S. Mulliken for suggesting the interpretation of the spectrum as a set of band sequences.



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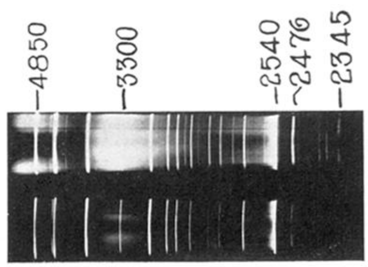
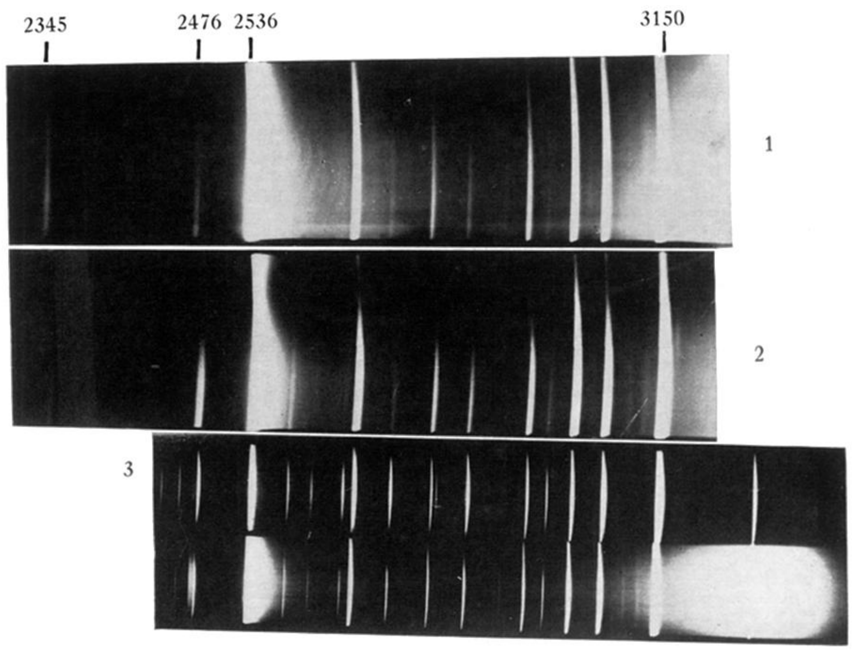


Fig. 3. Effect of heat on mercury bands.



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