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New Energy Levels in Au II, Hg III, Tl IV, Pb V and Bi VI

J. E. MACK AND M. FROMER, *Department of Physics, University of Wisconsin*

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All the previously unknown $5d^{10}$, $5d^96s$ and $5d^96p$ levels in all the stable members of the platinum-like isoelectronic sequence, and some $5d^96d$ and $5d^97s$ levels, have been identified. Several corrections are made to the literature on Au II, Hg III and Tl IV. The Pb V and Bi VI classifications verify Arvidsson's estimates of the stages of ionization for the individual lines. The $5d^96p|_0$ levels were found only in consequence of Goble's predictions from his solution of the four-vector problem. The dependence of the energy and intensity values upon the atomic number is very smooth, except for a branching effect explained by Goble. New d^9s screening numbers and Houston parameters are given. Ionization potentials are estimated, by a comparison method, up to 87.9 ± 0.7 volts for Bi VI. Analysis of the one (partly resolved) hyperfine structure pattern attributed to Bi VI yields a splitting factor $a(6s)=3.1\pm0.2$ cm^{-1}.

MODERN methods of excitation of extreme ultraviolet spark spectra are capable of stripping atoms of all kinds to stages with very simple spectra, and (except in the case of the lightest elements) to others as well, with very complicated spectra. The abundance of the lines thus excited leads to quite a high probability of fortuitous agreement in wave number differences, so that one frequently meets lines listed in the literature as belonging to ions removed by several stages of ionization from those to which they are later found to belong. A few investigations with the excitation controlled, especially by means of a variable series inductance,[1] have yielded reliable quantitative information about the stages of ionization of lines. Notable among these investigations is that of the spark spectra of lead and bismuth, by Arvidsson.[2] His success leaves no doubt as to the quantitative applicability of the method as far as the sixth spectrum at least. The first step in our investigation[3] was the completion of the classification of the $5d^{10}$, $5d^96s$ and $5d^96p$ levels of Pb V and Bi VI, except $5d^96p|_0$, whose later discovery is discussed below. The new Pb V and Bi VI levels are all derived from Arvidsson's lines, classified with few exceptions in exactly the stage of ionization to which they were assigned by Arvidsson. The exceptions never involve a discrepancy of more than one in z (where $z\equiv$Roman numeral). They occur mainly in the region of wavelengths much shorter than any heretofore classified in lead or bismuth; so they are not surprising, in view of the fact that Arvidsson's method of separation was a relative one, depending upon the presence of lines belonging to known stages.

Because of the relative excellence of the experimental material for these two elements, their platinum-like spectra were then known better than the earlier members of the isoelectronic sequence, so they presented an unusual opportunity for the verification of the levels already reported and the discovery of new ones, by interpolation, and in one lot of levels, by backward extrapolation from the fourth spark spectrum. Many of the better known rules for the classification of spectra are inapplicable in this sequence. In Pt I itself the configurations built upon the $5d^86s$ configuration of the spark spectrum are so mixed with those built upon the $5d^9$ configuration that, in general, the individual levels can scarcely be coordinated with corresponding levels in the spark spectra. (For this reason Pt I will not be considered again in this report.) In the finally verified sequence there are even instances of sharp breaks in the graph of relative energy as a function of the atomic number, within an isolated configuration. The reports up to Arvidsson's upon spectra in the sequence were all based upon experimental material considerably less modern than that given by Arvidsson. Altogether, then, it is not surprising that in extending our knowledge of the sequence it has been necessary not only to fill in the gaps, but also to make a critical examination of all the older data and rectify several misclassifications in Au II, Hg III and Tl IV. It has been found possible from a study of the existing data in the light of our new knowledge from

[1] A. Fowler, Phil. Trans. Roy. Soc. **A225**, 1 (1925); R. C. Gibbs, A. M. Vieweg and C. W. Gartlein, Phys. Rev. **34**, 406 (1929).

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

[3] A. T. Goble and J. E. Mack, Phys. Rev. **42**, 909 (1932). With the revisions mentioned in the next paragraph, the irregularities pointed out in this abstract disappear.

Arvidsson[2] on the one hand, and from Goble[3,4] on the other, to complete the identification of all the seventeen levels belonging to the configurations $5d^{10}$, $5d^9 6s$, and $5d^9 6p$ in each of the six stable elements of the sequence. In addition, the $5d^9 7s$ levels have been found in Pb V and Bi VI, and five possible $5d^9{}_{5/2}6d$ levels in Pb V.

Certain general properties of the spectra of this sequence are shown in the figures and tables of Goble's[4] paper just preceding this one. Except for a hyperbola-like branching effect in two pairs of levels (to be discussed below in connection with certain notational difficulties it introduces) the dependence of the energy values upon the atomic number is quite smooth. In fact, although the total spread of the $5d^9 6p$ configuration ranges up to almost sixty thousand units, in most cases the misplacement of a level by a hundred units would have caused a noticeable loss of regularity in the large scale original of Goble's Fig. 1.

No attempt is made in this report to interpret the energy distribution of the $5d^9 6p$ levels, or the intensities. The reader is referred to the Goble paper for a full treatment of these matters.

Table I, showing some other general properties, is almost self-explanatory. It includes certain values from the gold- and mercury-like sequences for comparison. In the configuration means the levels are weighted by the factor $2J+1$. Houston's[5] X's are calculated according to Laporte and Inglis'[6] Eq. (3′), where X' or X''' equals Goble's[4] $-2\zeta/a_1$. The slight negative change of the regular doublet screening number σ_{-5d} of Au II between $5d^9 6s$ and $5d^9 7s$ is probably a false effect due to the overlapping of $5d^9 7s$ and $5d^9 6d$. The discrepancy between X''' and X' in $5d^9 6s$ decreases regularly as $5d^8 6s^2$ recedes with increasing z. In Bi VI $5d^9 7s$ Houston's relationship is exactly fulfilled, the recorded discrepancy amounting to only 3 cm^{-1}, or less than the uncertainty in the values of the separations. This bespeaks a fortuitous balancing of perturbing effects or a remarkably weak interaction between $5d^9 7s$ and the neighboring (undiscovered) $5d^9 6d$.

The estimation of the ionization potentials (I. P., Table I) required a close study of neighboring and analogous spectra. The highest series member from which the ionization potential was estimated, and the estimating author, for the gold-like spectra, are shown in the line labeled "determined from." The hybrid method finally adopted for our sequence, which appeared to give the most plausible results there, was to calculate a first approximate Moseley ordinate $(\nu_{6s}/R)^{\frac{1}{2}}{}_{\text{Rydberg}}$ by applying the Rydberg formula to the first two members of the $5d^9{}_{5/2}ns|_3$ series, where possible, and to make the same slight correction, $\Delta(\nu_{6s}/R)^{\frac{1}{2}}$, to this ordinate as in the corresponding spectrum of the gold-like sequence, where the Moseley ordinates are almost identical and the corrections are known from higher terms. The absolute energies of the normal levels $5d^{10}|_0$, referred to the limits $5d^9|_{5/2}$, could then be evaluated directly from known spectrum lines. The method is almost tantamount to assuming the same Ritz correction in the platinum-like as in the gold-like spectrum of the same stage of ionization, but lends itself better to interpolation. The correction to the simple Rydberg value amounts to between three and four percent of the $6s$ term value. In Cu II, the only homologous spectrum where the absolute term values are known from its own series, the method yields results 0.4 percent too high. We suppose our estimates are reliable to about 1 percent.

The spectra are discussed separately below, except for the $5d^9{}_{3/2}6p_{3/2}|_0$ level, which is treated after Bi VI for all the spectra in common. In part A of each of the Tables II to VI there is given at the head of each column and row, the configuration with appropriate j and J values, and the relative energy, for a level. A self-explanatory jj notation is used throughout except for some notational expedients described in the next paragraph. In Au II and Hg III the energies are referred to $5d^9{}_{5/2}6s|_3$; in Tl IV, Pb V and Bi VI, to the normal level $5d^{10}|_0$. At each intersection, corresponding to a spectrum line, there is given the observed intensity, followed by the wave number discrepancy $\nu_{\text{obs}}-\nu_{\text{calc}}$. In Pb V and Bi VI, the intensity is preceded by a Roman numeral showing Arvidsson's estimate z_A, if any, of the stage of ionization to which the line belongs. In part B of each table, the experimental data for each line are taken from the author whose intensity estimate is shown farthest to the left (except where otherwise specified).

[4] A. T. Goble, Phys. Rev. this issue.
[5] W. V. Houston, Phys. Rev. **33**, 297 (1929).
[6] O. Laporte and D. R. Inglis, Phys. Rev. **35**, 1337 (1930).

TABLE I. *The x-ray doublets, Houston parameters and ionizing energy values, in the platinum-like spectra.*[1]

	Seq.	I		II		III		IV		V		VI
Spectrum	80	Hg I		Tl II		Pb III		Bi IV				
	79	Au I		Hg II		Tl III		Pb IV		Bi V		
	78	Pt I		Au II		Hg III		Tl IV		Pb V		Bi VI
Irregular doublets:												
$5d^{10}6s^2-5d^{10}6s6p_{\text{mean}}$	80	44855		61854		77875		93722				
$(6s-6p)_{80}-(6s-6p)_{79}$	—	4953		4283		3843		3532				
$5d^{10}6s-5d^{10}6p_{\text{mean}}$	79	39902		57571		74032		90190		106372		
$(6s-6p)_{79}-(6s-6p)_{78}$	—	3066		3279		3540		3946		4388		
$5d^96s_{\text{mean}}-5d^96p_{\text{mean}}$	78	[36836]		54292		70492		86244		101984		117900
Δ_1			+17456		+16200		+15752		+15740		+15916	
Δ_2				−1256		−448		−12		+176		
Regular doublets:												
$\Delta\nu_{-5d}(5d^96s^2)$	79	12274		15040								
$\sigma_{-5d}(5d^96s^2)$		43.560		42.708								
$\Delta\sigma_{-5d}(6s^2-6s)$	—		Au+0.327		Hg+0.315							
$\Delta\nu_{-5d}(5d^96s)$	78	10132		12727		15554		18624		21943		25522
$\sigma_{-5d}(5d^96s)$		44.215		43.233		42.393		41.661		41.015		40.437
Δ_1			−0.992		−0.840		−0.732		−0.646		−0.578	
$\Delta\sigma_{-5d}(6s-7s)$		[−1.95]		−0.054						+0.052		+0.071
$\Delta\nu_{-5d}(5d^97s)$		[7978]		12650						22055		25693
$\sigma_{-5d}(5d^97s)$		[46.17]		43.287						40.963		40.366
Δ_1			−2.88		←		−0.77×3		→		−0.597	
Houston parameters:												
$X'''(5d^9{}_{5/2}6s\|_2)$	78	[0.67]		2.055		2.053		1.914		1.751		1.598
$X'(5d^9{}_{3/2}6s\|_2)$		[3.02]		1.530		1.765		1.691		1.566		1.438
$X'''-X'$		[−2.35]		+0.525		+0.288		+0.223		+0.185		+0.160
Δ_1			+2.88		−0.237		−0.065		−0.038		−0.025	
$X'''(5d^9{}_{5/2}7s\|_2)$		0.308		0.310						0.3076		0.2978
$X'(5d^9{}_{3/2}7s\|_2)$		[0.424]		0.285						0.3154		0.2987
$X'''-X'$		−0.116		+0.025						−0.0078		−0.0009
Ionizing energies:												
$5d^{10}6s_{1/2}-5d^{10}7s_{1/2}$	79	54485		95714		139209		185100		233346		
$(\nu_{6s}/R)^{\frac{1}{2}}_{\text{Rydberg}}$		0.8396		1.1969		1.5068		1.7945		2.0644		
$\Delta(\nu_{6s}/R)^{\frac{1}{2}}$		−0.016		−0.023		−0.026		−0.030		−0.033		
$(\nu_{6s}/R)^{\frac{1}{2}}_{\text{best}}$		0.8238		1.174		1.481		1.764		(2.031)		
determined from		7d(MM)		12g(P)		7h(M)[2]		7h(M)[2]				
$5d^96s\|_3-5d^97s\|_3$	78	52379		93132						227672		277092
$(\nu_{6s}/R)^{\frac{1}{2}}_{\text{Rydberg}}$		0.8258		1.1834						2.0447		2.2998
$\Delta(\nu_{6s}/R)^{\frac{1}{2}}$		−0.016		(−0.023)						(−0.033)		(−0.035)
$(\nu_{6s}/R)^{\frac{1}{2}}_{\text{best}}$		0.810		1.160		(1.464)		(1.746)		2.012		2.265
Δ_1			+0.350		+0.304		+0.282		+0.266		+0.253	
$10^{-2}\nu_{6s}$		720		1477		2353		3343		4442		5630
$10^{-2}\nu_{5d}$		659		1617		2781		4094		5550		7125
$(\nu_{5d}/R)^{\frac{1}{2}}$		0.775		1.214		1.592		1.932		2.249		2.548
Δ_1			+0.439		+0.378		+0.340		+0.317		+0.299	
I. P., $5d^9{}_{5/2}(6s\rightarrow\infty)$, volts		8.88										
I. P., $5d^9{}_{5/2}(5d\rightarrow\infty)$, volts				19.95 ±0.2		34.3 ±0.3		50.5 ±0.4		68.5 ±0.5		87.9 ±0.7

[ ] These values in Pt I are irregular, due to the mixture of $5d^96s$ with $5d^86s^2$, and of $5d^96p$ with $5d^86s6p$ in many of the levels.
( ) Estimated values.
[1] In this and the following tables the values given without special references are taken from sources which may be found in Bacher and Goudsmit, *Atomic Energy States*, McGraw-Hill, 1932, or from the new material in this paper, below. Authors referred to only by their initials can be identified by the bibliographical references at the appropriate points in Bacher and Goudsmit.
[2] Kindly communicated privately by Professor McLay.

For each of the J values common to the $5d^9{}_{5/2}6p_{3/2}$ and $5d^9{}_{3/2}6p_{1/2}$ groups (*viz.*, $J=1$ and $J=2$) the crossing of the pure *jj* roots, shown by Goble,[4] is accompanied by a hyperbola-like branching of the pair of levels, with an interchange of the formally assigned approximate j values near the vertices. (See Goble's Fig. 2.) The vertices for the $J=1$ pair are so near to Tl IV that the wave function of the lower level there, according to Goble, shows no clear majority in favor of either *jj* assignment. For these reasons it has been found expedient to supplement the notation by adding a prime (′) for the higher and a double prime (″) for the lower level of each of

TABLE II. *A: Energy levels and transitions in Au II (supplementary to Bacher and Goudsmit, Table I, reference 1).*

Config. J / B & G symbol		$5d^{10}\|_0$	$5d^9{}_{3/2}6s\|_1$	$5d^86s^2\|_1$	$5d^9{}_{5/2}6d\|_1$ 1	$5d^9{}_{5/2}6d\|_1$ 5	$5d^9{}_{3/2}7s\|_1$
	ν(cm^{-1})	-14023**	12726.7*	?46710.0*	101008.8*	102256.4*	105781.2*
$5d^9{}_{5/2}6p_{3/2}\|_{1''}$	58364.5*	2 +1	old	—	old	old	—
$5d^9{}_{3/2}6p_{3/2}\|_0$	66606.5†		3 0	—	3 0.0	—	1 0.0
$5d^9{}_{3/2}6p_{1/2}\|_{1'}$	66620.2*	3 +4	old	—	(see IIB)	old	old
$5d^9{}_{3/2}6p_{3/2}\|_1$	70668.0*	3 −17	old	?old	—	old	old

Several putative levels not listed here may be found in B. V. Rao, Proc. Roy. Soc. **A142**, 118 (1933).
* Old level (MM).
** Replaces (ST)[1] $5d^{10}\,{}^1S_0=-15036$.
† Replaces (MM) $6p\ {}^3P_0=67574.5$.

? 46710_1 is one of a group of five (MM) levels evidently overlooked by B & G. The question mark is ours; with the repudiation of 67574.5_0 this supposed level is supported only by a single pair, and in any case one would expect the $d^8s^2|_1$ level to be near the middle $J=2$ level (probably 33471.6_2) of the configuration.

TABLE II. *B: Newly classified lines of Au II.*

BBF[2]	BB[2]	Intensity EH[3] spark	EH[3] arc	MM[4]	λ_{vac}	ν	
3					1181.00	84674	$5d^{10}\|_0-5d^9{}_{3/2}6p_{3/2}\|_1$
3					1239.97	80647	$5d^{10}\|_0-5d^9{}_{3/2}6p_{1/2}\|_{1'}$
	2				1381.44	72388	$5d^{10}\|_0-5d^9{}_{5/2}6p_{3/2}\|_{1''}$
	2				1852.54	53980	$5d^9{}_{3/2}6s\|_1-5d^9{}_{3/2}6p_{3/2}\|_0$
					λ_{air}		
		1	—		2551.90	39174.7	$5d^9{}_{3/2}6p_{3/2}\|_0-5d^9{}_{3/2}7s\|_1$
		3	1		2905.93	34402.3	$5d^9{}_{3/2}6p_{3/2}\|_0-5d^9{}_{5/2}6d\ \ 1\|_1$
		4	—	5	2907.07	34388.7	$5d^86s^2\|_3-5d^9{}_{3/2}6p_{3/2}\|_2$; $5d^9{}_{3/2}6p_{1/2}\|_{1'}-5d^9{}_{5/2}6d\ \ 1\|_1$, (overlooked in (MM) line list)

[1] R. A. Sawyer and K. Thomson, Phys. Rev. **38**, 2203 (1931).
[2] L. Bloch, E. Bloch and J. Farineau, J. de phys. et rad. **3**, 437 (1932); L. Bloch and E. Bloch, J. de phys. et rad. **6**, 160 (1925).
[3] F. Exner and E. Haschek, quoted in Kayser and Konen, *Handbuch der Spectroskopie*, VII.
[4] Table I, reference 1.

these pairs throughout the sequence, and to omit the j values entirely for the $1'$ and $1''$ levels of Tl IV. (The $J=2$ levels exchange j values between Hg III and Tl IV. If formal j values had been assigned in the Tl IV $J=1$ pair according to the minority plurality these two levels would have exchanged j values between Tl IV and Pb V.) Doctor Goble's advice as to the nature of the phenomena to be expected in the branching region has been invaluable. Of course the assignments of the doubtful j values were made on the basis of his calculations.

Au II (*Table II*). All the published $5d^96s$, $5d^96p$ and $5d^97s$ levels are verified except $5d6p|_0$. An alternative value for the normal level $5d^{10}|_0$ is proposed. The new value for the normal level fits into the scheme of Moseley ordinates (Table I) perhaps better than the old $((\nu_{5d}/R)^{\frac{1}{2}}{}_{\rm old}=1.218)$, but this in itself is hardly conclusive, since Moseley graphs for isoelectronic sequences generally show relatively sharp departures from linearity in the neighborhood of the neutral atom. A much more serious matter is the line list of the Blochs. In a number of instances the qualitative correctness of the ultraviolet line lists of those authors has been verified, although, obtained from a low dispersion instrument, the frequency values are not necessarily especially accurate. Although the three lines establishing the new level are far apart, their wave number agreement is well within the Blochs' own estimate of their absolute accuracy. Compared with the new level's (3, 3, 2), the intensities of the three expected transitions to the previously reported $5d^{10}|_0$ level are (0, 4, missing); this disparity in intensities is contrary to the behavior of almost all other known $d^{10}-d^9p$ line triads. (The case of Ag II will be treated elsewhere.) Unfortunately the BBF paper gives no hint as to how BBF intensities and BB intensities are to be compared.

Hg III[7] (*Table III*). Each of the changes improves the internal consistency of the spectrum, as well as being practically inevitable from the consideration of smoothness within the sequence. Replacement of the (MMC) ${}^1F_3$ relieves the analysis of an ambiguity in the Hg II line ν71408. The $d^{10}-d^9p$ lines were all stronger than any other mercury lines to the violet of λ1080 on Lang's plates, which extend to about λ600. There is hardly any doubt of the presence of a mercury

TABLE III. *A: Energy levels and transitions in Hg III (supplementary to Bacher and Goudsmit, Table I, reference 1).*

Config. J		$5d^{10}\|_0$	$5d^9{}_{5/2}6s\|_3$	$5d^9{}_{5/2}6s\|_2$	$5d^9{}_{3/2}6s\|_1$	$5d^9{}_{3/2}6s\|_2$
	ν(cm^{-1})	−42862	0*	3177*	15554*	18234*
$5d^9{}_{5/2}6p_{3/2}\|_{1''}$	75754**	8 0		old	old	old
$5d^9{}_{3/2}6p_{1/2}\|_{1'}$	83704*	8O −8		old	old	old
$5d^9{}_{3/2}6p_{3/2}\|_0$	86228				6 0	
$5d^9{}_{3/2}6p_{3/2}\|_3$	91737†		3 0	5 0	out	8 0
$5d^9{}_{3/2}6p_{3/2}\|_1$	92146	6 +1		3 −7	8 +1	5 +1
$5d^9{}_{3/2}6p_{3/2}\|_2$	93627§		2 0	4 +4	9− +1	8 −1

The best values for the (MMC) levels not listed here are: 60698_2, 62775_3, 75148_4, 75695_2, 78074_2, 78750_3.
* Old level (MMC).
** This (MMC)$^3P_1$, previously questioned, is verified by this investigation.
† Formerly (MMC)$^1D_2$; replaces (MMC) 89637_3.
§ Formerly (MMC)$^3D_1$.
out The line formerly classified (MMC) as the transition, now forbidden, between these levels, appears on Lang's plates at ν76173, $\nu_{obs}-\nu_{calc}=-10$ cm^{-1}.

TABLE III. *B: Newly classified lines of Hg III.*

L[7]	Intensity MMC	C[1]	λ_{vac}	ν	Designation
6		1	740.69	135009	$5d^{10}\|_0-5d^9{}_{3/2}6p_{3/2}\|_1$
8O		5O	790.15	126558	$5d^{10}\|_0-5d^9{}_{3/2}6p_{1/2}\|_{1'}$
8		3	843.06	118616	$5d^{10}\|_0-5d^9{}_{5/2}6p_{3/2}\|_{1''}$
2		—	1068.04	93627	$5d^9{}_{5/2}6s\|_3-5d^9{}_{3/2}6p_{3/2}\|_2$
3	5	1	1090.07	91737	$5d^9{}_{5/2}6s\|_3-5d^9{}_{3/2}6p_{3/2}\|_3$
4	4	1	1105.53	90454	$5d^9{}_{5/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_2$
3		—	1124.08	88962	$5d^9{}_{5/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_1$
5	4	0	1129.18	88560	$5d^9{}_{5/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_3$
9	10	4	1280.83	78074	$\begin{cases}5d^9{}_{3/2}6s\|_1-5d^9{}_{3/2}6p_{3/2}\|_2;\\5d^9{}_{5/2}6s\|_3-5d^9{}_{3/2}6p_{1/2}\|_{2'}\end{cases}$
8		2	1305.61	76593	$5d^9{}_{3/2}6s\|_1-5d^9{}_{3/2}6p_{3/2}\|_1$
8	6	3d	1326.40	75392	$5d^9{}_{3/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_2$
5		2d	1352.94	73913	$5d^9{}_{3/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_1$
8	8	2	1360.49	73503	$5d^9{}_{3/2}6s\|_2-5d^9{}_{3/2}6p_{3/2}\|_3$
6		4	1414.95	70674	$5d^9{}_{3/2}6s\|_1-5d^9{}_{3/2}6p_{3/2}\|_0$

Note: MMC have listed only their classified lines.
d Diffuse.
O (after intensity) Masked by an oxygen line (see text).
[1] J. A. Carroll, Phil. Trans. Roy. Soc. **A225**, 357 (1925).

line overlying the unresolved oxygen pair at λ790. Lang's intensities for the oxygen lines in this region on his mercury spark spectrum plates are 779 : 787 : 790 : 796 = 1 : 3 : 8 : 2*d*, while Edlén[7] gives their intensities as 9IV, 10IV : 15IV : 13IV, 16IV : 10II, respectively. Here we have placed Edlén's intensities and *z* values between the colons.

Tl IV (*Table IV*). After the classification of the $s\leftarrow p$ transitions (replacing our (Table I, reference 1) previous $5d^96s|_1$ level by Rao's (Table IV, reference 2)) and the prediction of the d^{10} level, it was our privilege to receive, in answer to our letter to Dr. Arvidsson, a list of measurements which, though not quite complete, effected a great improvement in the accuracy of our knowledge of the spectrum and tended to verify our scheme in detail. The columns headed by " A " in Table IV refer to this hitherto unpublished list, and for the lines listed in the column ν_A, the wavelengths are Arvidsson's; for the rest of the lines, the large discrepancies are no worse than might have been expected from the quality of the original data. There is a possibility that $5d^96s|_3$ and the $5d^9{}_{5/2}6p_{1/2}$ levels should be 10 or 12 cm^{-1} higher. Although no use is made in this paper of the hyperfine structure of Tl IV, the separations of some pairs are listed in Table IVA in parentheses after the wave number discrepancies, and in Table IVB in the column labeled $\delta\nu_A$, from Arvidsson's list. Of the ten to sixteen levels given in each of the three previous papers on this spectrum, not more than nine are verified in any case.

[7] We are greatly indebted to Professor Lang for generously sending us lists of readings from several mercury spark spectrum plates, which we have transformed to frequencies with respect to Paschen's Hg II and Edlén's (Zeits. f. Physik **85**, 85 (1933)) oxygen lines. The "L" in Table IIIB refers to these plates. The completeness and accuracy of the analysis presented here is due in no small measure to the availability of Lang's measurements. It is pleasing, however, to notice how closely compatible the older material of Carroll is with that of Lang. About forty of Lang's mercury spark spectrum lines of intensity more than 3, in the region $\lambda<2000$, remain unaccounted for.

TABLE IV. *A: Energy levels and transitions in Tl IV (complete).*

Config. J	ν(cm^{-1})	$\Delta\nu$	$5d^{10}$ 0	$5d^{9}_{5/2}6s$ 3		$5d^{9}_{5/2}6s$ 2		$5d^{9}_{3/2}6s$ 1		$5d^{9}_{3/2}6s$ 2
			0	75052*		78647*		93676**		96727*
					3595		15029		3051	
$5d^{9}_{5/2}6p_{1/2}\|_{2}$	147635*			7 − 0.9(4.7)		5 + 7		—		3 − 7
		2206								
$_{3}$	149841*			4 − 0.4(3.4)		8 + 1(3.8)				5 − 13
		16584								
$5d^{9}_{3/2}6p_{1/2}\|_{2''}$	166425†			0 + 0.4		5 − 5		5 − 1.6(3.0)		6 + 2(3.4)
		1074								
$5d^{9}6p\|\ _{1''}$	167499† (Note)		4 + 1.8			4 − 4		—		5 + 3(4.7)
		173								
$5d^{9}_{5/2}6p_{3/2}\|_{4}$	167672*			6 0.0						
		2662								
$5d^{9}_{5/2}6p_{3/2}\|_{2'}$	170334*			2 + 3		4 − 3		3 − 3		5 + 0.3(4.1)
		1938								
$5d^{9}_{5/2}6p_{3/2}\|_{3}$	172272*			4 − 9.0		4 + 4.5				1 + 3.1
		3018								
$5d^{9}6p\|\ _{1'}$	175290§ (Note)		10 − 1.5			3 + 0.8		2 − 11		3 − 10(4.6)
		5793								
$5d^{9}_{3/2}6p_{3/2}\|_{0}$	181083							3 0 (4.5?)		
		6584								
$_{3}$	187667			0 calc.		5 − 6				6 + 2
		566								
$_{1}$	188233†		7 − 1.3			3 − 24		2 + 0.3		2 − 6
		1911								
$_{2}$	190144†			2 − 16		0 calc.		3 + 0.3		4 − 0.2

* Old level (M (Table I, reference 1), and sometimes one or more of P[1], R[2] and S[3]).
** This level, discovered by Rao, replaces (M) 18865 (referred to 75052_3).
† Given by Rao, in some cases with different J.
§ Designation changed from (M) $5d^{9}_{5/2}6p_{3/2}|_{1}$ after Goble[4].
Note: See the special discussion in the text regarding the notation for levels 1″ and 1′.

[1] P. Pattabhiramayya, Ind. J. Phys. **3**, 523 (1929).
[2] K. R. Rao, Proc. Phys. Soc. London **41**, 361 (1929).
[3] Dr. G. K. Schoepfle has courteously kept us informed of his unpublished work in Tl IV, Pb V and Bi VI (Phys. Rev. **43**, 374 (1933); **45**, 747 (1934)). His results are largely, but not entirely, in harmony with ours.

TABLE IV. *B: Classified lines of Tl IV.*

Intensity C	Intensity M	Intensity A	λ_{vac}	ν A	ν CM	$\delta\nu$ A	Designation
		7	531.260	188231.7			$5d^{10}\|_{0}-5d^{9}_{3/2}6p_{3/2}\|_{1}$
		10	570.488	175288.5			$5d^{10}\|_{0}-5d^{9}6p\|_{1'}$
		4	597.012	167500.8			$5d^{10}\|_{0}-5d^{9}6p\|_{1''}$
	2	1	868.99		115076		$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{3/2}6p_{3/2}\|_{2}$
	—	1b	888.0	calc.			$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{3/2}6p_{3/2}\|_{3}$
	—	3	896.9	calc.			$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{2}$
	3	3	912.74		109560		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{1}$
	5	8	917.31		109014		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{3}$
4	6	30	1028.690	97211.0	97224		$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{5/2}6p_{3/2}\|_{3}$
3	4	20	1034.728	96643.8	96643		$5d^{9}_{5/2}6s\|_{2}-5d^{9}6p\|_{1'}$
3C?	4C? —	20	1036.610	96468.3	96477		$5d^{9}_{3/2}6s\|_{1}-5d^{9}_{3/2}6p_{3/2}\|_{2}$
2	5	10	1049.48		95285		$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{5/2}6p_{3/2}\|_{2'}$
2		10	1057.56	94557.3	94557		$5d^{9}_{3/2}6s\|_{1}-5d^{9}_{3/2}6p_{3/2}\|_{1}$
4	5	20	1068.04	93629.5	93623		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{5/2}6p_{3/2}\|_{3}$
4		20	1070.471	93416.8	93416		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{2}$
6	6	30	1079.68	92620.0	92617		$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{5/2}6p_{3/2}\|_{4}$
4	5		1079.70		91684		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{5/2}6p_{3/2}\|_{2'}$
2			1092.90		91500		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{1}$
—		4	1094.411	91373.4			$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{3/2}6p_{1/2}\|_{2''}$
6			1099.60		90942		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{3/2}6p_{3/2}\|_{3}$
4			1125.52		88848		$5d^{9}_{5/2}6s\|_{2}-5d^{9}6p\|_{1''}$
5			1139.30		87773		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{3/2}6p_{1/2}\|_{2''}$
3		2, 1d	1144.07		87407	4.5?	$5d^{9}_{3/2}6s\|_{1}-5d^{9}_{3/2}6p_{3/2}\|_{0}$
2		3, 2	1225.45		81603	4.6	$5d^{9}_{3/2}6s\|_{1}-5d^{9}6p\|_{1'}$
3	6		1273.03		78553		$5d^{9}_{3/2}6s\|_{2}-5d^{9}6p\|_{1'}$
3			1304.55		76655		$5d^{9}_{3/2}6s\|_{1}-5d^{9}_{5/2}6p_{3/2}\|_{2''}$
1C?	6	2	1323.660	75548.1	75542		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{5/2}6p_{3/2}\|_{3}$
4	7	7, 7	1337.103	74788.6	74784	3.4	$5d^{9}_{5/2}6s\|_{1}-5d^{9}_{5/2}6p_{1/2}\|_{3}$
5	7	3, 2	1358,56	73607.3	73606	4.1	$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{5/2}6p_{3/2}\|_{2'}$
5		2, 4	1374.620	72747.4	72747	3.0	$5d^{9}_{3/2}6s\|_{1}-5d^{9}_{3/2}6p_{1/2}\|_{2''}$
7	7	7, 7	1377.750	72582.1	72582	4.7	$5d^{9}_{5/2}6s\|_{3}-5d^{9}_{5/2}6p_{1/2}\|_{2}$
8	7	7, 7	1404.60		71195	3.8	$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{5/2}6p_{1/2}\|_{3}$
5		3, 2	1412.93		70775	4.7	$5d^{9}_{3/2}6s\|_{2}-5d^{9}6p\|_{1''}$
6		3, 3	1434.72		69700	3.4	$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{3/2}6p_{1/2}\|_{2''}$
5			1449.37		68995		$5d^{9}_{5/2}6s\|_{2}-5d^{9}_{5/2}6p_{1/2}\|_{2}$
5			1883.2		53101		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{5/2}6p_{1/2}\|_{3}$
3			1974.6		50901		$5d^{9}_{3/2}6s\|_{2}-5d^{9}_{5/2}6p_{1/2}\|_{2}$

A. Private communication from Arvidsson (see text).
C. (After intensity) masked by a carbon line.

TABLE V. *A: Energy levels and transitions in Pb V (complete).*

Config.	J	ν(cm^{-1})	$\Delta\nu$	$5d^{10}$ 0	$5d^9{}_{5/2}6s$ 3	$5d^9{}_{5/2}6s$ 2	$5d^9{}_{3/2}6s$ 1	$5d^9{}_{3/2}6s$ 2	$5d^9{}_{3/2}6s$ 4	$5d^9{}_{3/2}6s$ 3	$5d^9{}_{3/2}6s$ 4	$5d^9{}_{3/2}6s$ 2	$5d^9{}_{3/2}6s$ 2	$5d^9{}_{5/2}7s$ 3	$5d^9{}_{5/2}7s$ 2	$5d^9{}_{3/2}7s$ 1	$5d^9{}_{3/2}7s$ 2
				0	110768.0*	114705.3*	132711.4	135996.9*	?327433	?329573	?329935	?332358	?332501	338440	339234	360496	361073
					3937.3	18006.1	3285.7							794	21261	578	
$5d^9{}_{5/2}6p_{1/2}$	2	194803.3*			V {9 + 3.3; 0? −12.3}	V 6 0.0	:	:00 +7		V 5 −1		—	—	V 6 0	0 0	—	—
			2328														
	3	197131.2*			V 9 −0.7	V 7 +0.7		:00 +1	V 7 0	VI 4 +1	VI 2 0	2 −2	1 −1	V 2 +6	V 3 +1		—
			19937														
$5d^9{}_{3/2}6p_{1/2}$	2″	217068.4			V 1 +2	V 5? −1	V 8 +0.6	V 10 −0.7		—		—	0 −1	—	0 −3	1 −1	2b +10
			2420														
	1″	219488.2		V 1 −2		V 7 +1	V 1 −1.4	V 6 +1.4				—	—		—	III blend	—
			1581														
$5d^9{}_{5/2}6p_{3/2}$	4	221069*			V 10 0				V 1 +2	V 0 +2	0 0			V 3 0			
			2840														
	2′	223908.8*			V 7 0	V 9 0	V 4 +0.2	V 5 −0.6		—		V 2 −3	V 2 0	—	V 2 +1	—	—
			2602														
	3	226511.0*			V 15 −1	V 8 +1		V 3 0.0	V 2 −2	V 2 −1	V 1 0	0 0	0 0	V 1 0	0 +1		—
			1324														
	1′	227835.2**		V 10 +1		V 7 0	V 2 +0.1	V 5 0.0				IV 2 +3	V 1 0		1 +1	—	—
			9825														
$5d^9{}_{3/2}6p_{3/2}$	0	237660					V 4 0									V 1 −1	
			7001														
	3	244661			—	V 5 −1		V 7 0	—	—	—	—	—	—	VI 0 −1		VI 2 0
			616														
	1	245277		V 7 +1		VI 1 0	V 7 0	V 2 −2				V 3 +5	V 0 +2		—	1 +2	—
			2318														
	2	247595			1 +2	V 1 −1	V 7 −1	V 7 0		—		—	—	—	—	0 −2	0 0

* Old level (M) (Table I, reference 1). ** This level, previously question marked, is verified by this investigation. : Beyond Arvidsson's range; the lines recorded are Carroll's.

Pb V (Table V) and Bi VI (Table VI); (see below for hyperfine structure). All the previously reported levels are verified, but the values of some have been altered by a few wave numbers to fit the new data. Since the differences $5d^96s-5d^96p$ are known more accurately than the differences $5d^{10}-5d^96p$, where tenths of a unit are meaningless, the choice of d^{10} as the zero for the measurement of term values has entailed the additional arbitrary choice of a naught after the decimal point in the value of Pb V $5d^96s|_3$. The normal levels were found after the establishment of all the $5d^96p|_1$ levels. It was a most satisfactory verification of our schemes, and of the accuracy of Arvidsson's wave numbers, to find the lines $5d^{10}-5d^96p$ in each case including the strongest of the lines listed in the region $\lambda<700$A for all the spectra of the element; and moreover, to find the required differences of about 30,000 cm^{-1} among the three lines of wave number about 300,000 cm^{-1}, in each case satisfied within a total discrepancy range of 3 cm^{-1}.

The $5d^96p|_0$ level. Detailed justification is needed for our $5d^9{}_{3/2}6p_{3/2}|_0$ levels, especially because we list but one with a question mark although they give rise, in three of our five schemes, to only one line each. Previous to this investigation the level had been reported in Au II, but McLay and his collaborators had wisely omitted any attempt to place it in Hg III, and it had been proposed in Tl IV only as the result of an excessive extrapolation. It was not sought by us until Dr. Goble had kindly made a preliminary estimate of its position in Pb V from those of the other eleven levels in the configuration. The $5d^96p|_0$ energy was one of the constants wanted for his final calculation, so the product of the $J=1$ roots, referred to $5d^96p|_4$, was used in its place in the preliminary estimate. Then ν104949 was chosen as $5d^96s|_1-5d^96p|_0$, supported by the following three facts:

(1) It is the nearest Pb V$_{\text{Arvidsson}}$ line to the predicted position (below the preliminary estimate from five electrostatic parameters by 550 cm^{-1} and below that from three electrostatic parameters by 750 cm^{-1}).

(2) It leads with a discrepancy of 1 cm^{-1} to a Pb V$_{\text{Arvidsson}}$ line for $5d^96p|_0-5d^97s|_1$, the level's only other possible transition in our scheme.

(3) Since there is only one each of the levels of

TABLE V. *B: Classified lines of Pb V.*

Intensity A	Intensity M	Intensity C	λ_{vac}	ν	z_A	Designation
7			407.700	245278	V	$5d^{10}{}_0-5d^9_{3/2}6p_{3/2}\vert_1$
10			438.911	227837	V	$5d^{10}{}_0-5d^9_{5/2}6p_{3/2}\vert_{1'}$
1			455.61	219486	V	$5d^{10}{}_0-5d^9_{3/2}6p_{1/2}\vert_{1''}$
0			692.37	144431		$5d^9_{5/2}6p_{1/2}\vert_2-5d^9_{5/2}7s\vert_2$
2b	1		694.37	144015		$5d^9_{3/2}6p_{1/2}\vert_{2''}-5d^9_{3/2}7s\vert_2$
6			696.20	143637	V	$5d^9_{5/2}6p_{1/2}\vert_2-5d^9_{5/2}7s\vert_3$
1			697.22	143427		$5d^9_{3/2}6p_{1/2}\vert_{2''}-5d^9_{3/2}7s\vert_1$
3	2O		703.71	142014	V	$5d^9_{5/2}6p_{1/2}\vert_3-5d^9_{5/2}7s\vert_2$
2	1		707.64	141315	V	$5d^9_{5/2}6p_{1/2}\vert_3-5d^9_{5/2}7s\vert_3$
2	2		709.20	141004	III	{ $5d^9_{3/2}6p_{1/2}\vert_{1''}-5d^9_{3/2}7s\vert_1$; Pb III $6s6p\ ^3P_0-6s6d\ ^3D_1$
1			730.84	136829		$5d^9_{5/2}6s\vert_3-5d^9_{3/2}6p_{3/2}\vert_2$
1			738.72	135369		$5d^9_{5/2}6p_{1/2}\vert_2-?332501_2$
2	1		739.51	135225		$5d^9_{5/2}6p_{1/2}\vert_3-?332358_2$
5	4		742.01	134769	V	$5d^9_{5/2}6p_{1/2}\vert_2-?329573_3$
1			752.51	132889	V	$5d^9_{5/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_2$
2	1p		752.99	132804	VI	$5d^9_{5/2}6p_{1/2}\vert_3-?329935_4$
4	4		755.05	132442	VI	$5d^9_{5/2}6p_{1/2}\vert_3-?329573_3$
1	1		765.86	130572	VI	$5d^9_{5/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_1$
7	6	0	767.45	130302	V	$5d^9_{5/2}6p_{1/2}\vert_3-?327433_4$
5	1		769.50	129955	V	$5d^9_{5/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_3$
1			814.10	122835	V	$5d^9_{3/2}6p_{3/2}\vert_0-5d^9_{3/2}7s\vert_1$
0			818.58	122163		$5d^9_{3/2}6p_{1/2}\vert_{2''}-5d^9_{5/2}7s\vert_2$
3	2	00	852.00	117371	V	$5d^9_{5/2}6p_{3/2}\vert_4-5d^9_{5/2}7s\vert_3$
2	1		859.02	116412	VI	$5d^9_{3/2}6p_{3/2}\vert_3-5d^9_{3/2}7s\vert_2$
15	7	5	863.99	115742	V	$5d^9_{5/2}6s\vert_3-5d^9_{5/2}6p_{3/2}\vert_3$
0			866.31	115432		$5d^9_{3/2}6p_{1/2}\vert_{2''}-?332501_2$
2	0		867.11	115326	V	$5d^9_{5/2}6p_{3/2}\vert_{2'}-5d^9_{5/2}7s\vert_2$
1	0		867.90	115221		$5d^9_{3/2}6p_{3/2}\vert_1-5d^9_{3/2}7s\vert_1$
7	5	3	870.45	114883	V	$5d^9_{3/2}6s\vert_1-5d^9_{3/2}6p_{3/2}\vert_2$
0			881.23	113478		$5d^9_{3/2}6p_{3/2}\vert_2-5d^9_{3/2}7s\vert_2$
7}	5	4	{ 883.85	113141	V	$5d^9_{5/2}6s\vert_3-5d^9_{5/2}6p_{3/2}\vert_{2'}$
7}			883.94	113130	V	$5d^9_{5/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_{1'}$
0			885.75	112899		$5d^9_{3/2}6p_{3/2}\vert_2-5d^9_{3/2}7s\vert_1$
0			887.12	112724		$5d^9_{5/2}6p_{3/2}\vert_3-5d^9_{5/2}7s\vert_2$
7	5	3	888.37	112566	V	$5d^9_{3/2}6s\vert_1-5d^9_{3/2}6p_{3/2}\vert_1$
1			893.42	111929	V	$5d^9_{5/2}6p_{3/2}\vert_3-5d^9_{5/2}7s\vert_3$
8	6	4	894.40	111807	V	$5d^9_{5/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_3$
7	5		896.07	111598	V	$5d^9_{3/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_2$
1			897.67	111400		$5d^9_{5/2}6p_{3/2}\vert_{1'}-5d^9_{5/2}7s\vert_2$
10	8	7	906.61	110301	V	$5d^9_{5/2}6s\vert_3-5d^9_{5/2}6p_{3/2}\vert_4$
2	0		915.10	109278	V	$5d^9_{3/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_1$
9	6	3	915.72	109204	V	$5d^9_{5/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_{2'}$
0			918.56	108866		$5d^9_{5/2}6p_{3/2}\vert_4-?329935_4$
7	5	3	920.27	108664	V	$5d^9_{3/2}6s\vert_2-5d^9_{3/2}6p_{3/2}\vert_3$
2	1		920.87	108593	V	$5d^9_{5/2}6p_{3/2}\vert_{2'}-?332501_2$
0			921.61	108506	V	$5d^9_{5/2}6p_{3/2}\vert_4-?329573_3$
2			922.12	108446	V	$5d^9_{5/2}6p_{3/2}\vert_{2'}-?332358_2$
1			940.15	106366	V	$5d^9_{5/2}6p_{3/2}\vert_4-?327433_4$
1	1		940.72	106302	V	$5d^9_{5/2}6s\vert_3-5d^9_{3/2}6p_{1/2}\vert_{2''}$
0			943.49	105990		$5d^9_{5/2}6p_{3/2}\vert_3-?332501_2$
0		00?	944.76	105847		$5d^9_{5/2}6p_{3/2}\vert_3-?332358_2$
4	4		952.84	104949	V	$5d^9_{3/2}6s\vert_1-5d^9_{3/2}6p_{3/2}\vert_0$
7	6	5	954.34	104785	V	$5d^9_{5/2}6s\vert_2-5d^9_{3/2}6p_{1/2}\vert_{1''}$
1	1−	00?	955.42	104666	V	$5d^9_{5/2}6p_{3/2}\vert_{1'}-?332501_2$
2			956.70	104526	IV	$5d^9_{5/2}6p_{3/2}\vert_{1'}-?332358_2$
1			966.89	103424	V	$5d^9_{5/2}6p_{3/2}\vert_3-?329935_4$
2	1	0?	970.30	103061	V	$5d^9_{5/2}6p_{3/2}\vert_3-?329573_3$
5?	8C	4C	976.93?	102362	V?	$5d^9_{5/2}6s\vert_2-5d^9_{3/2}6p_{1/2}\vert_{2''}$
2			990.88	100920	V	$5d^9_{5/2}6p_{3/2}\vert_3-?327433_4$
2		0	1051.26	95123.9	V	$5d^9_{3/2}6s\vert_1-5d^9_{5/2}6p_{3/2}\vert_{1'}$
0			1057.40	94571.6	VI	$5d^9_{3/2}6p_{3/2}\vert_3-5d^9_{5/2}7s\vert_2$
5	4	2	1088.87	91838.3	V	$5d^9_{3/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_{1'}$
4	2	1d	1096.52	91197.6	V	$5d^9_{3/2}6s\vert_1-5d^9_{5/2}6p_{3/2}\vert_{2'}$
3	1	00	1104.80	90514.1	V	$5d^9_{3/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_3$
5	8−	5d−	1137.51	87911.3	V	$5d^9_{3/2}6s\vert_2-5d^9_{5/2}6p_{3/2}\vert_{2'}$
0	0		1146.45	87225.8	V	$5d^9_{3/2}6p_{3/2}\vert_1-?332501_2$
3	4	0	1148.29	87086.0	V	$5d^9_{3/2}6p_{3/2}\vert_1-?332358_2$
1			1152.40	86775.4	V	$5d^9_{3/2}6s\vert_1-5d^9_{3/2}6p_{1/2}\vert_{1''}$
9	8	8	1157.91	86362.5	V	$5d^9_{5/2}6s\vert_3-5d^9_{5/2}6p_{1/2}\vert_3$
8	6	6	1185.43	84357.6	V	$5d^9_{3/2}6s\vert_1-5d^9_{3/2}6p_{1/2}\vert_{2''}$
9	6	7	1189.93	84038.6	V	$5d^9_{5/2}6s\vert_3-5d^9_{5/2}6p_{1/2}\vert_2$
6	5	2	1197.71	83492.7	V	$5d^9_{3/2}6s\vert_2-5d^9_{3/2}6p_{1/2}\vert_{1''}$
7	6	5	1213.20	82426.6	V	$5d^9_{5/2}6s\vert_2-5d^9_{5/2}6p_{1/2}\vert_3$
10	5	3	1233.49	81070.8	V	$5d^9_{3/2}6s\vert_2-5d^9_{3/2}6p_{1/2}\vert_{2''}$
6	3	2	1248.47	80098.0	V	$5d^9_{5/2}6s\vert_2-5d^9_{5/2}6p_{1/2}\vert_2$

b Broad. C (after intensity) Uncertain; masked by a carbon line. d Diffuse. O (after intensity) Uncertain; masked by an oxygen line. − (after intensity) Unresolved blend with another line, resolved by Arvidsson.

extreme J value in each of the configurations we are considering, the intensity sum rules degenerate in this case to show that the transition $d^9s|_1-d^9p|_0$ has one-ninth the *a priori* probability of $d^9s|_3-d^9p|_4$, or, being in the same spectral region, a photographic magnitude roughly less by three. The experimental intensity values, using the above lines, which were chosen without regard to their intensities, form the quite satisfactory set:

$$5d^96s|_1-5d^96p|_0 : 5d^96s|_3-5d^96p|_4 : : 4 : 10;$$
$$5d^96p|_0-5d^97s|_1 : 5d^96p|_4-5d^97s|_3 : : 1 : 3.$$

The Γ-sum rule, or spur degeneracy, leads to the expectation that the difference between the line frequencies $5d^96s|_1-5d^96p|_0$ and $5d^96s|_3-5d^96p|_4$ depends especially smoothly upon the atomic number; or, in Goble's language, this difference is simply $\delta+\frac{1}{2}[5a_1(d^9s)-5a_1(d^9p)]$, where δ is the electrostatic energy measuring in LS coupling the interval $^3P-{}^3F$, and the difference between the values of the minus d electron's ls interaction energy $5a_1/2$ in the two configurations is ordinarily neglected.

Most fortunately, Hg ν70674 was the only unclassified mercury line on Lang's plates sufficiently strong to be considered for $5d^96s|_1-5d^96p|_0$, within 1500 cm^{-1}. This pointed to Tl ν87407, although the less likely appearing ν87573 was not eliminated until Arvidsson reported that the former was definitely a Tl IV line, whereas a study of a reproduction of one of his plates with several exposures using different inductances, shows that the latter is a pair separated by some 30 cm^{-1}, both components probably belonging to a higher stage of ionization than IV. The Bi VI

TABLE VI. *A: Energy levels and transitions in Bi VI (complete).*

Config.	J	ν(cm^{-1})	$\Delta\nu$	$5d^{10}$ 0	$5d^9_{5/2}6s$ 3	$5d^9_{5/2}6s$ 2	$5d^9_{3/2}6s$ 1	$5d^9_{3/2}6s$ 2	$5d^9_{5/2}7s$ 3	$5d^9_{5/2}7s$ 2	$5d^9_{3/2}7s$ 1	$5d^9_{3/2}7s$ 2
				0	149495*	153737*	175017	178479	426587	427483	452280	452914
			$\Delta\nu$			4242	21310	3462		896	24797	634
$5d^9_{5/2}6p_{1/2}$	2	244721*			VI 10_{18} 0	VI 4? 0	—	:	VI 3 +2	0 +3	—	—
	3	247165*	2444		VI 10b 0	VI 10_{20} 0		—	—	—		—
$5d^9_{3/2}6p_{1/2}$	2″	270603	23438		—	V 5 0	VI 8_{14} −0.4	VI 7? +2	—	0 +2	1 −1	VI 2 +1
	1″	274158	3555	V 7 +1		VI 6 0	1 +0.4	VI 4 +8.7 VI 4 +4.1 VI 4 −0.6 VI 4 −6.4		—	—	00 −9
$5d^9_{5/2}6p_{3/2}$	4	277866	3708		VI 8 0				VI 3 −2			
	2′	280939*	3073		VI 4 0	VI 7 0	—	2b −1	1 −3	1 0	—	—
	1′	284036	3097	V 10 −2		VI 5 −0.5	—	V 3b−x +1		1 0	—	—
	3	284058*	22		VI 10b +3	VI 6 −0.7		V x −21	2 +2	1 0		—
$5d^9_{3/2}6p_{3/2}$	0	? 298861	14833				VI 3 0				—	
	3	305272	6381		—	V 3 −1		VI 7 0	—	—		VI 4 −1
	1	305903	630	V 8b 0		1 +4	VI 3 −1	2d −3		—	1 0	—
	2	308613	2711		1 +14?	1 0	VI 7 −1	VI 4 0	—	—	—	0 +10

* Old level (A).[2]

? (Before energy value) Existence of level is uncertain.

TABLE VI. *B: Classified lines of Bi VI.*

Intensity	λ_{vac}	ν	z_A	Designation
8b	326.901	305903	V	$5d^{10}{}_0-5d^9_{3/2}6p_{3/2}\|_1$
10	352.070	284034	V	$5d^{10}{}_0-5d^9_{5/2}6p_{3/2}\|_{1'}$
7	364.752	274159	V	$5d^{10}{}_0-5d^9_{3/2}6p_{1/2}\|_{1''}$
0	547.15	182765		$5d^9_{5/2}6p_{1/2}\|_2-5d^9_{5/2}7s\|_2$
2	548.51	182312	VI	$5d^9_{3/2}6p_{1/2}\|_{2''}-5d^9_{3/2}7s\|_2$
3	549.85	181868	VI	$5d^9_{5/2}6p_{1/2}\|_2-5d^9_{5/2}7s\|_3$
1	550.42	181679		$5d^9_{3/2}6p_{1/2}\|_{2''}-5d^9_{3/2}7s\|_1$
00	559.45	178747		$5d^9_{3/2}6p_{1/2}\|_{1''}-5d^9_{3/2}7s\|_2$
1	628.41	159132		$5d^9_{5/2}6s\|_3-5d^9_{3/2}6p_{3/2}\|_2$?
0	637.42	156882		$5d^9_{3/2}6p_{1/2}\|_{2''}-5d^9_{5/2}7s\|_2$
1	645.68	154876		$5d^9_{5/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_2$
1	657.16	152170		$5d^9_{5/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_1$
3	659.92	151534	V	$5d^9_{5/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_3$
3	672.41	148719	VI	$5d^9_{5/2}6p_{3/2}\|_4-5d^9_{5/2}7s\|_3$
4	677.32	147641	VI	$5d^9_{3/2}6p_{3/2}\|_3-5d^9_{3/2}7s\|_2$
1	682.39	146544		$5d^9_{5/2}6p_{3/2}\|_{2'}-5d^9_{5/2}7s\|_2$
1	683.15	146381		$5d^9_{3/2}6p_{3/2}\|_1-5d^9_{3/2}7s\|_1$
1	686.60	145645		$5d^9_{5/2}6p_{3/2}\|_{2'}-5d^9_{5/2}7s\|_3$
0	692.95	144311		$5d^9_{5/2}6p_{3/2}\|_2-5d^9_{3/2}7s\|_2$
1	697.12	143447		$5d^9_{5/2}6p_{3/2}\|_{1'}-5d^9_{5/2}7s\|_2$
1	697.23	143425		$5d^9_{5/2}6p_{3/2}\|_3-5d^9_{5/2}7s\|_2$
2	701.60	142531		$5d^9_{5/2}6p_{3/2}\|_3-5d^9_{5/2}7s\|_3$
10b	743.13	134566	VI	$5d^9_{5/2}6s\|_3-5d^9_{5/2}6p_{3/2}\|_3$
7	748.53	133595	VI	$5d^9_{3/2}6s\|_1-5d^9_{3/2}6p_{3/2}\|_2$
4	760.78	131444	VI	$5d^9_{5/2}6s\|_3-5d^9_{5/2}6p_{3/2}\|_{2'}$
3	764.03	130885	VI	$5d^9_{3/2}6s\|_1-5d^9_{3/2}6p_{3/2}\|_1$
6	767.340	130320.3	VI	$5d^9_{5/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_3$
5	767.468	130298.5	VI	$5d^9_{5/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_{1'}$
4	768.44	130134	VI	$5d^9_{3/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_2$
8	778.99	128371	VI	$5d^9_{5/2}6s\|_3-5d^9_{5/2}6p_{3/2}\|_4$
2d	784.80	127421		$5d^9_{3/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_1$
7	786.15	127202	VI	$5d^9_{5/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_{2'}$
7	788.69	126793	VI	$5d^9_{3/2}6s\|_2-5d^9_{3/2}6p_{3/2}\|_3$
3	807.47	123844	VI	$5d^9_{3/2}6s\|_1-?5d^9_{3/2}6p_{3/2}\|_0$
6	830.42	120421	VI	$5d^9_{5/2}6s\|_2-5d^9_{3/2}6p_{1/2}\|_{1''}$
5	855.68	116866	V	$5d^9_{5/2}6s\|_2-5d^9_{3/2}6p_{1/2}\|_{2''}$
3b	947.35	105558	V	$5d^9_{3/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_3$; $5d^9_{3/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_{1'}$
2b	976.00	102459		$5d^9_{3/2}6s\|_2-5d^9_{5/2}6p_{3/2}\|_{2''}$
1	1008.66	99141.4		$5d^9_{3/2}6s\|_1-5d^9_{3/2}6p_{1/2}\|_{1''}$
10b	1023.860	97669.60	VI	$5d^9_{5/2}6s\|_3-5d^9_{5/2}6p_{1/2}\|_3$
4	1045.066	95687.7	VI	$5d^9_{3/2}6s\|_2-5d^9_{3/2}6p_{1/2}\|_{1''}$
4	1045.117	95683.1	VI	
4	1045.168	95678.4	VI	
4	1045.231	95672.6	VI	
8_{14}	1045.183	95585.6	VI	$5d^9_{3/2}6s\|_1-5d^9_{3/2}6p_{1/2}\|_{2''}$
10_{18}	1050.130	95226.3	VI	$5d^9_{5/2}6s\|_3-5d^9_{5/2}6p_{1/2}\|_2$
10_{20}	1070.34	93428.2	VI	$5d^9_{5/2}6s\|_2-5d^9_{5/2}6p_{1/2}\|_3$
7?	1085.47	92126.0	IIIa VI	$5d^9_{3/2}6s\|_2-5d^9_{3/2}6p_{1/2}\|_{2''}$
4?	1099.09	90984.3	VI	$5d^9_{5/2}6s\|_2-5d^9_{5/2}6p_{1/2}\|_2$

a Found in the bismuth arc. b Broad. d Diffuse. ? (after designation) Wave number discrepancy casts doubt upon designation.

line chosen as $5d^96s|_1-5d^96p|_0$ seemed by far the most probable choice on purely experimental grounds (intensity and z_A) though unfortunately $5d^96p|_0-5d^97s|_1$, which might have been hoped for, is not in Arvidsson's list. A difficulty with this choice in Bi VI is treated in the next paragraph. Extrapolation back to Au II by third differences predicted $5d^96s|_1-5d^96p|_0$ at about ν53943 instead of MMC's ν54848. Trial with the nearest line, 37 cm^{-1} away, led to the discovery of the $5d^96p|_0$ level shown in Table II. Even objectively considering the Au II spectrum alone, this level appears more convincing than the one repudiated.

TABLE VII.

Calculated:							
$F(d^9s)\leftarrow F(d^9p)$	$13/2\leftarrow 11/2$		$11/2\leftarrow 9/2,\ 11/2$		$9/2\leftarrow 7/2,\ 9/2,\ 11/2$		$\begin{cases} 7/2\leftarrow 7/2,\ 9/2 \\ 5/2\leftarrow 7/2 \end{cases}$
$\nu-\nu_0$	0		$6\frac{1}{2}A_s-3\frac{1}{4}A_p$		$12A_s-34/9A_p$		$18A_s-33/7A_p$
Intensity (energy)	(7)		(6)		(5)		(7)
$\Delta\nu$		$6.50A_s-3.25A_p$		$5.50A_s-0.53A_p$		$6.00A_s-0.96A_p$	
Observed:							
Intensity (blackening)	(4)		(4)		(4)		(4)
$\Delta\nu$		5.8 cm^{-1}		4.7 cm^{-1}		4.6 cm^{-1}	
$\therefore A_s$		+0.75 cm^{-1}		+0.83 cm^{-1}		+0.72 cm^{-1}	

Goble's graph[4] (Fig. 4) of the parameters separately calculated with the aid of data from this paper shows that, although the dependence of each upon Z appears quite smooth, three of them, *viz.* γ, δ and ϵ, decrease in magnitude between Pb V and Bi VI. Though perhaps not out of the question, such a decrease is surprising. The equations used in evaluating γ and ϵ from the experimental data involved these quantities only in the sums $\delta+\gamma$ and $\delta+\epsilon$ respectively, so an increase in the magnitude of the negative quantity δ would automatically have increased the magnitudes of γ and ϵ simultaneously. The desirability of this triple change leads one to suspect that either the Bi VI $5d^96s|_1-5d^96p|_0$ line has somewhat ($\sim 10^3$ cm^{-1}) higher frequency than the ν123844 selected by us, or the approximation achieved in Goble's theory is insufficient to render this detail intelligible (e.g., perhaps $a_1(d^9p)\neq a_1(d^9s)$, masking the behavior of δ). The fairly strong evidence of the Bi VI data, together with the previously mentioned constancy of the differences, favors the latter alternative.

On the strength of all the above discussion, we feel justified in calling all the $5d^96p|_0$ levels in the sequence pretty well established except perhaps the one in Bi VI.

Hyperfine structure in Bi VI. Several of Arvidsson's Bi VI lines show noticeable breadth, as indicated by the letter b or by a numerical subscript giving the approximate breadth in cm^{-1}, accompanying the intensity. Only one of them, $5d^9{}_{3/2}6s|_2-5d^9{}_{3/2}6p_{1/2}|_{1''}$, is partly resolved, but from that one we may obtain an indication of the magnitude of the hyperfine structure splitting factor $a(6s_{1/2})$. Values in cm^{-1} of certain splitting factors in the bismuth spectra are as follows:[8,9]

	Bi I	II	III	IV	V	VI
$a(6p_{1/2})$	0.375	0.464	0.66			(1.1±0.4)
$a(6s_{1/2})$		1.60	1.80	2.34	2.6	*3.1±0.2*

Assuming the $a(6p_{1/2})$ value in parentheses (which was obtained by extrapolation) and the negligibility of $a(5d^9{}_{3/2})$, we shall now derive the $a(6s)$ value shown in italics.[10] We are justified in assuming jj coupling, so the levels' splitting factors have the following values:

$$A(5d^9{}_{3/2}6p_{1/2}|_1)(\equiv A_p)=-\tfrac{1}{4}a(6p_{1/2}),$$
$$A(5d^9{}_{3/2}6s|_2)(\equiv A_s)=+\tfrac{1}{4}a(6s).$$

Instead of showing five components on account of the predominance of A_s, it is not surprising that the line appeared to Arvidsson in only four, for, on account of the negative value of A_p, the two closest (and faintest) groups come within $3\frac{1}{2}A_s-10|A_p|$ of each other. Calculating the intensities of the nine individual components by the Kronig-Russell-Sommerfeld-Hönl-Dirac formulas, and assuming that Arvidsson measured the centers of gravity of the energy distributions, we have the groupings given in Table VII, measuring from the strongest (lowest frequency) component. From the data given there, we obtain:

$$a(6s_{\frac{1}{2}})=4A_s=3.1\text{cm}^{-1}\pm\sim 6 \text{ percent}.$$

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

[9] A. B. McLay and M. F. Crawford, Phys. Rev. **44**, 986 (1933).

[10] But our results are almost independent of these assumptions. For instance, had we neglected the splitting of the d^9p term entirely ($A_p=0$, below) the mean result for $a(6s_{1/2})$ would have been 3.35 cm^{-1}. The $J=1$ levels of the interesting groups $5d^9{}_{3/2}6s^26p_{1/2}|_{1,\,2}$ and $5d^9{}_{5/2}6s^26p_{3/2}|_{1,\,2,\,3,\,4}$ in Bi IV, as identified by McLay and Crawford[9] (misled by Mack, cf. Table IV A, footnote §), show hyperfine splitting of $+1.5\pm0.4$ and -1.5 ± 0.5 cm^{-1}, respectively, which appears to lead to a negative value of $a(6p_{1/2})$. These levels, however, have a distribution strikingly (but not surprisingly) similar to that of the same groups minus the $6s^2$ shell, in Tl IV, and Goble[4] shows that just these Tl IV levels are badly intermingled. So the only conclusion we can draw about the a's from the splitting of these Bi IV levels is that $-a(6p_{1/2})-3a(6p_{3/2})+5a(5d^9{}_{3/2})+7a(5d^9{}_{5/2})=0\pm3.6$ cm^{-1}. The Bi VI level with which we are concerned is much more nearly pure $5d^9{}_{3/2}6p_{1/2}$.