Miller, and Sawyer[7] as 189, 244 cm^{-1}. If the two levels $\nu\nu$122,866.03 and 163,180.20 are the $^1P_1$ terms of the configurations $5p^5(^2P_{\frac{1}{2}})6s$ and $5p^5(^2P_{\frac{1}{2}})7s$, respectively, then application of the Rydberg formula gives a value of 202,263 cm^{-1} for the $^1S_0$ term. This new value is preferable since all the terms in the preceding paper are then positive when referred to $^1S_0$.

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[7] O. Laporte, G. R. Miller, and R. A. Sawyer, Phys. Rev. **39**, 458 (1932).

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On the Spectra of Hg II and Hg III

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The structure of many lines of ionized mercury in the region 6000–2200A has been investigated by means of apparatus of high resolving power. Many of the lines have been found to possess complex structure. The structures found are presented in the form of graphs, in which approximate distances and intensities of components are given. In a few cases more exact values of the distances are indicated. From the data collected in Table I and Fig. 2 the isotope shifts in 47 energy levels of Hg II and the hyperfine structure splittings in ten of them have been roughly determined (Table II). The isotope shift and hyperfine splitting are very small for levels of the configuration $5d^{10}nx$ (where nx designates electronic orbits higher than $6s$), and quite considerable for levels of the type $5d^96snx$. In the latter case shifts of about 0.3 cm^{-1} between consecutive even isotopes Hg 200 and 202, and hyperfine splittings amounting to from 0.4 to 1.3 cm^{-1}, have been found. Some levels of the configuration $5d^{10}nx$ show perturbation in the isotope shift; the levels $15°_{3/2}$ and $25°_{5/2}$ reveal a strong perturbation of the same kind. The data collected in Table III, Fig. 3, and Fig. 4 present the results in the cases of lines for which no correct classification seems to be known. They belong, mostly at least, to Hg II, and possibly some of them to Hg III. The results show the necessity of rejecting the existing classification of these lines (Hg II and Hg III) and some of the term values previously given for Hg II by Paschen, by Naude, and by Venkatesachar and Subbaraya. A discussion taking into account also the conditions of excitation reveals many doubts about the correctness of an extension of the analysis of the spectrum of Hg III reported by Johns. The most interesting among the lines studied are lines with isotope shifts which are the highest among all known spectra, and most of which at the same time possess no observable hyperfine structure. Since a discussion shows that probably they do not belong to Hg III, their presence furnishes evidence for the existence of two previously unknown sets of levels in Hg II, belonging to configurations $5d^86s^2nx$ and $5d^9nxn'x'$, by which the presence of a considerable number of hitherto unclassified lines can be understood.

INTRODUCTION AND EXPERIMENTAL

SPECTRA of most of the elements have been investigated for hyperfine structure and isotope shift. Astonishingly enough, the spectra of singly and multiply ionized mercury have not been studied, although the spectrum of neutral mercury has been the object of many studies. Only in the singly ionized mercury spectrum has the structure of a few lines (λ7945; 6150, 4797, 3984, 2848, and 2262) been reported before. This lack of data was undoubtedly connected with the difficulty of obtaining these spectra with high intensity. On the other hand, the study of line structures in these spectra is interesting not only for itself, but is promising also as a means of determining the classification of lines of unknown origin.

The present writer in the spring of 1939 succeeded in obtaining at the Institute of Theoretical Physics, Joseph Pilsudski University, a spectrum of singly ionized mercury of extremely high intensity. The source of light consisted of a hollow cathode discharge tube operated at a very low pressure of helium. The details of the construction of this tube have been described fully in a former paper[1] in which results of other experiments carried out with the same tube have been reported. By using different Fabry-Perot etalons,

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* A great part of the experimental work was done at the Institute of Theoretical Physics, Joseph Pilsudski University, Warsaw (Poland).

[1] S. Mrozowski, Phys. Rev. **58**, 332 (1940).

the structures of a considerable number of lines of Hg II in the region λ6000–2200 were observed. The relative intensities and distances of components in all the lines were hastily and roughly evaluated at the time; because of lack of time, the structure of only three of them, λ2815, 2848, and 3984A, were measured exactly. In view of the considerable interest of the hyperfine structure of a forbidden line of a quadrupole type (λ2815) the results of the analysis of these three lines were published in a separate paper two years ago.[2] This paper contains details concerning the operation of the source and a description of the apparatus used. It should be mentioned that, although completeness in references to former work of other investigators was attempted, a paper by Venkatesachar and Sibaiya[3] was unfortunately overlooked. This omission has been pointed out in a recent letter by Dr. Sibaiya.[4] The relation of the results of Venkatesachar and Sibaiya to mine has recently been discussed.[5]

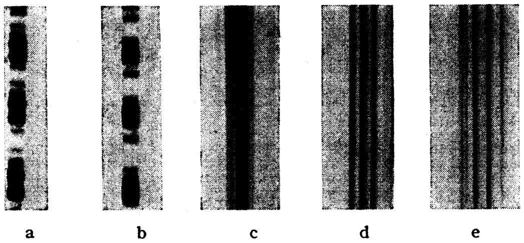

FIG. 1. (a) λ2916.37 Fabry-Perot etalon, 4.2-mm spacer (comp. Fig. 2); (b) λ2935.92 Fabry-Perot etalon, 4.2-mm spacer (comp. Fig. 2); (c) λ3549.42 Second order of 30-foot grating (comp. Fig. 2); (d) λ3090.60 Second order of 30-foot grating (comp. Fig. 4, type B); (e) λ3312.31 Second order of 30-foot grating (comp. Fig. 4, type B*).

At first the publication of all other data obtained for the spectrum of ionized mercury was postponed to the time when exact measurement would be made. But in the meantime a critical analysis, carried out here in Chicago, of the data available at present revealed several points of interest (especially the probable existence of two hitherto unknown sets of levels in Hg II). The exact values of distances of the components (to one percent) are important only for the calculation of the exact energy level separation; all important conclusions concerning the general problems of classification of levels can in this case be obtained just as well from the approximate as from the exact data.[6] The original plates were left at the Institute of Theoretical Physics in Warsaw, and there is little hope that the exact measurements can be carried out in the near future. In view of this situation the author decided to present in this paper all results obtained up to now, although he is fully aware of the incompleteness of this work. In a few cases more exact data have been obtained, and are inserted in the corresponding figures. For the lines λ2916 and λ2936, the measurements were performed on two enlargements made in Warsaw from plates taken with etalons of 4.2 and 7-mm separation (the first one is reproduced in Fig. 1, a and b). A few other lines have been photographed in the first order (λ4797, 5128, and 5210) and in the second order (λ2481, 2572, 2809, 2982, 3091, 3110, 3312, 3385, 3452, 3549, and 3557) of the 30-foot Chicago grating (resolving power in the second order around 300,000). Unfortunately, the relatively low intensity of the source did not

TABLE I. Classified lines of Hg II without structure.

Line	Classification	Width in 10^{-3} cm^{-1}	Line	Classification	Width in 10^{-3} cm^{-1}
2224.71	$6^2P^\circ_{1\frac{1}{2}}-6^2D_{2\frac{1}{2}}$	*D*	3006.57	$6^2D_{2\frac{1}{2}}\ -7^2F^\circ_{3\frac{1}{2}}$	*
2252.78	$6^2P^\circ_{1\frac{1}{2}}-6^2D_{1\frac{1}{2}}$	*D*	3191.03	$7^2P^\circ_{\frac{1}{2}}\ -9^2D_{1\frac{1}{2}}$	*
2260.26	$7^2S_{\frac{1}{2}}\ -6^2P^\circ_{\frac{1}{2}}$	*D*	3277.87	$16^\circ_{3\frac{1}{2}}\ -4_{2\frac{1}{2}}$	*
2339.37	$5^\circ_{4\frac{1}{2}}\ -3_{3\frac{1}{2}}$	~70	3317.30	$7^2P^\circ_{\frac{1}{2}}\ -10^2S_{\frac{1}{2}}$	~120
2345.55	$6^\circ_{1\frac{1}{2}}\ -4_{2\frac{1}{2}}$	*D*	3524.19	$6^2D_{1\frac{1}{2}}\ -6^2F^\circ_{2\frac{1}{2}}$	*
2407.35	$7^\circ_{3\frac{1}{2}}\ -4_{2\frac{1}{2}}$	~70	3605.80	$\left\{\begin{matrix}6^2D_{2\frac{1}{2}} & -6^2F^\circ_{3\frac{1}{2}}\\ 7^2P^\circ_{1\frac{1}{2}} & -9^2D_{2\frac{1}{2}}\end{matrix}\right\}$	*
2414.13	$8^\circ_{2\frac{1}{2}}\ -4_{2\frac{1}{2}}$	~85	3806.38	$7^2P^\circ_{\frac{1}{2}}\ -8^2D_{1\frac{1}{2}}$	*
2514.79	$7^2S_{\frac{1}{2}}\ -9^2P^\circ_{\frac{1}{2}}$	*	4404.86	$5^2F^\circ_{3\frac{1}{2}}\ -9^2G$	~150
2545.33	$11^\circ\ -5_{2\frac{1}{2}}$	*◇	4454.33	$5^2F^\circ_{2\frac{1}{2}}\ -9^2G$	~150
2691.13	$6^2D_{1\frac{1}{2}}\ -8^2F^\circ_{2\frac{1}{2}}$	*	4552.89	$6^2D_{1\frac{1}{2}}\ -8^2P^\circ_{\frac{1}{2}}$	~180
2732.60	$6^2D_{2\frac{1}{2}}\ -8^2F^\circ_{3\frac{1}{2}}$	*	4762.22	$5^2F^\circ_{2\frac{1}{2}}\ -8^2G$	~200
2749.83	$7^2P^\circ_{\frac{1}{2}}\ -11^2D_{1\frac{1}{2}}$	*	5222.81	$5^2F^\circ_{3\frac{1}{2}}\ -7^2G$	⩽80[x]
2788.40	$\left\{\begin{matrix}7^2P^\circ_{\frac{1}{2}} & -12^2S_{\frac{1}{2}}\\ 11^\circ & -4_{2\frac{1}{2}}\end{matrix}\right\}$	*	5677.17	$6^2D_{2\frac{1}{2}}\ -5^2F^\circ_{3\frac{1}{2}}$	†
2909.36	$7^2P^\circ_{\frac{1}{2}}\ -10^2D_{1\frac{1}{2}}$	~130	7944.66	$7^2P^\circ_{\frac{1}{2}}\ -7^2S_{\frac{1}{2}}$	‡
2955.13	$6^2D_{1\frac{1}{2}}\ -7^2F^\circ_{2\frac{1}{2}}$	~180			

D Width equal to the Doppler width.

* Total width of the line $\leq 100\times 10^{-3}$ cm^{-1}. Not investigated with higher resolving power.

† Overlapped with a neighboring line. Width uncertain, studied only with lower resolving power.

‡ Not studied in this work. Data taken from H. Schüler and E. G. Jones, Zeits. f. Physik **76**, 14 (1932). Width not given by them.

[x] On both sides of the line there are wings visible which undoubtedly belong to hyperfine structure. It shows an anomalously great splitting of one of the levels involved in this transition.

◇ Classified by Jones in Hg III as 11 −22°.

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[2] S. Mrozowski, Phys. Rev. **57**, 207 (1940).

[3] B. Venkatesachar and L. Sibaiya, Proc. Ind. Acad. Sci. **1**, 8 (1934). They investigated the lines λ3984, 2848, and 2262.

[4] L. Sibaiya, Phys. Rev. **58**, 925 (1940).

[5] S. Mrozowski, Phys. Rev. **59**, 104 (1941).

[6] These are exact probably to around 5 percent, the errors are certainly smaller than 10 percent.

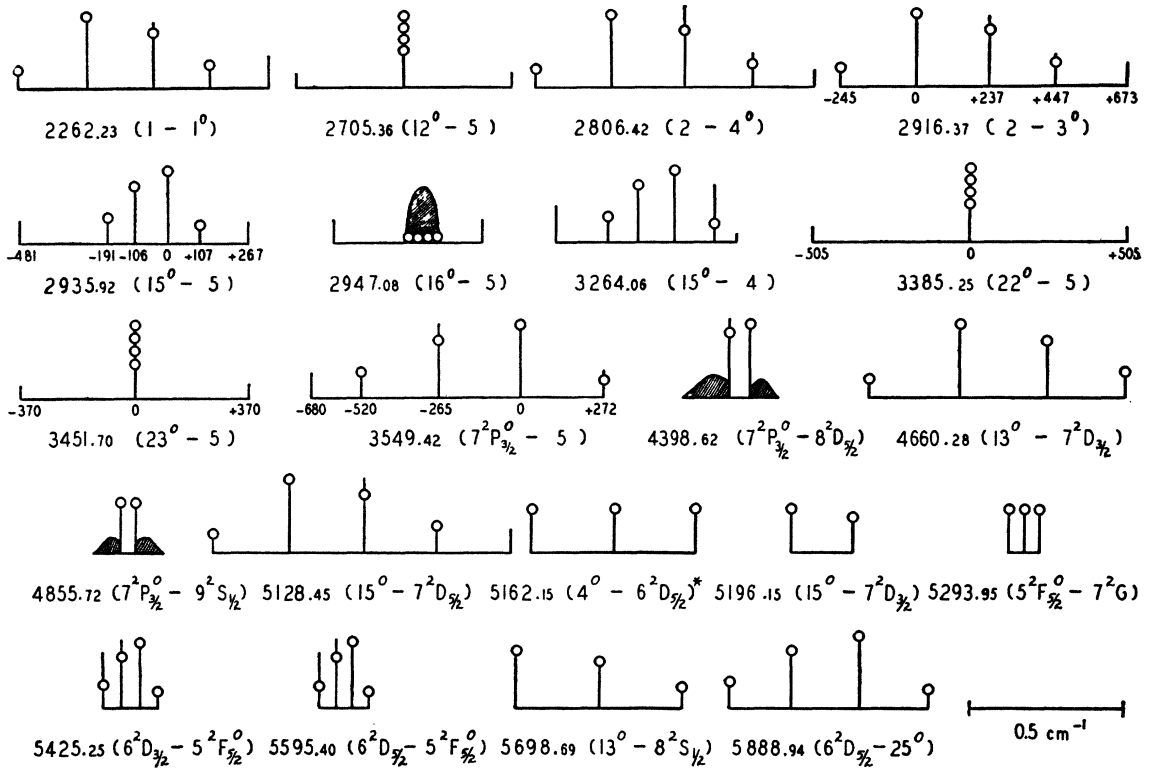

FIG. 2. Structure of classified lines of Hg II. The correlation of components to even isotopes is indicated by circles. The height of lines below the circles corresponds to relative concentration of isotopes $Hg^{198}\sim 10$ percent, $Hg^{200}\sim 24$ percent, $Hg^{202}\sim 29.5$ percent, $Hg^{204}\sim 7$ percent. In cases where the direction of the correlation is not certain, all circles are indicated on the same level. For λ5162.15 only the first of two alternate classifications proposed by McLennan, McLay, and Crawford (reference 8) has been adopted, since the second one $16^\circ - 7^2D_{5/2}$ leads to an isotope shift in $7^2D_{5/2}$ incompatible with the structure of λ5128.45 (see Table II).

permit getting particularly good pictures and extending the investigations to other weaker lines. The reason for the failure of the hollow cathode used here to give intense spectrum was its horizontal position. The presence of the drop of liquid mercury at the end of the cathode axis in the older arrangement[2] seems to make possible the running of the discharge at much lower pressures of helium, thus giving a much brighter spectrum of Hg II. Some of the pictures obtained with the grating are reproduced in Fig. 1.

RESULTS

Structure of Classified Lines of Hg II

In Table I are collected all formerly classified lines found to be single, use of which has been made in determination of the isotope shifts of levels in Hg II (Table II). The classification of the Hg II lines has been taken from the papers by Paschen[7] (the $5d^{10}nx$ set of levels) and by McLennan, McLay, and Crawford[8] (the $5d^96snx$ set of levels and the intercombinations). In Fig. 2 are presented in the form of graphs the structures found for all classified lines; these data have been used in preparation of Table II. In most of the cases the correlation of components to the even isotopes of mercury (198–204) can be found easily by inspection. The odd isotopes (199 and 201) possess in most cases an observable hyperfine splitting; according to the unsymmetrical position of their centers of gravity additional components appear outside of the lightest mercury isotope line (198), the other components being overlapped with the lines belonging to heavier even isotopes. The components belonging to even

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[7] F. Paschen, Ber d. Preuss. Akad. d. Wiss. **32**, 536 (1928).

[8] J. C. McLennan, A. B. McLay, and M. F. Crawford, Proc. Roy. Soc. **134**, 41 (1932).

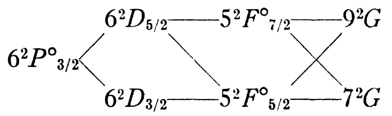
TABLE II. Isotope shifts and hyperfine separations in the levels of Hg II.

Level		Configuration	Isotope shift Hg^{200}–Hg^{202} in 10^{-3} cm^{-1}	H.f.s. Hg^{199} in 10^{-3} cm^{-1}
$6^2S_{\frac{1}{2}}$	0	$6s$	$+226$	$+1358$
$1_{2\frac{1}{2}}$	35514	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}$	$+508$	$+118$
$2_{1\frac{1}{2}}$	50554	$5d^9{}_{1\frac{1}{2}}6s_{\frac{1}{2}}$	$+530$	$+183$
$6^2P^\circ{}_{\frac{1}{2}}$	51485	$6p_{\frac{1}{2}}$	0	
$6^2P^\circ{}_{1\frac{1}{2}}$	60608	$6p_{1\frac{1}{2}}$	assumed 0	$+49$
$1^\circ{}_{2\frac{1}{2}}$	79704	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{\frac{1}{2}}$	$+295$	$\sim +700$
$3^\circ{}_{2\frac{1}{2}}$	84834	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{\frac{1}{2}}$	$+290$	$\sim +780$
$4^\circ{}_{1\frac{1}{2}}$	86177	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{\frac{1}{2}}$	$+290$	$\sim +780$
$5^\circ{}_{4\frac{1}{2}}$	92566?	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{1\frac{1}{2}}$	$\approx +310$ or $+290$*	
$6^\circ{}_{1\frac{1}{2}}$	94091	$5d^9{}_{1\frac{1}{2}}6s_{\frac{1}{2}}6p_{\frac{1}{2}}$	$+310$	
$7^\circ{}_{3\frac{1}{2}}$	95186	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{1\frac{1}{2}}$	$+290$	?
$8^\circ{}_{2\frac{1}{2}}$	95302	$5d^96s6p$	$+285$	?
$7^2S_{\frac{1}{2}}$	95714	$7s_{\frac{1}{2}}$	0	$\sim +320$
11°	100859	$5d^96s6p$	$\sim +300$	
$12^\circ{}_{1\frac{1}{2}}$	103183	$5d^96s6p$	$+290$	$\sim +1150$
$13^\circ{}_{\frac{1}{2}}$	103872	$5d^96s6p$	$+290$	$(\sim 0?)$
$6^2D_{1\frac{1}{2}}$	104983	$6d_{1\frac{1}{2}}$	0	
$6^2D_{2\frac{1}{2}}$	105543	$6d_{2\frac{1}{2}}$	0	
$15^\circ{}_{1\frac{1}{2}}$	106085	$5d^96s6p$	$+190$	~ -400
$16^\circ{}_{3\frac{1}{2}}$	106213	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}6p_{1\frac{1}{2}}$	$+320$	$\sim +880$
$7^2P^\circ{}_{\frac{1}{2}}(19^\circ{}_{\frac{1}{2}})$	108298	$7p_{\frac{1}{2}}$†	~ 0	
$22^\circ{}_{1\frac{1}{2}}$	110603	$5d^96s6p$†	$\sim +295$	$\sim +1300$
$23^\circ{}_{3\frac{1}{2}}$	111172	$5d^96s6p$†	$\sim +295$	$\sim +1120$
$7^2P^\circ{}_{1\frac{1}{2}}(24^\circ{}_{1\frac{1}{2}})$	111970	$7p_{1\frac{1}{2}}$†	$+25$	
$8^2S_{\frac{1}{2}}$	121416	$8s_{\frac{1}{2}}$	$+30$	
$25^\circ{}_{2\frac{1}{2}}$	121959	$5d^96s6p$†	$+220$	$(\sim 0?)$
$5^2F^\circ{}_{3\frac{1}{2}}$	123152	$5f_{3\frac{1}{2}}$	~ 0	
$5^2F^\circ{}_{2\frac{1}{2}}$	123409	$5f_{2\frac{1}{2}}$	$+60$	
$7^2D_{1\frac{1}{2}}$	125324	$7d_{1\frac{1}{2}}$	0	
$7^2D_{2\frac{1}{2}}$	125578	$7d_{2\frac{1}{2}}$	-50	
$8^2P^\circ{}_{\frac{1}{2}}$	126954	$8^2p_{\frac{1}{2}}$	± 50	
$9^2S_{\frac{1}{2}}$	132559	$9^2s_{\frac{1}{2}}$	$+50 \pm 25$	
$6^2F^\circ{}_{3\frac{1}{2}}$	133268	$6f_{3\frac{1}{2}}$	~ 0	
$6^2F^\circ{}_{2\frac{1}{2}}$	133350	$6f_{2\frac{1}{2}}$	~ 0	
$8^2D_{1\frac{1}{2}}$	134562	$8d_{1\frac{1}{2}}$	$\sim\sim 0$	
$8^2D_{2\frac{1}{2}}$	134698	$8d_{2\frac{1}{2}}$	$+90$	
$3_{3\frac{1}{2}}$	135299	$5d^9{}_{2\frac{1}{2}}6s_{\frac{1}{2}}7s_{\frac{1}{2}}$	$\approx +290$ or $+310$*	
$9^2P^\circ{}_{\frac{1}{2}}$	135467	$9p_{\frac{1}{2}}$	0	
$4_{2\frac{1}{2}}$	136712	$5d^96s_{\frac{1}{2}}7s_{\frac{1}{2}}$	$+310$	$\sim +880$
$10^2S_{\frac{1}{2}}$	138434	$10s_{\frac{1}{2}}$	$\sim \pm 30$	
$7^2F^\circ{}_{3\frac{1}{2}}$	138793	$7f_{3\frac{1}{2}}$	~ 0	
$7^2F^\circ{}_{2\frac{1}{2}}$	138812	$7f_{2\frac{1}{2}}$	± 50	
7^2G	139042	$7g$	$+10$	
$9^2D_{1\frac{1}{2}}$	139627	$9d_{1\frac{1}{2}}$	$\sim\sim 0$	
$9^2D_{2\frac{1}{2}}$	139695	$9d_{2\frac{1}{2}}$	$\sim +25$	
$5_{2\frac{1}{2}}$	140135	$5d^96s_{\frac{1}{2}}7s_{\frac{1}{2}}$	$+295$	$\sim +420$
$8^2F^\circ{}_{3\frac{1}{2}}$	142127	$8f_{3\frac{1}{2}}$	~ 0	
$8^2F^\circ{}_{2\frac{1}{2}}$	142131	$8f_{2\frac{1}{2}}$	~ 0	
8^2G	142293	$8g$	0	
$10^2D_{1\frac{1}{2}}$	142660	$10d_{1\frac{1}{2}}$	$\sim \pm 30$	
9^2G	144402	$9g$	± 30	
$11^2D_{1\frac{1}{2}}$	144653	$11d_{1\frac{1}{2}}$	$\sim\sim 0$	

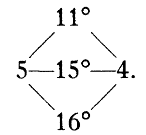
Remarks: All isotope shifts have been determined under the assumption of zero isotope shift for the level $6^2P^\circ{}_{3/2}$. Of the two classifications given for the line λ2788.40 (Table I) only the second one has been adopted, as no traces of the next line in the series $7^2P^\circ{}_{\frac{1}{2}} - 13^2S_{\frac{1}{2}}$ have been observed. Use of both classifications of λ3605.80 has been made, although it is very probable, that only one of them is correct (single structure of this line). The isotope shifts in 5° and 3 have been obtained by assuming for one of these levels a reasonable value of the shift and then calculating for the other level the corresponding shift from the width of the line λ2339.37. Two equally reasonable assumptions can be made (*). The values of hyperfine structure separations in the levels $7^2S_{\frac{1}{2}}$ and 2 have been calculated from the formulas of Goudsmit (reference 10). The latter has been used in evaluation of the splittings in the levels 3° and 4°. The absence of any hyperfine structure in the strong lines λ2407.35 and 2414.13 is rather strange. Therefore in the case of the levels 7° and 8° interrogation marks have been inserted. The absence of hyperfine structure in the lines λ4660.28 and 5888.94 indicates a very small hyperfine separation of the levels 13° and 25°, which seems rather improbable. It seems possible however that the structures observed are incomplete.

isotopes are marked on the top with small circles. For a few weak lines, whose structure has been obtained very incompletely in view of insufficient exposure, the direction of the correlation is not certain, and this uncertainty has been made visible by putting all circles at the same level.

From the data of Table I and Fig. 2 isotope shifts of levels for the isotope 200 relative to 202, and the approximate hyperfine structure separation of levels in the isotope 199 have been determined and are presented in Table II. The level designations and the corresponding electronic configurations are taken from the paper of McLennan, McLay, and Crawford.[8] Data formerly obtained by the author[2] for a few levels in Hg II have been included. For the isotope shifts the level $6^2P^\circ{}_{3/2}$ has been chosen as reference level and its isotope shift has been assumed to be equal to zero. From this level all given levels (with the exception of two levels 5° and 3) can be reached by way of lines observed with instruments of high resolving power. In several cases very good cross checking was possible, as for instance in the case



and



For some lines with uncertain direction of shift (Fig. 2 and broad lines of Table I) the more probable correlation has been chosen, except when the direction of the shift could be determined by cross checking (which was possible for example in the case of the line $16^\circ{}_{7/2} - 5_{5/2}$). In general the possible limits of error probably do not exceed 10 percent; for the levels in which shifts can be obtained in several ways and for intermediate levels the values are a little more reliable. The relative shifts in the levels $6^2S_{\frac{1}{2}}$, $1_{5/2}$, $6^2P^\circ{}_{3/2}$, $7^2S_{\frac{1}{2}}$, $7^2P^\circ{}_{\frac{1}{2}}$, $7^2P^\circ{}_{3/2}$, and $5_{5/2}$ are determined with highest degree of precision. Some values possess a considerable uncertainty due to a

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† Correlation to electronic configuration not given in the paper of McLennan, McLay, and Crawford, reference 8.

possible accumulation of errors. Especially in cases when use has been made of single lines with unknown width (Table I), there is a possibility of a larger error. Such cases are marked with one or two signs ∼ according to the number of such single lines involved in evaluation of the shifts given.

The results are in best agreement with the currently accepted explanation of isotope shifts. These shifts are caused by the differences in the distribution of electric fields in the neighborhood of the nuclei of different isotopes and are proportional to the density of electrons in the immediate vicinity of the nucleus. Therefore the most important contribution to the isotope shift originates from the *s* electrons. The total isotope shifts are quite considerable, but they cannot be determined; since we are only interested in changes produced by the outer electrons we will choose as a reference configuration the configuration of the ground level of Hg III $5d^{10}$. In Hg II then only very small positive shifts are expected for levels belonging to the configuration $5d^{10}nx$, where *nx* designates electronic orbits higher than 6*s*. In Table II a zero shift has been adopted for the level $5d^{10}6p$; this means, that in order to get shifts relative to the configuration $5d^{10}$, a constant positive number Δ has to be added to all values given in Table II. According to the theory, the shift produced by the 7*s* electron (the shifts for 7*s* and 6*p* are equal, see Table II) has to be about 4.2 times smaller than in the case of 6*s* (the ratio has to be equal to $(n'_{\mathrm{eff}}/n''_{\mathrm{eff}})^3$). This means that $(226+\Delta)/\Delta=4.2$ and $\Delta\overset{\frown}{=}70$. This value seems to be quite reasonable, since in this case all negative shifts would disappear from Table II. Köhler[9] claims that in the case of Tl II the relative contributions of the electrons in higher *s* orbits have been shown to be in agreement with theory. This seems to be not well founded, since his statement about the non-influence of the perturbing state $5d^{10}6p^{2}\,{}^1S_0$ is untenable. This state has a considerably smaller isotope shift than the series of states $5d^{10}6sns$ investigated by Köhler ($n=7, 8, 9$), probably around 200 units (10^{-3} cm^{-1}) less, because of the absence of an electron in the 6*s* orbit. The increasing interaction with the term $6p^{2}\,{}^1S_0$ tends to lower the shift in levels $6sns\,{}^1S_0$ with increasing *n*. How a big part of the observed decrease must be ascribed to this perturbation is at present impossible to evaluate, but the investigations of Hg II show (1) that perturbations give rise to considerable changes in isotope shift, which would be entirely sufficient to explain the whole effect found by Köhler; (2) there is no evidence of a $1/n_{\mathrm{eff}}^3$ decrease of shift in the series of levels $5d^{10}ns$ ($n=7, 8, 9, 10$) in Hg II (however the decrease could be masked by increasing effect of possible perturbations by high $5d^9 6snx$ terms). Therefore, since the theoretical proportionality to $1/n_{\mathrm{eff}}^3$ has not yet been checked experimentally in any of the spectra of heavy elements, there is no basis for the assumption $\Delta\overset{\frown}{=}70$ in Hg II. But if the value -50 of the shift found for $7^2D_{5/2}$ is right, at least Δ should not be smaller than $+50$. We therefore adopt the value $\Delta=50$ in the following, with a possible error of ± 30.

For all the levels belonging to the configuration $5d^{10}nx$ shifts ranging from 0 to 140 are obtained. Among them the higher values are probably caused by perturbations, as will be explained below. For most of the levels belonging to the configuration $5d^9 6snx$ the isotope shifts obtained lay in the range 335–370 (two exceptions 15° and 25° are caused probably by perturbations), almost the whole shift is due to the contribution of the 6*s* electron. The increase by around 60 units of the shift caused by the 6*s* electron in comparison with the configuration $5d^{10}6s$ ($226+\Delta=275$) is connected with the absence of one 5*d* electron and a consequent increase of the strength of binding of the 6*s* electron. The two sets of levels $5d^{10}nx$ and $5d^9 6snx$ perturb each other; it is easy to see that the perturbations can only result in an increase of the shift in perturbed $5d^{10}nx$ levels and a corresponding decrease in perturbed $5d^9 6snx$ levels. According to this we understand in principle the occurrence of exceptionally high shifts in some of the $5d^{10}nx$ levels and abnormally low shifts in the levels 15° and 25°. The set of levels $5d^9 6snx$ is known very incompletely, and therefore it is not possible to study these perturbations in detail. In the case of the level 25° the perturbation is probably caused by the level $5^2F_{5/2}$ and vice versa, but the case of the level 15° is obscure, as there are no appropriate levels of the configuration $5d^{10}nx$ in the neighborhood. The relatively high shifts in the levels $6^2P^{\circ}_{3/2,\,1/2}$ are also difficult to understand. The levels $7^2P^{\circ}_{3/2,\,1/2}$ show also relatively high shifts

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[9] P. Köhler, Zeits. f. Physik **113**, 306 (1939).

which are probably caused by perturbation, but this perturbation is by far not as great as predicted by McLennan, McLay, and Crawford[8] and not so great as to make the correlation with the configuration $5d^{10}nx$ doubtful.

The values of the hyperfine structure separations of levels in Table II are far less accurate than the isotope shifts. Both isotopes of mercury 199 and 201 have many hyperfine structure components and only the strongest ones have been obtained on the plates. The adopted method of evaluation of splittings of levels has been the following: It has been assumed that the strong component lying outside of the sequence of the even isotopes at the side of lower masses belongs to the more abundant isotope 199. From the approximate distance of this component from the center of gravity (situated between Hg^{198} and Hg^{200}, very close to the first one), and the separation of one of the levels involved, the separation of the other level could be found. The applicability of the formulas of Hill for relative intensities in a hyperfine structure multiplet had to be assumed. Naturally, such procedure gives only very rough values. The separations in $6^2S_{\frac{1}{2}}$, $1_{5/2}$, and $6^2P^\circ_{3/2}$ were exactly determined and the calculated value for $7^2S_{\frac{1}{2}}$ roughly checked by the author previously.[2] Since the value found for $1_{5/2}$ is exactly equal to the value computed from the formula of Goudsmit,[10] the separation of the level $2_{3/2}$ has been calculated using the same formula. This last value was the starting point for evaluation of splitting in levels 3° and 4°. The hyperfine structure of the perturbed level 15° is inverted, as the structure of the line λ2936 shows; the value of splitting finds a very good check in the chain $7^2P^\circ_{3/2}(\sim 0) \leftrightarrow 5_{5/2}(\sim 420) \leftrightarrow 15^\circ_{3/2}(\sim -400) \leftrightarrow 7^2D_{5/2}(\sim 0)$. It can be hoped that the rough values of hyperfine separations here reported will help to correlate definite j values to different electrons in different levels of the configuration $5d^96snx$.

TABLE III. Unclassified lines of Hg II (or Hg III) without structure.*

2263.64	3315.93[7]	3776.26[14]
2467.62[1]	3358.78[8]	4140.38
2525.98	3402.77[9]	4227.29[15]
2552.87[2]	3420.04[10]	4230.13[16]
2574.86[3]	3492.77[11]	4261.88
2627.90[4]	3532.63	4264.65[17]
2781.93[5]	3606.92	4282.75
2796.13[6]	3630.61	4284.70[18]
2797.43	3638.39[12]	4825.62[19]
2873.24	3684.91	5204.78
2939.03	3774.52[13]	

* Total width of the line $\leqslant 100 \times 10^{-3}$ cm^{-1}, if not stated otherwise in a reference below. Unit for shift and width in references is 10^{-3} cm^{-1}.

[1] Classified by Naudé as $2_{1\frac{1}{2}} - {}^4P_{\frac{1}{2}}$ (expected isotope shift of ∼230 or more). Existence of ${}^4P_{\frac{1}{2}}$ level doubtful (see reference 8).

[2] Classified by Naudé as ${}^4P_{5/2} - {}^4D^2{}_{5/2}$, (expected isotope shift of ∼0), but existence of the level ${}^4D^2{}_{5/2}$ doubtful (see reference 8).

[3] Classified by Naudé as $15^\circ_{1\frac{1}{2}} - {}^4D^3{}_{\frac{1}{2}}$ (expected isotope shift of ∼100 or less). Existence of level ${}^4D^3{}_{\frac{1}{2}}$ doubtful (see reference 8).

[4] Wide line (∼800) without structure. Classified by Paschen as $13^\circ_{\frac{1}{2}} - 11^2S_{\frac{1}{2}}$ (expected total isotope shift ∼300). Level $11^2S_{\frac{1}{2}}$ doubtful (see text below).

[5] Classified by Johns as 13 − 36° of Hg III (expected isotope shift of ∼400).

[6] Classified by Paschen as $13^\circ_{\frac{1}{2}} - 9^2D_{1\frac{1}{2}}$ (expected isotope shift of ∼300).

[7] Total width of ∼300.

[8] Two components in distance of ∼1000. Probably two independent single lines.

[9] Total width of ∼200. Classified by Naudé as $12^\circ_{1\frac{1}{2}} - 9^2S_{\frac{1}{2}}$ (expected isotope shift of ∼230).

[10] Classified by Johns as 84° − 37 of Hg III.

[11] Classified by Naudé as ${}^4F_{\frac{1}{2}} - 6^2D_{2\frac{1}{2}}$ (expected isotope shift ∼300).

[12] Classified by Venkatesachar and Subbaraya as $1^\circ_{2\frac{1}{2}} - {}^2D^3{}_{5/2}$ (expected isotope shift ∼0), but the existence of the level ${}^2D^3{}_{5/2}$ doubtful (see text below).

[13] Classified by Naudé as $2_{1\frac{1}{2}} - {}^4P_{5/2}$ (expected isotope shift ∼230 or more). Existence of level ${}^4P_{5/2}$ doubtful (see reference 8).

[14] Two components in distance of ∼800. Probably two independent single lines. Classified by Paschen and McLennan, McLay, and Crawford as $15^\circ_{1\frac{1}{2}} - 9^2S_{\frac{1}{2}}$ (expected isotope shift ∼140); by Venkatesachar and Subbaraya as $1^\circ_{2\frac{1}{2}} - 6T$ (expected isotope shift ∼300 for a transition $5d^96s6p - 5d^96p^2$).

[15] Classified by Johns as 82° − 34 of Hg III (expected isotope shift ∼0).

[16] Classified by Johns as 82° − 33 of Hg III (expected isotope shift ∼0).

[17] Classified by Johns as 15 − 81° of Hg III (expected isotope shift ∼100).

[18] Classified by Venkatesachar and Subbaraya as $1^\circ_{2\frac{1}{2}} - {}^2D^2{}_{2\frac{1}{2}}$ (expected isotope shift ∼0), but existence of the level ${}^2D^2{}_{2\frac{1}{2}}$ doubtful (see text below).

[19] Total width of ∼120.

Structure of Unclassified Lines of Hg II and Possibly Hg III

In Table III and Figs. 3 and 4 are presented results obtained for all remaining lines studied which have not been classified yet or for which the proposed classification seems to be in error. As can be seen, the results have given for Hg II in general a confirmation of the analysis of Paschen[5] (the $5d^{10}nx$ set of levels) and a very good one of the work of McLennan, McLay, and Crawford.[8] There are only some doubts about the level $11^2S_{\frac{1}{2}}$ (in Paschen's notation 6S), since all three lines observed λ2628, 2974, and 3338 in which this level is involved, are shown to be classified incorrectly. All in all the classification of only 2 lines by McLennan, McLay, and Crawford, and of 11 lines by Paschen has to be discarded. The classification of 9 lines by Naudé[11] has been proven to be incorrect, 6 of them involving levels whose existence has been put into doubt by the work of McLennan, McLay, and Crawford.[8] In

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[10] S. Goudsmit, Phys. Rev. 43, 636 (1933).

[11] S. M. Naudé, Ann. d. Physik 3, 1 (1929).

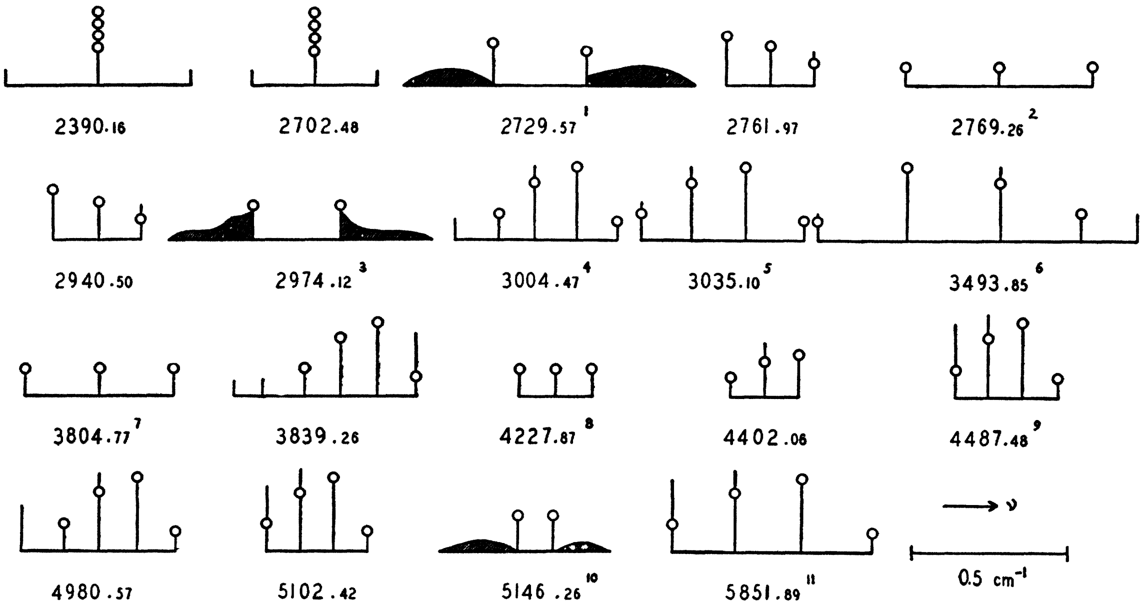

FIG. 3. Structure of unclassified lines of Hg II (possibly partly Hg III). The correlation of components to the even isotopes is marked similarly to the Fig. 2. (1) Classified by Paschen as $15°-10^2D_{5/2}$, the structure found would require an isotope shift in $10^2D_{5/2}$ of ~ -100. (2) If the wave-length of this line is correct the classification of McLennan, McLay, and Crawford as $14°-5$ is untenable (the isotope shift in 14° would be ~ 0). There remains the possibility however, that the structure observed belongs to λ2770.88 (the author was not able to check it once more on the original plate). (3) Classified by Paschen as $7^2P_{\frac{1}{2}}-11^2S_{\frac{1}{2}}$, or $15°-9^2D_{5/2}$, in the first case the line should be single, in the second the isotope shift should be ~ 200 thus considerably smaller than observed. (4) Classified by Naudé as $4°-{}^4D^2{}_{\frac{1}{2}}$, the isotope shift in ${}^4D^2{}_{\frac{1}{2}}$ would be ~ 420, which seems much too high. The existence of the level ${}^4D^2{}_{\frac{1}{2}}$ is doubtful (see reference 8). (5) Classified by Naudé as $7^2P_{3/2}-{}^4D^3{}_{\frac{1}{2}}$, the isotope shift in ${}^4D^3{}_{\frac{1}{2}}$ would be ~ 200, which seems possible, but the existence of the level ${}^4D^3{}_{\frac{1}{2}}$ is doubtful (see reference 8). (6) Classified by Paschen and McLennan, McLay, and Crawford as $15°-8^2D_{5/2}$, but the isotope shift seems to be too big (~ 280 instead of ~ 100). (7) Classified by Naudé as $8^2P-{}^4D^2{}_{3/2}$, the isotope shift in ${}^4D^2{}_{3/2}$ would be $\sim 240 \pm 50$ which seems possible, but the existence of the level ${}^4D^2{}_{3/2}$ is doubtful (see reference 8). (8) Classified by Johns as $81°-33$ in Hg III (expected isotope shift ~ 0). (9) Classified by Venkatesachar and Subbaraya as $1°-{}^2D^3{}_{3/2}$, the isotope shift in ${}^2D^3{}_{3/2}$ would be ~ 410, which seems too high. The existence of the level ${}^2D^3{}_{3/2}$ is doubtful (see text). (10) Classified by Johns as 10–12° in Hg III (expected isotope shift ~ 750). (11) Classified by Paschen as $25°-6^2G$, but the direction of the observed isotope shift is opposite to the expected. Classified by Johns as 21–82° in Hg III (expected isotope shift ~ 0).

view of such good agreement of my data with the results of McLennan, McLay, and Crawford three other lines classified by Naudé,[11] but involving levels in their opinion not well established have been included in Table II and Figs. 3 and 4, although the classification of Naudé is not in disagreement with the structure observed. Several new term values have been reported by Venkatesachar and Subbaraya,[12] but of all of them only one seems to be well established and is included in Table II ($1°_{5/2}$). Their new term ${}^2\bar{D}_{3/2}$ of the configuration $5d^96s6p$, the terms ${}^2D_{3/2}{}^2$, ${}^2D_{5/2}{}^3$ and ${}^2D_{3/2}{}^3$ of $5d^96s7s$, the term ${}^4\bar{P}_{\frac{1}{2}}$ of $5d^96s6d$ and the terms $6T$ and $7T$ of $5d^96p^2$ if correct would possess on the basis of the present results isotope shifts incompatible with shifts expected for such configurations (even taking into account possible large perturbations). The remaining 5 new terms, although one of them would show a reasonably great isotope shift, in view of the very poor agreement of calculated and measured frequencies and of the use of doubtful terms previously reported by Naudé (see above) should also be discarded.

The big number of relatively strong lines of Hg II for which no classification could be found up to now is rather striking. Of all the 132 lines investigated only 54 have been hitherto classified correctly. Among the unclassified lines a whole group of lines has been found (Fig. 4), which in view of their extremely high isotope shift (the biggest shifts till now observed in any spectrum with the exception of H and B II only), cannot be fitted into the two known sets of levels of Hg II.

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[12] B. Venkatesachar and T. S. Subbaraya, Zeits. f. Physik **73**, 412 (1931).

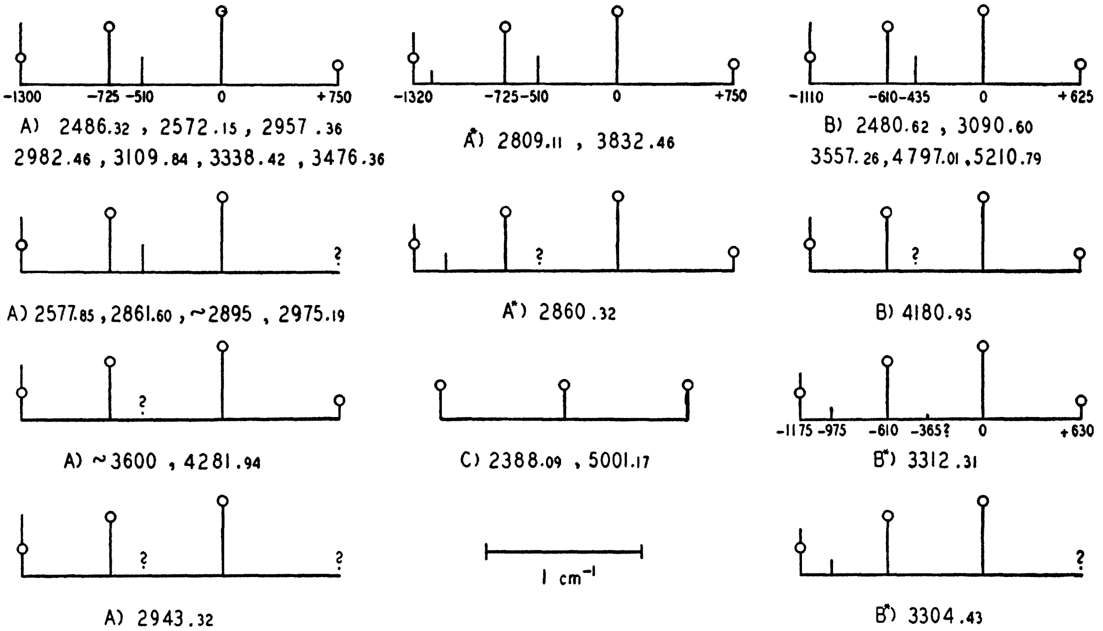

FIG. 4. Structure of unclassified lines, probably belonging to transitions of the type $5d^86s^2nx\rightarrow 5d^96pnx$ in Hg II. The correlation of components to different isotopes is marked similarly to the Fig. 2. All lines fall into three types *A*, *B*, and *C*, according to the magnitude of the isotope shift, the lines with evidence of hyperfine structure splitting are marked by asterisks. In view of the extremely high isotope shift, all previous attempts of classification should be discarded, with the possible exception of the two lines λ3312 and λ3557 classified by Johns in Hg III. λ2388, classified by Johns as 11–23° in Hg III. Expected isotope shift ~400. λ2480 classified by Naudé as $4P_{5/2}-{}^4D^2{}_{3/2}$. Level $^4D^2{}_{3/2}$ is doubtful (see reference 8). λ2957, classified by Naudé as $4P_{5/2}-{}^4D^2{}_{3/2}$. Level $^4D^2{}_{7/2}$ is doubtful (see reference 8). Classified also by Johns as 10−16° in Hg III; expected isotope shift ~400. λ2982 classified by Paschen as $21°-10^2D_{5/2}$, and by Naudé as $^4\bar{D}_{\frac{1}{2}}-5$. This line was not classified by McLennan, McLay, and Crawford, as was erroneously stated in my former paper, reference 2. λ3090, classified by Paschen as $15°-10^2S_{\frac{1}{2}}$. λ3304, classified by Venkatesachar and Subbaraya as $^4F_{7/2}-{}^2D^3{}_{5/2}$. λ3312, classified by Paschen as 15°−A, also by Johns as 1°−13 in Hg III (in the last case expected isotope shift ~700, which seems to be right). λ3338, classified by Paschen as $7^2P_{3/2}-11^2S_{\frac{1}{2}}$. λ3557, classified by Venkatesachar and Subbaraya as $1°-{}^2D^2{}_{3/2}$. Also classified by Johns as 2°−13 in Hg III (in the last case expected isotope shift ~700, which seems to be right). λ3832, classified by Venkatesachar and Subbaraya as $^2D^3{}_{5/2}-6^2F_{7/2}$. λ4281, classified by Venkatesachar and Subbaraya as $^4D_{\frac{1}{2}}-{}^4\bar{P}_{\frac{1}{2}}$. λ5210, classified by Johns as 28−87° in Hg III. Expected isotope shift ~100.

Therefore, the question arises, if they do belong to Hg II at all. All unclassified lines investigated by the author have been reported previously by Naudé[11] and included by him in a table of observed lines of Hg II (with the exception of the two new lines here reported at ~λ2895 and ~λ3600, whose exact wave-length the author, not having the original plates at his disposal, was not able to determine). But since Ellis and Sawyer[13] have shown, that in the case of Tl, higher spark spectra (Tl III and Tl IV) appear weakly in a hollow cathode discharge in He, the appearance of relatively strong higher spark spectra of mercury in the experiments of Naudé and of the author in discharges in pure mercury vapor at very low pressures seems possible.

A few years ago a considerable extension of the analysis of the spectrum of Hg III was published by Johns,[14] where also a part of the lines from the table of Naudé have been included. But of the 13 lines classified by Johns and observed in this work, only 5 have a structure compatible with the type of transition assigned by Johns. Some of the levels involved belong to highly excited levels of Hg III according to Johns, but at the same time several of the stronger lines emitted from lower levels of Hg III are definitely absent in my spectrograms (for instance λ2724.39 6−10° and λ4973.49 6−5°). Many of the lines classified by Johns as $d^8s^2-d^9p$ transitions are not reported by him to possess a wide structure, although extremely high isotope shifts are expected (see

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[13] C. B. Ellis and R. A. Sawyer, Phys. Rev. **49**, 145 (1936).

[14] W. M. Johns, Can. J. Research **15**, 193 (1937).

below). In view of these inconsistencies which cast doubts upon Johns' extension of the term scheme of Hg III it seemed to be interesting to forget Johns' classification for a while and to try to fit at least the lines with extremely high shifts into the level scheme of Hg III independently. From the direction of the isotope shift in these lines (Fig. 4) it is clear that the big shifts belong to the upper levels; these upper levels can belong only to the configuration $5d^8 6s^2$ of Hg III or $5d^8 6s^2 nx$ of Hg II, as can be seen from Table IV, where the approximate isotope shifts for different configurations are collected (configurations involving $5d^7$ are much less probable in the case of the excitation used, see footnote 15). The lower levels of the lines mentioned should have very small isotope shift (around zero) in the case of lines of type *A*, and in the case of lines type *B* these levels should belong to the same type of configuration, but should be perturbed (shift increased by around 115 units). In Hg III the lowest levels of the type, $5d^9 6p$ have been known for a long time and are well established. But trials revealed that no new differences of frequencies could be found among the lines of Fig. 4 which would be equal to the distance of the levels in question ($5d^9 6p$). The only two lines classified by Johns as transitions $5d^8 6s^2 \rightarrow 5d^9 6p$ in Hg III (λ3312 and 3557) emitted according to him from the same upper level (13_2), show a difference in behavior: the first one is fairly intense in a discharge in helium and has been reported by Paschen,[7] the second one is absent in presence of larger amounts of helium, and its intensity increases very rapidly with removal of the helium from the discharge tube (see the table in Naudé's work[11]). All the difficulties mentioned above seem to point out that the lines of Fig. 4 actually belong to Hg II. Their upper levels should belong to the configuration $5d^8 6s^2 nx$.[15] Since transitions to the levels of the configuration $5d^{10} nx$ are forbidden (this being also the reason why they are not broadened by autoionization), their final levels should be of the type $5d^9 6pnx$. This would explain why all attempts to find a classification for these lines failed: Two till now unknown sets of levels in Hg II are involved. In order to extend the analysis of the spectrum of Hg II, to remove the uncertainty concerning the origin of these lines with high isotope shifts and concerning the level scheme of Hg III given by Johns, investigations of the Zeeman effect seem to be necessary. It should be very helpful to re-measure at the same time the wave-lengths of all the lines in question, since the data reported previously seem to be not very accurate.

TABLE IV. Electronic configurations and approximate isotope shifts (in 10^{-3} cm^{-1}) in mercury. The values in parenthesis are extrapolations.

Hg IV	$5d^7 6s^2$	(~1200)	$5d^8 6s$	(~500)	$5d^9$	(~0)
Hg III	$5d^7 6s^2 nx$	(~1200)	$5d^8 6s\ nx$	(~500)	$5d^9 nx$	~0
	$5d^8 6s^2$	~775	$5d^9 6s$	~350	$5d^{10}$	=0 assumed
Hg II	$5d^8 6s^2 nx$	~775	$5d^9 6s\ nx$	~350	$5d^{10} nx$	~0
	$5d^9 6s^2$	~560	$5d^{10} 6s$	~275		
Hg I	$5d^9 6s^2 nx$	~560*	$5d^{10} 6s\ nx$	~275		
	$5d^{10} 6s^2$	~450				

* The isotope shift in such terms has not been investigated, the value given is a prediction.

It is a pleasure to me to take this opportunity to thank Professor C. Bialobrzeski in Warsaw for his great interest in this work.

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[15] The excitation of these levels in the discharge tube proceeds partly by excitation of a $5d$ electron in a metastable Hg$^+$ ion ($5d^9 6s^2$), but the main process is the direct excitation of one $5d$ electron accompanied by the ejection of a second $5d$ electron from the neutral Hg atom. The results of W. Bleakney [Phys. Rev. **35**, 139 (1930)] seem to indicate that the probability of the first process for the probable average velocities of electrons in the low pressure discharge used is about 7 times bigger than for the second process. However, the low concentration of metastable ions makes the second process predominant. The excitation of the states $5d^7 6s^2 nx$ of HgIII or $5d^7 6s^2$ of HgIV, to be of importance, requires electrons of considerably higher velocity which are probably present in this kind of discharge only in very small numbers.