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Multiplet and Hyperfine Structure Analyses of Bi IV. Discussion of Perturbation Effects

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Three hundred and sixty lines of Bi IV, excited in an electrodeless discharge, have been classified. Twenty-seven terms of $6snx$ configurations, four terms of $6p^2$ and six terms of $5d^9\,6s^2\,6p$ have been identified. Evidence of perturbation of $6s5f$ and $6s7p$ by $5d^9\,6s^2\,6p$ and of $6s6d$ by $6p^2$ is presented. The perturbation of $6s6d$ by $6p^2$ in Bi IV and other members of the Hg I sequence is shown to agree qualitatively with Bacher's theory of $sd-p^2$ interactions. The hyperfine structure intervals of many of the terms of Bi IV have been evaluated. They are compared with the theoretical formulae for hyperfine structure separations and shown to be consistent with our multiplet analysis. Anomalous hyperfine structure has been observed in $6s7p_{\frac{1}{2}}$. This is interpreted as a coupling effect due to the approximate equality of the multiplet and hyperfine structure separations of $6s7p_{\frac{1}{2}}$. Goudsmit and Bacher's theory of hyperfine structure perturbations due to a change in coupling is applied to the four hyperfine levels of $6s7p_{\frac{1}{2}}$. Their theory accounts for the observed distribution of these levels and for the appearance of forbidden transitions.

I. Introduction

In 1930 Arvidsson[2] reported the identification of 1317A as the resonance line $6s^2\,{}^1S_0-6s6p\,{}^3P_1{}^\circ$ of Bi IV, and of 1103A as a combination of $6s6p\,{}^3P_1{}^\circ$ with a higher level. Later Smith[3] tentatively classified 873A as the other resonance line $6s^2\,{}^1S_0-6s6p\,{}^1P_1{}^\circ$. Last year in a more complete paper Arvidsson[4] established the above levels ${}^1S_0$, ${}^3P_1{}^\circ$ and ${}^1P_1{}^\circ$ with greater certainty; identified $6s6p\,{}^3P_2{}^\circ$; and established, but did not name, a few higher even terms. He observed large hyperfine structure in some of the lines, and from the triplet splitting of a few of these evaluated the total interval of $6s6p\,{}^3P_1{}^\circ$ as about 12.5 cm^{-1}.

We report here the results of an extensive analysis of Bi IV wave-lengths. We have established many new terms and confirmed all of Arvidsson's terms except one, number "8" in his Table III. This term appears to be unreal, since the excitation of one of the three lines used by him to establish it is too high and the other two have been classified by us in Bi III.[5] We have assigned configurations to all the terms now known and evaluated the hyperfine structure intervals of many of them.

II. Experimental

The experimental data on Bi IV were obtained in the same investigation as that on Bi II and Bi III.[6] The spectra of bismuth were photographed by us in the region 1000A to 10,000A. For the extreme ultraviolet a vacuum grating spectrograph was used. Equipped with a two-meter N.P.L. grating, this spectrograph has an average dispersion of 8.75A per mm. A Hilger El spectrograph with interchangeable quartz and glass optical systems was employed to investigate the near ultraviolet and visible regions; and a Hilger constant deviation spectrograph for the infrared.

The spectra were excited by an electrodeless discharge in bismuth vapor. The source was a quartz tube, one inch in diameter and two feet long, containing metallic bismuth which was vaporized by heating the tube in an electric oven. When the source was used with the vacuum spectrograph one end of the tube was left open and attached directly by a taper to the slit of

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[2] G. Arvidsson, Nature **126**, 565 (1930).

[3] S. Smith, Nature **127**, 855 (1931).

[4] G. Arvidsson, Ann. d. Physik **12**, 787 (1932).

[5] M. F. Crawford and A. B. McLay, Paper on Bi II and III, in press.

[6] J. C. McLennan, A. B. McLay and M. F. Crawford, Proc. Roy. Soc. **A129**, 579 (1930). Also reference 5.

the instrument. The discharge was produced by passing a high frequency oscillating current through an exciting coil of fifty turns wound around the tube. The oscillating circuit consisted of the exciting coil, a capacity of 0.003 mf, and an adjustable spark gap, all in series; and was energized by a 2 kva, 60,000 volt transformer.

The advantages of this type of source are as follows: first, lines of Bi I, II, III, IV, and even Bi V, can be easily excited and differentiated by observing their behavior when the vapor pressure and the exciting circuit are varied; second, the individual components of complex lines are narrow enough to permit hyperfine structure measurements.

A number of plates were taken with the vacuum grating spectrograph, each with a different excitation. The exposures varied from one to six hours depending on the experimental conditions. Inspection of the intensities of a given line on the various plates usually showed very definitely in which ion of bismuth it originated. The same procedure was followed in the investigation of the region above 2000A. The exposures, however, were shorter ranging from fifteen minutes to two hours.

All lines between 1000A and 10,000A were measured. The wave-lengths of prominent carbon, nitrogen, oxygen and mercury lines, which appeared on the plates, served to check the accuracy of our measurements. In general, our wave numbers are reliable to within 1 or 2 cm^{-1}. This accuracy is adequate for the term analysis. The hyperfine separations, however, are much more accurate than the absolute values of the wave numbers.

In addition to our data Arvidsson's[4] wave-lengths from 1486A to 175A and his excitation and intensity estimates have been used and found very satisfactory.

III. Multiplet Structure

The term structure of Bi IV is presented in Table I. The hyperfine structure intervals of many terms are also given. A numerical designation of terms is used. The levels previously established by Arvidsson[4] are included, since most of them are interpreted here for the first time and all are needed for the identification of newly classified lines. The classified wave-lengths of Bi IV are listed in Table II. The wave numbers are as measured; the wave-lengths are given only to facilitate identification of the lines on a spectrogram. Since accurate intensity estimates could not be made because of the large wave-length range involved and the diversity of the line widths, the total intensity of each multiplet term combination is expressed qualitatively only. The relative intensities of the components of each hyperfine structure pattern, however, are more accurate. The values assigned apply within a given pattern only. Since the terms 8°, 9°, 10°, 11°, are hyperfine structure levels of $6s7p_{\frac{1}{2}}$ (see footnote, Table I), their combinations are grouped as a single hyperfine structure pattern.

There is considerable evidence to justify the configuration assignments as they are given in Table I. The mean energies of the configurations and their multiplet separations are consistent with the values predicted by extrapolation from energy levels of Hg I,[4a] Tl II[4b] and Pb III[4a] and of the spectra of the other ions of bismuth. The configuration assignments are also consistent with the hyperfine structure data (see Section V).

There is, however, evidence (see Section IV) of perturbation of a number of terms due to overlapping of configurations. The properties of a term when so perturbed cannot be completely described by a single configuration. However, as most of the perturbed terms show predominantly the characteristics of the configurations assigned to them, we consider the assignments sufficiently significant to warrant their use.

The only even term predicted in the energy range 0 to 270,000 cm^{-1} that has not been identified is $6p_{1\frac{1}{2}}6p_{1\frac{1}{2}}(J=0)$. It is predicted a little higher than 11_2. But its combinations with $2_1°$ and $4_1°$, which should be in the extreme ultraviolet, have not been identified among Arvids-

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[4a] Bacher and Goudsmit, *Atomic Energy States*. Also unpublished data of authors.

[4b] J. C. McLennan, A. B. McLay and M. F. Crawford, Proc. Roy. Soc. **A125**, 570 (1929). S. Smith, Phys. Rev. **35**, 235 (1930). J. C. McLennan and M. F. Crawford, Proc. Roy. Soc. **A132**, 10 (1931).

son's wave-lengths.[4] Its combinations with other known terms are probably beyond 10,000A. The even term designation 12 is reserved for this unidentified term.

Ten odd terms besides those of $6s7p$ have been established in the range 224,000 to 238,000 cm^{-1}. They undoubtedly arise from the $6s5f$ and $5d^9\,6s^2\,6p$ configurations. An unambiguous differentiation of three of these terms, 17_3°, 18_3°, 21_3°, two from $6s5f$ and one from $5d^9_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$, could not be made; hence both configurations are assigned to all three in Table I. The hyperfine structure intervals of 19_2° and 20_4° show that these two are $6s5f$ terms. That the remaining

TABLE I. *Terms of Bi IV.*

Configuration[1]	Term[2]	Value[3] cm^{-1}	Total hfs interval
$6s^2$	1_0	0 [4]	
$6s6p$	1_0°	70963	
	2_1°	75926	12.5±0.5
	3_2°	96423	13. ±3.
	4_1°	114602	
$6p_{\frac{1}{2}}6p_{\frac{1}{2}}$	2_0	166552	
$6s6d$	3_2	184160	2.5±0.5
$6p_{\frac{1}{2}}6p_{1\frac{1}{2}}$	4_1	185014	small
$6s6d$	5_1	197151	−6.2±0.2
$6s7s$	6_1	197446	16.0±0.2
$6s6d$	7_2	197829	7.0±0.5
	8_3	199769	13. ±1.
$6s7s$	9_0	201581	
$6p_{\frac{1}{2}}6p_{1\frac{1}{2}}$	10_2	202434	−2.5±0.5
$6p_{1\frac{1}{2}}6p_{1\frac{1}{2}}$	11_2	217823	small
$5d^9_{1\frac{1}{2}}\,6s^2\,6p_{\frac{1}{2}}$	7_2°	224292	3.0±0.5
$6s7p_{\frac{1}{2}}$ [5]	8°	224584.6	$(F=4\frac{1}{2})$ 15.6±0.1
	9°	224600.2	$(F=3\frac{1}{2})$ 6.8±0.1
	10°	224607.0	$(F=4\frac{1}{2})$ 4.9±0.1
	11°	224611.9	$(F=5\frac{1}{2})$
$5d^9_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$	12_4°	225617	
$5d^9_{1\frac{1}{2}}\,6s^2\,6p_{\frac{1}{2}}$	13_1°	228127	1.5±0.4
$5d^9_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$	14_2°	230637	3. ±1.
$6s7p_{1\frac{1}{2}}$	15_1°	231913	−4.2±0.2
	16_2°	232627	11. ±1.
$5d^9_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$ and $6s5f$	17_3°	233238	small
	18_3°	233955	small
	21_3°	236518 [6]	small
$6s5f$	19_2°	235172	−7. ±1.
	20_4°	235657	13. ±4.[7]
$5d^9_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$	22_1°	237701	−1.5±0.5
$6s8s$	13_1	266674	14.2±0.2
$6s7d$	14_1	267576	−6.4±0.4
	15_2	267856	10. ±1.
$6s8s$	16_0	268191	
$6s7d$	17_3	268690	13. ±1.
	18_2	269758	−6.5±1.

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[1] Evidence for the configuration assignments is discussed in the context.

[2] The numbers 5° and 6° have been reserved for the two terms of $5d^9_{2\frac{1}{2}}\,6s^2\,6p_{\frac{1}{2}}$, as yet unidentified; and 12 for the one unidentified term of the $6p^2$ group.

[3] The value assigned to each term whose hfs splitting has been determined is that of its middle $(F=4\frac{1}{2})$ hfs level. In regard to the values of the $6s7p_{\frac{1}{2}}$ terms see reference 5. Accuracy of term values is about ±2 cm^{-1}.

[4] The value of this term relative to $6s\ ^2S$ of Bi V is about 365,500 cm^{-1}, obtained by applying a Rydberg formula to $6s6d$ 8_3 and $6s7d$ 17_3.

[5] 8°, 9°, 10°, 11°, are the four hfs levels of $6s7p_{\frac{1}{2}}$. Because of perturbation (see Section V) the J's lose their significance and only F values can be assigned to these levels. Their combinations are governed by the Laporte and F selection rules and are independent of the J rule.

[6] This term is not listed in the order of its term value; the usual order has been altered to facilitate grouping.

[7] The partially resolved line patterns involving this term indicate that it has a large total hfs interval.

TABLE II. *Classified wave-lengths.*

Order of Int.	λ I.A. (mean)	Classification	ν cm⁻¹	Relative int. and character of hfs components	Remarks
m	5347	$11_2-21_3^\circ$	18696		
w	5029	$11_2-22_1^\circ$	19877		
w	4509	10_2-8° 10_2-9° 10_2-10° 10_2-11°	22150 65.0 73.0 78.5	1 10 7 10	
m	4342	9_0-8° 9_0-9° 9_0-10° 9_0-11°	23005.3 19.2 26.0 31	— 10 6 —	—strong O II line near this component —red edge of strong Bi II line here
w	4077	$8_3-7_2^\circ$	24523 29	B —	—strong O II line at violet edge
w	4027	8_3-8° 8_3-9° 8_3-10° 8_3-11°	24815 32 37 40	3b 6b 5b 10b	
m	3891	$10_2-13_1^\circ$	25693	b	
s	3868	$8_3-12_4^\circ$	25848	B	
m	3778	$7_2-7_2^\circ$	26464	B	—merged with O II line
m	3766	$9_0-13_1^\circ$	26546		
s	3734	7_2-8° 7_2-9° 7_2-10° 7_2-11°	26756 72 77 80	1b 4b 6b 10b	
m	3724	$6_1-7_2^\circ$	26839 46.5 52.4	10b 6b 5b	—also classified in Bi II
s	3682	6_1-8° $5_1-7_2^\circ$ $6_1-9^\circ, 10^\circ, 11^\circ$	27130.4 39 41.5 46 53 57.4 61.7 66.1 68.3	5 8b 3b 10 8b 6 2 6 4	
s	3643	5_1-8° 5_1-9° 5_1-10° 5_1-11°	27430.3 33.1 36.5 45.9 48.6 52.9 58.7 60.3 63.7	6 8 10 2 3 5 0? 4 2	
w	3545	$10_2-14_2^\circ$	28202	B	
m	3391	$10_2-15_1^\circ$	29479	b	
w	3346	$22_1^\circ-14_1$	29874	B	
m?	3299	$7_2-13_1^\circ$	30296.3 98.3 301	10 8 8B	— classified in Bi II, the patterns of the Bi II and Bi IV lines probably nearly coincide
m	3296	$9_0-15_1^\circ$	30330 32 34	10 9 8	
w	3279	$22_1^\circ-16_0$	30491		
m	3259	$6_1-13_1^\circ$	30672.0 80 86.5	10 8b 8	
m	3245	$10_2-17_3^\circ$	30804	b	
s	3239	$8_3-14_2^\circ$	30865	B	
m	3227	$5_1-13_1^\circ$	30973 76 80	6b 7b 10b	
w	3190	$21_3^\circ-15_2$	31334.3 35.8 37.6 39.8 42.5	5 6 7 8 10	
m	3171	$10_2-18_3^\circ$	31522	b	
m	3118	$22_1^\circ-18_2$	32059	B	
m	3085	$19_2^\circ-14_1$	32404	B	—merged with strong band component
w	3058	$19_2^\circ-15_2$	32678 82 85 88 94	10b 3b 2b 2b 8b	—merged with band component —merged with band component
m	3054	$10_2-19_2^\circ$	32737	B	—also classified in Bi II
m	3047	$7_2-14_2^\circ$	32808	B	
s	3042	$8_3-16_2^\circ$	32860	B	
m	3026	$20_4^\circ-17_3$	33033	B	
s	3012	$6_1-14_2^\circ$	33183.3 90.5 96.1	10b 9b 9b	
w	3007	$21_3^\circ-18_2$	33236.8 39.0 40.9 42.6 44.1	10 8 7 6 5	
m	2987	$8_3-17_3^\circ$	33461.9 64.6 67.0 69.1 70.9 72.5 73.8	10 7 6 6 6 5 4	
m	2985	$5_1-14_2^\circ$	33481.2 85.0 90.0	9b 9b 10b	
m	2949	$18_3^\circ-15_2$	33897.4 99.3 901.2 03.5 06.0	4 5 6 7 10	
s	2936	$16_2^\circ-13_1$	34042 48 52 55	—B 10 4 5b	—also classified in Bi II
s	2933	$7_2-15_1^\circ$ $10_2-21_3^\circ$	34078 85 89	1 10B 0b	
s	2924	$8_3-18_3^\circ$	34179.7 82.4 84.8 86.9 88.8 90.4 91.7	10 7 6 6 6 5 4	
m	2901	$6_1-15_1^\circ$	34455.7 58.0 64.5 68.7 74.0 75.9	10 9 8 8 8 7	
w	2888	$17_3^\circ-15_2$	34615 19.4 22.0	10B 5 8	
m	2875	$15_1^\circ-13_1$ $5_1-15_1^\circ$	34753 59 61 63 65 68.9 71.2	8b 10b 2 9b 8b 3 4	—merged with a band component —merged with a band component
m	2873	$7_2-16_2^\circ$	34800	B	
s	2842	$6_1-16_2^\circ$	35172.4 75.3 79 81.1 85 88.3	2 5 10b 4 10b 3	
m	2838	$16_2^\circ-15_2$	35225	B	
m	2835	$10_2-22_1^\circ$	35266	b	
m	2823	$7_2-17_3^\circ$	35405.6 07.6 09.3 10.8 12.1	10 8 7 6 5	

TABLE II—(*Continued.*)

Order of Int.	λ I.A. (mean)	Classification	ν cm⁻¹	Relative int. and character of hfs components	Remarks
w	2792	$18_3^\circ-18_2$	35799.0 801.3 05	9 6 10B	
s	2786	$8_3-20_4^\circ$	35888	B	
m	2782	$15_1^\circ-15_2$	35934.4 36.2 38.7 41.2 43.9 46.4 49.4	6 2 5 6 7 4 10	—probably not a Bi line —diffuse structure from this line to Bi I line=35954.5
m	2774	$14_2^\circ-13_1$	36033.4 38.4 44.4	9b 9b 10b	
s	2772	$16_2^\circ-17_3$	36061	B	
m	2768	$9_0-22_1^\circ$	36118		
s	2767	$7_2-18_3^\circ$	36122.1 24.3 26.2 27.9 29.4	10 8 7 6 5	
m	2756	$15_1^\circ-16_0$	36275.5 77.4 79.7	6 8 10	
w	2737	$17_3^\circ-18_2$	36520	B	—about five components resolved but too faint to measure
w	2720	$8_3-21_3^\circ$	36751	B	—about seven components resolved but too faint to measure
w	2692	$16_2^\circ-18_2$	37122 28 32 34 36	10B 2b 3b 1 1b	—also classified in Bi II
w	2686	$14_2^\circ-15_2$	37215 17 19 22	6b 5b 6b 10b	
s	2677	$7_2-19_2^\circ$	37335.0 37.2 39.9 41.4 44.9 48	10 4 3 8 8 9B	
m	2650	$6_1-19_2^\circ$	37714.0 25.6 35.4	10B 9B 8B	
m	2642	$15_1^\circ-18_2$	37845	B	—C II line at violet edge
s	2629	$5_1-19_2^\circ$	38020	B	
m	2627	$14_2^\circ-17_3$	38049.6 51.5 52.9 54.3 55.9 58.0 59.0	6b 5 5 6 7 10 2	
w	2593	$13_1^\circ-13_1$	38541 46.8 48.3 55	7 4 4 10	
m	2584	$7_2-21_3^\circ$	38685.0 87.5 89.1 90.9 92.5	10 8 7 6 5	
w	2555	$14_2^\circ-18_2$	39116 18 21 23 25	10b 2b 6b 6b 5b	
w	2545	$4_1-7_2^\circ$	39278	b	
w	2534	$13_1^\circ-14_1$	39444.0 47.5 49.0 51.7	10 4 4 7	
m	2525	4_1-8° 4_1-9° 4_1-10° 4_1-11°	39571.5 86.8 93 99	10 2 — —	 —strong unclassified Bi II line here —strong Bi I line here
m	2516	$13_1^\circ-15_2$	39725.0 26.7 28.6 30.7 33.0	5 4 5 6 10	
w	2507	$7_2-22_1^\circ$	39867.0 69.8 72.4 74.0 75.7	10 8 6 5 5	
w	2495	$13_1^\circ-16_0$	40066	—	—superimposed on faint classified Bi II line
w	2491	$3_2-7_2^\circ$	40132		
m	2483	$6_1-22_1^\circ$	40245.5 54.6 62.0	10 8b 8	
m	2472	3_2-8° 3_2-9° 3_2-10° 3_2-11°	40425.7 42.3 47.9 51.8	2b 10b 7b 9b	
w	2465	$5_1-22_1^\circ$	40546.1 48.5 51.5	8 6b 10	
m	2401	$13_1^\circ-18_2$	41627.3 29.9 32.0 33.9 36	10 6 5 4 4b	
s	2376	$\left.\begin{array}{r}11^\circ\\10^\circ\\9^\circ\end{array}\right]-13_1$	42060.8 62.6 67.6 70.4 73.8 75.2	3 8 5 10 7 9	
		$8^\circ-13_1$	83.2 89.6 97.5	10 9 8	
s	2326	$11^\circ-14_1$	42960.2 63.7	6 5	—band component at red edge
		$10^\circ-14_1$	68.2 71.5	3 7	—might be band line
		$9^\circ-14_1$	75.2 78.2	5 3	
		$8^\circ-14_1$	87.3 90.8 93.7	10 8 6	—band component at red edge —band at violet edge
m	2321	$12_4^\circ-17_3$	43073	B	—structure confused by band components
w	2319	$4_1-13_1^\circ$	43112		
s	2311	$\left.\begin{array}{r}11^\circ\\10^\circ\\9^\circ\end{array}\right]-15_2$	43246 48 49.5 51.1 53 55	6 6 10 7 5 3	
		$8^\circ-15_2$	68.7 70.7 73.0	0 1 2	
w	2295	$7_2^\circ-15_2$	43565	B	—about five components, too faint to measure satisfactorily
m	2293	$11^\circ-16_0$ $10^\circ-16_0$ $9^\circ-16_0$ $8^\circ-16_0$	43580.2 85.0 91.8 608	8 7 10 1	
m	2274	$3_2-13_1^\circ$	43966		
w	2251	$7_2^\circ-17_3$	44399	B	—structure too faint to measure well; stronger line of unknown origin superimposed on red end
—	2214	$11^\circ-18_2$ $10^\circ-18_2$ $9^\circ-18_2$	45145 53 62	— — —	—Hg III line here —Bi II line here —Bi III line here

TABLE II—(*Continued.*)

Order of Int.	λ I.A. (mean)	Classification	ν cm⁻¹	Relative int. and character of hfs components	Remarks
					This Bi IV pattern is either too faint to be observed or masked by the lines indicated
w	2199	$7_2^\circ-18_2$	45465	b	observed only on grating plates; dispersion too small to detect structure
w	2151	$3_2-14_2^\circ$	46476	—	
w	2099	$4_1-16_2^\circ$	47615	b	
m	2093	$3_2-15_1^\circ$	47748.3 52.0 54.8	10b 8b 6b	
	(*vac.*)				
w	1925.0	$4_1^\circ-2_0$	51949		
m	1910.0	$3_2-21_3^\circ$	52357		
w	1867.8	$3_2-22_1^\circ$	53538		
w	1722.9	$2_0-\left[\begin{smallmatrix}9^\circ\\10^\circ\\11^\circ\end{smallmatrix}\right]$	58042	b	—also classified in Bi III
Arv.[1]					
w 2	1437.6	$4_1^\circ-3_2$	69559		
2	1420.2	$4_1^\circ-4_1$	70412		
s 60	1317.0	$1_0-2_1^\circ$	75920 25.8 32.9	20 20 20	
3	1211.4	$4_1^\circ-5_1$	82548		
1	1207.1	$4_1^\circ-6_1$	82836.1 43.7 54.0	0 0 1	
0	1201.5	$4_1^\circ-7_2$	83228	b	
w 7	1149.7	$4_1^\circ-9_0$	86980		
m 6	1139.8	$3_2^\circ-3_2$	87737	b	
6	1138.6	$4_1^\circ-10_2$	87830		
w 7	1128.8	$3_2^\circ-4_1$	88591	b	
s 24	1103.4	$2_1^\circ-2_0$	90620.0 27.1 32.5	8 8 8	
2	992.8	$3_2^\circ-5_1$	100718 100737	1 1	
8	989.8	$3_2^\circ-6_1$	101027		
5	986.1	$3_2^\circ-7_2$	101408		
8	968.8	$4_1^\circ-11_2$	103222		
9	967.6	$3_2^\circ-8_3$	103349		
15	943.3	$3_2^\circ-10_2$	106002.9 09.2 15.0	5 5 5	number of components questioned by Arvidsson
12	923.9	$2_1^\circ-3_2$	108231.2 36.8 41.4	4 4 4	
9	916.7	$2_1^\circ-4_1$	109081.9 89.3 94.2	3 3 3	
8	876.8	$1_0^\circ-4_1$	114051		
15	872.6	$1_0-4_1^\circ$	114600		
12	824.9	$2_1^\circ-5_1$	121217.2 30.4	6 6	
4	823.7	$3_2^\circ-11_2$	121399	b	
9	822.9	$2_1^\circ-6_1$	121512.5 20.0 26.1	3 3 3	number of components questioned by Arvidsson
10	820.3	$2_1^\circ-7_2$	121899	b	
1	795.8	$2_1^\circ-9_0$	125653		
8	792.5	$1_0^\circ-5_1$	126188		
6	790.6	$1_0^\circ-6_1$	126476.9 82.8 91.6	2 2 2	
6	790.5	$2_1^\circ-10_2$	126500.4 07.8 14.2	2 2 2	
1	704.7	$2_1^\circ-11_2$	141898		
1	651.1	$4_1^\circ-16_0$	153591		
2	644.5	$4_1^\circ-18_2$	155159		
3	587.4	$3_2^\circ-13_1$	170253		
3	580.5	$3_2^\circ-17_3$	172265		
2	524.2	$2_1^\circ-13_1$	190752		
2	521.0	$2_1^\circ-15_2$	191935		
2	508.6	$1_0^\circ-14_1$	196607		
5	445.2	$1_0-\left[\begin{smallmatrix}9^\circ\\10^\circ\\11^\circ\end{smallmatrix}\right]$	224607		
5	438.3	$1_0-13_1^\circ$	228130		
6	431.2	$1_0-15_1^\circ$	231911		
6	420.7	$1_0-22_1^\circ$	237701		

b, Broad. s, strong. m, medium. w, weak.
B, Very broad; hfs partially resolved but difficult to measure.
[1] Data from G. Arvidsson's paper, Ann. d. Physik 12, 787 (1932).

five and one of 17_3°, 18_3°, 21_3°, are the six terms of the (jj) sub-groups $5d^9{}_{1\frac{1}{2}}\,6s^2\,6p_{\frac{1}{2}}$ and $5d^9{}_{2\frac{1}{2}}\,6s^2\,6p_{1\frac{1}{2}}$, is evident from their relative distribution and their J values. The differentiation of each sub-group is based on a comparison with the corresponding terms of the very similar $5d^9\,6p$ configurations of the Pt I sequence unambiguously interpreted by Mack[7] on the basis of near (jj) coupling.

We have not been able to identify the terms of the lowest and the highest (jj) sub-group of $5d^9\,6s^2\,6p$. The approximate positions of these are estimated at about 205,000 cm^{-1} and 250,000 cm^{-1}, respectively. Thus most of the combinations of the two terms of the lowest sub-group with $6s6d$, $6s7s$, and $6p^2$ terms are probably in the red beyond the range of the available data, and their combinations with known higher even terms are probably weak. Combinations of the four terms of the highest sub-group with known even terms are probably weak. The numeral designations 5° and 6° are reserved for the two terms ($J=2$, 3) of the deepest sub-group since they are predicted among known terms. The terms of the highest sub-group are predicted above any known odd terms.

The multiplet structures of the various configurations are described and their special features indicated in the following.

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[7] J. E. Mack, Phys. Rev. 34, 17 (1929). Also a private communication.

(1) $6s6p$—The order of the J values is as predicted by simple theory; the energy distribution of the terms is consistent with Houston's equations[8] and characteristic of intermediate coupling.

(2) $6s6d$—The order of the J values is abnormal; one term 4_2 is below the other three which are in the order of their J values. This abnormality is also found in $6s6d$ and $6s7d$ of Hg I and Tl II and in $6s6d$ of Pb III and in many *sd* configurations of lighter elements; it is discussed more fully in Section IV.

(3) $6s7p$—The hyperfine structure intervals of the terms indicate near (*jj*) coupling, and their relative distribution except for two minor deviations is also consistent with this coupling. The $6s7p_{\frac{1}{2}}$ terms are almost coincident but it is doubtful if the coupling is as complete as the coincidence indicates. In all probability a small term perturbation effect is also involved (see Section IV). The $6s7p_{1\frac{1}{2}}$ terms are close together as expected; but are inverted, due undoubtedly to perturbation by adjacent terms (see Section IV).

(4) $6s7d$—The discussion in (1) applies to this configuration and also to $6s7d$ of Pb III. This is in contrast to $6s7d$ of Hg I and Tl II (see (2) above).

(5) $6s5f$—The distribution of terms is abnormal regardless of the ambiguity of its $J=3$ terms. If 21_3° is chosen as one of these and either 17_3° or 18_3° as the other, the distribution is very similar to that in $6s5f$ of Tl II and Pb III. The abnormal distribution is undoubtedly due to perturbation effects (see Section IV).

(6) $5d^9\,6s^2\,6p$—The distribution of the terms, which has already been discussed, shows that the coupling is near (*jj*).

(7) $6p^2$—The mean energies of the sub-groups indicate an approach to (*jj*) coupling, but the separation between the two terms 4_1 and 10_2 of $6p_{\frac{1}{2}}6p_{1\frac{1}{2}}$ is larger than expected for (*jj*) coupling. The large separation can be explained as a perturbation effect (see Section IV).

IV. Multiplet Perturbations

It is significant that $6s6p$ and $6s7d$ terms which are comparatively isolated show normal distributions, whereas $6s7p$, $6s5f$ and $6s6d$ terms, of which the first two overlap $5d^9\,6s^2\,6p$ and the third overlaps $6p^2$ and $6s7s$, show abnormal distributions. It is probable that the abnormalities are due to perturbations of the type suggested by Bacher.[9]

The interaction of $5d^9\,6s^2\,6p$ with $6s7p$ and $6s5f$ is sufficient to account qualitatively for the observed perturbations in these configurations. The unusually small separation between the $6s7p_{\frac{1}{2}}$ states can be explained as due to the perturbing effect of 13_1°; the inversion of the $6s7p_{1\frac{1}{2}}$ terms as due to the mutual perturbation of 13_1°, 15_1° and 22_1°, and of 14_2° and 16_2°; and the abnormal distribution of the $6s5f$ terms as due to mutual perturbation of 17_3°, 18_3°, and 21_3°. The perturbation effects are less noticeable in the $5d^9\,6s^2\,6p$ terms than in the $6s7p$ and $6s5f$ terms, since the $5d^9$ and $6p$ doublet intervals are much larger than the $7p$ and $5f$ intervals.

Since the $5d^9\,6s^2\,6p$ terms of Hg I, Tl II, and Pb III are not as well known as those of Bi IV, we cannot trace their effect on the $6s7p$ and $6s5f$ terms as the relative separations of the groups change with ionization and nuclear charge.

The interaction of $6p^2$ with $6s6d$, which is expected to be large according to Bacher,[9] qualitatively explains the abnormal distribution of the $6s6d$ terms of Bi IV and the other members of the Hg I sequence. Sufficient data on the $6p^2$ and $6s6d$ terms of these spectra are available to compare their relative energies. They are tabulated in Table III. Only the $J=2$ terms of $6p^2$ are given, since they represent approximately the c.g. of the whole group and are mainly responsible for the perturbation of $6s6d$. Mutual perturbation of the $J=1$ terms of the two configurations is not immediately evident. One of the $6s6d$ terms with $J=2$ is for all the cases considered within the relatively narrow so-called triplet, and its displacement from the normal position is not large compared to the variation in the separation of the other $J=2$ term from the triplet. Accordingly, for this qualitative comparison the triplet is represented by its normal c.g. (calculated from the total triplet separation by the (LS) interval rule) which is

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[8] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[9] R. F. Bacher, Phys. Rev. **43**, 264 (1933).

TABLE III. *Relative energies of sd, p^2 configurations of Hg I sequence.*

Level		Hg I†	Tl II†	Pb III†	Bi IV
$6s7d$ —	normal c.g. of $J=1, 2, 3$	5718	21540	43436	69522
	$J=2$	5671	20337	44950*	71036
$6p_{1\frac{1}{2}}6p_{1\frac{1}{2}}$ $J=2$		——	18774	20082*	19101
$6p_{\frac{1}{2}}6p_{1\frac{1}{2}}$ $J=2$		23233*	12263	6468	3712
$6s6d$ —	normal c.g. of $J=1, 2, 3$	0	0	0	0
	$J=2$	-60	-1394	-6466	-14562

* Unpublished data of authors.

† Data from Bacher and Goudsmit *Atomic Energy States.*

taken as the datum level in Table III. The $6s7d$ configurations are also included for comparison.

With increasing ionization $6p^2$ drops from above $6s7d$ in Hg I to just above $6s6d$ in Bi IV. As the $6p^2$ configuration approaches $6s6d$, the $J=2$ term of the latter diverges much more rapidly from the c.g. of the other three than normally expected for increasing ionization. The unusually rapid divergence is undoubtedly due to the interaction of the $6s6d$ and $6p^2$ configurations. The order of magnitude and the direction of the effect are as predicted by Bacher's treatment of $sd-p^2$ interactions,[9] thus qualitatively confirming his theory. The presence of this effect accounts for the fact that the $6s6d$ intervals are not consistent with Houston's[8] equations.

In Pb III and Bi IV $6p^2$ is relatively remote from $6s7d$, and as expected the $6s7d$ terms in both spectra are in normal order and agree with Houston's equations. In Hg I and Tl II there is probably some interaction of $6p^2$ and $6s7d$, since the order of the latter terms is abnormal. Houston has shown that the $6s7d$ terms of Hg I deviate somewhat from his predictions. The corresponding terms of Tl II according to our calculations fit fairly well with a negative value of X; but their hyperfine structures[10] indicate some perturbation of the $J=2$ terms. It is, however, difficult to draw any definite conclusions about the significance of the observed distribution of the $6s7d$ terms of Hg I and Tl II, since there is a possibility of perturbation by other configurations in addition to $6p^2$.

In Bi IV there is a possibility of interchanging the term assignments of 3_2 and 10_2. The change would give a normal order for the $6s6d$ terms, agreeing fairly well with Houston's equations, but an unsatisfactory distribution of the $6p^2$ terms. The hyperfine structure intervals of the individual terms with $J=2$ are consistent with this alternative assignment but for overlapping configurations only sum relations and not the equations for the individual levels are applicable. The sum relations taken over all $J=2$ terms of $6s6d$ and $6p^2$ are consistent with either assignment. The given assignment, however, can be adequately correlated with the unambiguously identified $6s6d$ and $6p^2$ terms of Hg I, Tl II, and Pb III, whereas the alternative cannot. This evidence, together with the fact that the distribution as given can be accounted for by Bacher's theory, is the basis for our unique configuration assignments $6s6d$ 3_2 and $6p_{\frac{1}{2}}6p_{1\frac{1}{2}}$ 10_2. However, on account of the sharing of some characteristics these terms are only approximately described by the configurations assigned.

There is evidence of a slight mutual perturbation of the adjacent terms $6s6d$ 5_1 and $6s7s$ 6_1. The prominence of the combination line $6s7s$ 6_1-6s5f $19_2{}^\circ$, which, although permitted by the Laporte rule, involves a single electron transition with $\Delta l=3$, indicates that 5_1 and 6_1 share some of their combining characteristics. The absence of the similar transition $6s5f$ $19_2{}^\circ-6s8s$ 13_1 shows that the $\Delta l=3$ type of transition is normally not prominent when the terms are unperturbed. The mutual perturbation of 5_1 and 6_1 is not noticeable in their hyperfine structure intervals.

V. HYPERFINE STRUCTURE

Although all the hyperfine structure intervals have a limit of error of 0.1 cm^{-1} or greater, most of them are so large that they can be compared somewhat critically with theory. The comparison, presented in this section, shows: (1) that the hyperfine structure levels 8°, 9°, 10°, 11°, arising from $6s7p_{\frac{1}{2}}$ exhibit perturbation of the

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[10] J. C. McLennan, A. B. McLay and M. F. Crawford, Proc. Roy. Soc. **A133**, 652 (1931).

type (violation of interval rule and intensity relations) found in Hg I by Schüler and Jones[11] and explained by Goudsmit and Bacher;[12] (2) that for our configuration assignments the observed interval factors are consistent with the theory of hyperfine structure separations;[13] and (3) that the mutual perturbation of overlapping configurations of the same parity affect the interval factors of the states with the same J values.

$6s7p_{\frac{1}{2}}$—Normally one expects first the two electrons of $6s7p_{\frac{1}{2}}$ to couple giving two multiplet states with J values 0 and 1, and then each of these J's to couple with the nuclear moment, $J=0$ giving one hyperfine structure level with $F=4\frac{1}{2}$ and $J=1$ giving three levels with $F=3\frac{1}{2}$, $4\frac{1}{2}$, $5\frac{1}{2}$. For this coupling the three levels arising from $J=1$ should obey the interval rule, and all four levels should combine according to the J and F selection rules and the normal intensity formulae.[14] In Bi IV, however, the interaction between the two electrons, $6s$ and $7p_{\frac{1}{2}}$, is small and of the same order of magnitude as their resultant interaction with the magnetic nucleus. For this case the J's lose their significance as quantum numbers and only F values can be assigned to the levels. Accordingly the four levels of $6s7p_{\frac{1}{2}}$ are not expected to exhibit the characteristics predicted for normal coupling. A theoretical treatment of hyperfine structure perturbation due to a change in coupling has been published by Goudsmit and Bacher.[12] Their theory is applied in the following.

Expressions for the hyperfine structure interactions can be readily derived for the two extreme cases where the hyperfine structure is much smaller and where it is much larger than the separation between the two J states. The relative energies of the four hyperfine structure levels of $6s7p_{\frac{1}{2}}$ for the extreme cases are given in Table IV. Here X represents the distance between the two J states in the absence of hyperfine structure, and a_{6s} is the interaction constant that governs the magnitude of the interaction of the $6s$ electron with the magnetic nucleus. In these equations the interaction of the $7p_{\frac{1}{2}}$ electron with the nuclear moment $(a_{7p}(\frac{1}{2})=0.1)$[15] is neglected, since it is about 1/25 of that of the $6s$ electron and only introduces a correction of the order of the error in the observed intervals.

TABLE IV. *hfs levels of* $6s7p_{\frac{1}{2}}$ *for (jj) coupling.*

Level	$a_{6s} \ll X$	$X=0$
$F=5\frac{1}{2}$	$E=0$	$E=0$
$=4\frac{1}{2}$	$E=-11/4\cdot a_{6s}$	$E=0$
$=3\frac{1}{2}$	$E=-5a_{6s}$	$E=-5a_{6s}$
$=4\frac{1}{2}$	$E=-X-9/4\cdot a_{6s}$	$E=-5a_{6s}$

The information in Table IV is sufficient to determine[16] the coefficients of the set of equations the roots of which give the relative energies of the levels for any intermediate values of a_{6s} and X. These equations are:

$$F=5\tfrac{1}{2};\quad E=0 \tag{1}$$

$$=4\tfrac{1}{2};\quad E^2+E(X+5a_{6s})+11/4\cdot X\cdot a_{6s}=0 \tag{2}$$

$$=3\tfrac{1}{2};\quad E+5a_{6s}=0. \tag{3}$$

The values of X and a_{6s} can be determined from the two levels with $F=5\frac{1}{2}$ and $3\frac{1}{2}$ and either of the levels with $F=4\frac{1}{2}$. The values of X and a_{6s} obtained from the relative energies of 11°, 9° and 8° are $X=20.4$ cm^{-1}, $a_{6s}=2.34$ cm^{-1}. These values when substituted in Eq. (2) give the position of 10° as 4.81 cm^{-1} below 11°. The good agreement of this predicted value with the observed position of 10°, 4.9 ± 0.1 cm^{-1} below 11°, shows that the hyperfine structure perturbation in $6s7p_{\frac{1}{2}}$ is a coupling effect due to the approximate equality of the multiplet and hyperfine structure separations of $6s7p_{\frac{1}{2}}$. The magnitude of the perturbation is such that 10° is displaced from its normal position, 6.43 cm^{-1} below 11° as calculated by the interval rule, to its observed position, 4.9 cm^{-1} below 11°.

A value of a_{6s} determined from the hyperfine splitting of a term of another configuration could be used in the equations but as the value

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[11] H. Schüler and E. G. Jones, Zeits. f. Physik **77**, 701 (1932).

[12] S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933). See also H. Casimir, Zeits. f. Physik **77**, 811 (1932).

[13] S. Goudsmit and R. F. Bacher, Phys. Rev. **34**, 1501 (1929) and S. Goudsmit, Phys. Rev. **37**, 663 (1931).

[14] E. L. Hill, Proc. Nat. Acad. Sci. **15**, 779 (1929).

[15] R. A. Fisher and S. Goudsmit, Phys. Rev. **37**, 1057 (1931).

[16] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

of a_{6s} obtained from other terms is not overly accurate this alternative method has not been used. Although the value $a_{6s}=2.34$ derived from $6s7p_{\frac{1}{2}}$ might not be very reliable, since in its derivation the coupling was assumed strictly (jj) and the interaction constant of $7p_{\frac{1}{2}}$ neglected, it is probably the best obtainable from the present data; and is consistent within the limits of the experimental errors with the interval factors of the terms of the other configurations (see Table V). This value of a_{6s} in Bi IV also compares favorably with the values of a_{6s} in other spectra of bismuth,[15] namely: Bi II, 1.60; Bi III, 1.80; Bi IV, 2.34; Bi V, 2.6.

Anomalies in the combinations of 8°, 9°, 10°, 11°, have been observed, as expected for perturbations of this type. The relative intensities of the hyperfine components of the combinations of 8° and 10° with $J=1$ terms, which are permitted by the J rule, indicate that 8° and 10° share their characteristics as expected. Forbidden combinations of 8°, which normally would be characterized by $J=0$, with $J=0$ and $J=2$ terms have been observed; the ratio of the sum of the intensities of the hyperfine structure components involving 8° to the sum of the intensities of the components involving 9°, 10°, 11° (normally characterized by $J=1$) is of the order of the ratio 1/14 predicted by Eq. (4) of Goudsmit and Bacher's paper.[12] Combinations of 8°, 9°, 10°, 11°, with the term 8_3, all of which are normally forbidden, have also been observed as weak lines.

In all respects the hyperfine structure of $6s7p_{\frac{1}{2}}$ confirms Goudsmit and Bacher's theory.

The hyperfine structure of other terms of Bi IV are discussed in the following. The value $a_{6s}=2.34$ deduced from $6s7p_{\frac{1}{2}}$ is used in the appropriate separation formulae[13] to predict the interval factors (A) of the terms. The predicted

TABLE V. *hfs interval factors.*

Formula		A(calc.)	A(obs.)	Remarks
$6s7p_{1\frac{1}{2}}$	$A(15_1{}^\circ)=-\frac{1}{4}a_{6s}$	−0.585	−0.42*	Coupling (jj). Since $a_{7p}(1\frac{1}{2})=0.01$, it is neglected[15]
	$A(16_2{}^\circ)=\frac{1}{4}a_{6s}$	0.585	0.55	
$6s7d$	$A(14_1)=-\frac{1}{4}a_{6s}$	−0.585	−0.64	Coupling intermediate, a_{7d} is neglected
	$A(15_2)+A(18_2)=1/12\cdot a_{6s}$	0.195	0.18	
	$A(17_3)=1/6\cdot a_{6s}$	0.390	0.43	
$6s5f$	$A(19_2{}^\circ)=-1/6\cdot a_{6s}$	−0.390	−0.35	Coupling intermediate, a_{5f} is neglected
	$A(20_4{}^\circ)=1/8\cdot a_{6s}$	0.292	0.3	
$6s6p$	$A(2_1{}^\circ)=\frac{1}{2}a_{6s}+\frac{1}{2}a_{6p}(\frac{1}{2})$	1.5	1.3†	Coupling intermediate, $a_{6p}(\frac{1}{2})=0.7$ $a_{6p}(1\frac{1}{2})=0.01$ [15]
	$A(3_2{}^\circ)=\frac{1}{4}a_{6s}+3/4\cdot a_{6p}(1\frac{1}{2})$	0.59	0.65	
$6s6d$	$A(5_1)=-\frac{1}{4}a_{6s}$	−0.585	−0.62	a_{6d} is neglected; independent of coupling
	$A(8_3)=1/6\cdot a_{6s}$	0.390	0.43	
$6s6d$ and $6p^2$	$A(3_2)+A(7_2)+A(10_2)+A(11_2)=1/12\cdot a_{6s}+\frac{1}{4}a_{6p}(\frac{1}{2})$	0.37	0.35	Mutual perturbation of the two configurations. a_{6d} & $a_{6p}(1\frac{1}{2})$ neglected

* Although the agreement for this term is not as good as for the other terms, the observed interval has the right sense and order of magnitude. Strictly this term should not be treated alone but should be summed with $13_1{}^\circ$ and $22_1{}^\circ$ since they mutually perturb. Although the intervals of $13_1{}^\circ$ and $22_1{}^\circ$ are known, the predicted sum of the interval factors of the three terms cannot be computed for comparison since sufficient data are not available to determine the interaction constant of $5d^9$.

† The observed interval factor of this term is smaller than the value calculated by means of the (jj) formula. This is as expected since the coupling is intermediate tending to (jj). The interval of $4_1{}^\circ$ is needed for a more critical discussion of the hyperfine structure of $6s6p$.

values are compared in Table V with the observed values.

The interaction constants a_{7s} and a_{8s} can be determined from the intervals of $6s7s\ 6_1$ and $6s8s\ 13_1$ and the value $a_{6s}=2.34$ as follows:

$$A(6_1)=\tfrac{1}{2}a_{6s}+\tfrac{1}{2}a_{7s}=1.60, \quad \text{hence} \quad a_{7s}=0.86;$$

$$A(13_1)=\tfrac{1}{2}a_{6s}+\tfrac{1}{2}a_{8s}=1.42, \quad a_{8s}=0.50.$$

The value of $a_{7s}=0.86$ determined from Bi IV is larger than $a_{7s}=0.47$ obtained from Bi III[15] by an amount of the order expected when the decrease in screening is considered. The value of $a_{8s}=0.50$ relative to the value of a_{7s} is of the order expected. These values, however, are not very accurate.

The data presented above show that the hyperfine structure of Bi IV is consistent with our configuration assignments. The intervals, however, are hardly accurate enough for a rigorous determination of the interaction constants of the various electrons. Hence we are preparing to investigate the hyperfine structure with a new twenty-one foot grating.

In conclusion the authors wish to thank Professor E. F. Burton, Director of the laboratory, for his interest in this investigation.