The Classification of the First Spark Spectrum of Lead: Pb II

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The spectrum of Pb II as excited in a Schüler hollow cathode discharge in helium has been photographed in the region from 800A to 10,000A. With these data the classification given by Fraülein H. Gieseler (Zeits. f. Physik **42**, 265 (1927)) has been corrected and extended. 247 lines have been classified, which locate 89 levels below the ionization level of the ion. These include the *s*, *p*, *d*, *f* and *g* series based on $6s^2$, extending to values of n of from 14 to 19, and all levels of the other configurations which are expected below ionization. The assignment of these levels is checked by series considerations, by Zeeman effect data, by hyperfine structure data, by comparison with the similar spectra Ge II and Sn II, and by the agreement with the regular and irregular doublet laws in the isoelectronic sequence with Tl I and Bi III. The observed anomalous location of a number of the levels is shown to be explained qualitatively by the perturbations expected between the even levels.

MEASUREMENTS of the lead spectrum have been obtained by various experimenters, notably Eder and Valenta,[1] Exner and Haschek,[2] Thalén,[3] and Klein[4] in the visible and ultraviolet, Randall[5] in the infrared, and Carroll,[6] Lang,[7] and Arvidsson[8] in the vacuum region. The sources used in these investigations included arc in air and vacuum, spark in air and vacuum, and electrodeless discharge. The only important work on the classification of the Pb II spectrum was done by Fraülein H. Gieseler.[9] She photographed the ultraviolet and visible region of the emission from a Schüler hollow cathode tube and supplemented these data with vacuum region measurements by various workers. 72 lines were used to establish 36 levels, several of which appear to be erroneous in the light of the present investigation.

Theory predicts the level $6s^26p\ ^2P_{\frac{1}{2}}$ as the lowest state of singly ionized lead. Predicted excited states include the several series *ms*, *mp*, *md*, *mf*, $\cdots$ when both $6s$ electrons remain unexcited; and, when one of these is raised to an excited state, configurations of the types $6s6p^2$, $6s6p6d$, $6s6d^2$, etc. By a consideration of the energy values in Pb III[11] corresponding to the excitation of a $6s$ electron to $6p$, $6d$, etc., states, it becomes apparent that the levels from $6s6p6d$, $6s6d^2$, etc., lie considerably above the ionization potential of Pb II. The same is true of the possible configurations $6s6p7s$, etc., on the basis of a Ritzian formula calculation. This leaves only the $6s^2mx$ series and the $6s6p^2$ levels to be expected below ionization. The $6s6p^2$ configuration gives rise to the eight levels $^4P_{\frac{1}{2},\,1\frac{1}{2},\,2\frac{1}{2}}$, $^2D_{1\frac{1}{2},\,2\frac{1}{2}}$, $^2P_{\frac{1}{2},\,1\frac{1}{2}}$, and $^2S_{\frac{1}{2}}$ in Russell-Saunders notation, and of course to an equal number of levels in any coupling.

EXPERIMENTAL

The excitation produced in a Schüler hollow cathode discharge in a rare gas atmosphere tends to be limited by the energy of the reactions between metal ions and metastable rare gas atoms, or between metal atoms and rare gas ions.[10] Since the ionization energy of Pb I is about 60,000 cm^{-1} and that of Pb II about 120,000 cm^{-1}, it is evident that a discharge in helium (metastable state 160,000 cm^{-1}; ionization energy 198,000 cm^{-1}) should excite all levels of Pb II, but none of Pb III. Hence this arrangement was chosen as a source in the present investigation. Two mercury vapor pumps in series circulated helium through the discharge tube and suitable liquid air and charcoal traps. A high voltage direct-current generator served as a source of potential (700 to 1000 volts), but the ballast resistance in series with the discharge decreased considerably the effective voltage at the terminals of the tube. The current used was approximately 125 m.a. Cathodes of molybdenum and of iron

[1] Eder and Valenta, Wellenlängenmessungen, Wien, Ber. **119**, 519 (1910).
[2] Exner and Haschek, Wellenlängentabellen, Leipzig, 1904.
[3] Thalén, Nova acta reg. soc sc. Upsal. **3**, 6 (1868).
[4] Klein, Zeits. f. Wiss. Phot. **12**, 16 (1913).
[5] Randall, Astrophys. J. **34**, 1 (1911).
[6] Carroll, Trans. Roy. Soc. **A225**, 357 (1925).
[7] Lang, Trans. Roy. Soc. **A224**, 371 (1924).
[8] Arvidsson, Ann. d. Physik **12**, 787 (1932).
[9] Gieseler, Zeits. f. Physik **42**, 265 (1927).
[10] Sawyer, Phys. Rev. **36**, 44 (1930).

were used at different times. In each case a few of the strongest lines due to the cathode material showed in the emission. The lead (chemically pure) was laid within the cylindrical cathode in small pieces which promptly melted in the heat of the discharge. Photographs were taken under two conditions of discharge. In the first the discharge was started in the normal helium pressure. The inflow of helium was then almost completely shut off, and within a few seconds the pumps removed the helium to a point at which the discharge changed from a yellowish appearance to a deep blue. Under these conditions it appeared that the discharge was carried primarily by the lead vapor; the helium lines remained, but were considerably weakened. This method of operation gave a number of lines which are classified by Smith[11] as Pb III and Pb IV. The second condition of discharge involved the continued circulation of the helium throughout the time of the photograph; in this case the lines due to higher ionization were much weaker or entirely absent.

The spectrum was photographed from 800A to 10,000A. From 800A to 2400A a normal incidence concave grating vacuum spectrograph was used. This instrument[12] (1 m radius, 14,400 lines per inch) had a dispersion of about 17A/mm. Between 2100A and 5500A two Hilger quartz instruments were used (types E–1 and E–3), and from 5100A to 10,000A a spectrograph of design similar to the E–1, with glass optical system, was utilized. In the vacuum photographs He, Hg and H lines appeared as impurity lines and were used as standards. Iron arc comparison spectra were applied to all other photographs except those in the infrared, where a neon tube was used. In addition, plates from the first order of a 21-foot concave grating, covering the region 2200A to 10,000A, were kindly loaned by Dr. J. L. Rose, of New York University. The excitation for these photographs was also a hollow cathode discharge in helium. All plates were measured on a Gaertner comparator. The calculated wavelengths in air were reduced to wave numbers by means of Kayser's table. For wavelengths greater than 2100A the wave number values are probably correct to about one wave per centimeter; for shorter wavelengths the error may be as high as 10 or 15 cm^{-1}, especially for weak lines.

Data and Classification

The above experimental work provided 340 lines in the vacuum region (ν185,000 to ν47,000) and about 730 lines in the region from ν47,000 to ν10,000. About 60 of the strongest of these lines have been classified by Gieseler and Grotrian[13] in Pb I, and a smaller number by Smith[11] and others in Pb III or Pb IV. The 247 lines now classified in Pb II are listed in Table I. Fourteen of these lines, lying in the vacuum region, were also observed by Arvidsson.[8] His measurements, which are more accurate than is claimed for the vacuum data of the present work, are included in Table I and used for the location of the $6p\,^2P$ levels. The classified lines determine 89 levels; these are tabulated in Table II, with their effective quantum numbers in the case of series members. It will be noted that the effective quantum numbers of the two odd series $6s^2mp\,^2P$ and $6s^2mf\,^2F$ are very regular as they approach a limiting value for large m, though all ^2F members are inverted. The even series $6s^2mg\,^2G$ is also regular; its doublets are unresolved. The other two even series $6s^2ms\,^2S$ and $6s^2md\,^2D$ show pronounced irregularities in the lower members; these irregularities are explained below in terms of perturbations from the intermingling levels from the $6s6p^2$ configuration.

In determining the ionization potential of Pb II, use has been made of the series limits of the ^2F and ^2G series; these limits are located to within less than 1 cm^{-1}. Thus the value of the ionization potential (121,243 cm^{-1}) is determined within the error involved in the vacuum data on transitions to the lowest term $6s^26p\,^2P_{\frac{1}{2}}$. By using Arvidsson's data[8] for these lines (for which his estimate of probable error is 2 or 3 cm^{-1}), the ionization potential is correct to 2 or 3 cm^{-1}. The location of the next series, $6s^2mh\,^2H$, could be predicted very closely, but transitions from the low members were out of experimental range, and those from the higher members were not observed.

Comparison of the Pb II spectrum with the similar spectra of Ge II[14] and Sn II[14] has been

[11] Smith, Phys. Rev. **34**, 393 (1926); **36**, 1 (1930).
[12] Sawyer, J. O. S. A. **15**, 307 (1927).
[13] Gieseler and Grotrian, Zeits. f. Physik **39**, 377 (1926).
[14] Bacher and Goudsmit, *Atomic Energy States* (1932).

TABLE I. *Classified lines in Pb II.*

Classification	λ(A)	ν(cm⁻¹)	Intensity	Δν	Notes
$7D_{1\frac{1}{2}} - 9P_{\frac{1}{2}}$	9864.2	10139	00	−1	
$5G - 9F_{2\frac{1}{2}}$	9440.1	10593	1	−2	
$5F_{2\frac{1}{2}} - 5G$	9063.7	11030	10	0	$x\ h_0$
$5F_{3\frac{1}{2}} - 5G$	9050.7	11045	10	0	$x\ h_0$
$8D_{2\frac{1}{2}} - 10F_{3\frac{1}{2}}$	8723.1	11461	3	2	
$9P_{\frac{1}{2}} - 12D_{1\frac{1}{2}}$	8721.3	11463	0	0	
$6F_{2\frac{1}{2}} - 8G$	8719.7	11465	5	0	h_0
$6F_{3\frac{1}{2}} - 8G$	8710.1	11478	7	0	h_0
$8P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	8550.6	11692	2	0	
$7P_{1\frac{1}{2}} - p^2\,{}^2D_{2\frac{1}{2}}$	8545.0	11699	7	1	h_6
$7P_{1\frac{1}{2}} - 8S_{\frac{1}{2}}$	8395.6	11908	10	0	h_{12}
$p^2\,{}^2D_{1\frac{1}{2}} - 8P_{\frac{1}{2}}$	8335.0	11994	6	1	h_7
$8D_{1\frac{1}{2}} - 10F_{2\frac{1}{2}}$	8152.0	12263	0	0	
$9P_{\frac{1}{2}} - 13D_{1\frac{1}{2}}$	8013.0	12476	00	1	
$8D_{2\frac{1}{2}} - 11F_{3\frac{1}{2}}$	7973.2	12538	00	0	
$9P_{1\frac{1}{2}} - 14D_{2\frac{1}{2}}$	7906.8	12644	0	2	
$8P_{\frac{1}{2}} - 10S_{\frac{1}{2}}$	7777.8	12853	2	0	
$6F_{2\frac{1}{2}} - 9G$	7739.8	12916	2	0	h_0
$6F_{3\frac{1}{2}} - 9G$	7732.3	12930	4	−1	h_0
$8P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$	7679.4	13018	1	1	
$6F_{3\frac{1}{2}} - 12D_{2\frac{1}{2}}$	7664.8	13043	0	1	
$8P_{1\frac{1}{2}} - 9D_{2\frac{1}{2}}$	7632.2	13098	10	0	h_0
$7D_{2\frac{1}{2}} - 7F_{3\frac{1}{2}}$	7558.7	13226	10	−1	h_{13}
$7D_{2\frac{1}{2}} - 7F_{2\frac{1}{2}}$	7553.7	13234	1	0	
$8D_{2\frac{1}{2}} - 12F_{3\frac{1}{2}}$	7499.6	13330	00	0	
$p^2\,{}^2D_{2\frac{1}{2}} - 6F_{3\frac{1}{2}}$	7193.6	13897	20	−1	h_6
$p^2\,{}^2D_{2\frac{1}{2}} - 6F_{2\frac{1}{2}}$	7187.1	13910	2	−1	
$6F_{2\frac{1}{2}} - 10G$	7165.1	13953	2	−1	h_0
$6F_{3\frac{1}{2}} - 10G$	7158.7	13965	2	0	h_0
$6F_{3\frac{1}{2}} - 13D_{2\frac{1}{2}}$	7114.7	14051	0	1	
$8P_{\frac{1}{2}} - 9D_{1\frac{1}{2}}$	7050.7	14179	9	1	h_0
$7D_{1\frac{1}{2}} - 7F_{2\frac{1}{2}}$	7013.2	14255	10	−1	$xxx\ h_0$
$7D_{2\frac{1}{2}} - 10P_{1\frac{1}{2}}$	6872.0	14548	0	−1	
$6F_{2\frac{1}{2}} - 11G$	6791.7	14720	2	−1	h_0
$7P_{\frac{1}{2}} - 8S_{\frac{1}{2}}$	6790.8	14722	10	−1	h_{12}
$6F_{3\frac{1}{2}} - 11G$	6785.9	14732	3	0	h_0
$7S_{\frac{1}{2}} - 7P_{\frac{1}{2}}$	6660.0	15011	50	0	$x\ h_8\ Z$
$7D_{1\frac{1}{2}} - 10P_{\frac{1}{2}}$	6569.4	15218	5	−2	
$8S_{\frac{1}{2}} - 9P_{\frac{1}{2}}$	6558.7	15243	3	−1	
$6F_{2\frac{1}{2}} - 12G$	6533.1	15302	4	0	h_0
$6F_{3\frac{1}{2}} - 12G$	6527.8	15315	5	0	h_0
$8P_{1\frac{1}{2}} - 11S_{\frac{1}{2}}$	6518.2	15337	8	−1	h_0
$7D_{1\frac{1}{2}} - 10P_{1\frac{1}{2}}$	6422.9	15565	0	2	
$6F_{2\frac{1}{2}} - 13G$	6345.0	15756	5	0	h_0
$6F_{3\frac{1}{2}} - 13G$	6339.8	15769	3	0	h_0
$8S_{\frac{1}{2}} - 9P_{1\frac{1}{2}}$	6311.5	15840	9	0	
$p^2\,{}^2D_{2\frac{1}{2}} - 9P_{1\frac{1}{2}}$	6229.7	16048	10	0	h_6
$6F_{2\frac{1}{2}} - 14G$	6203.7	16115	1*d*	0	h_0
$6F_{3\frac{1}{2}} - 14G$	6198.8	16128	1*d*	0	h_0
$8P_{1\frac{1}{2}} - 10D_{1\frac{1}{2}}$	6181.9	16172	7	−1	h_0 (*a*)
$8P_{1\frac{1}{2}} - 10D_{2\frac{1}{2}}$	6160.0	16229	10	0	h_0
$6F_{2\frac{1}{2}} - 15G$	6094.0	16405	0*d*	0	h_0
$6F_{3\frac{1}{2}} - 15G$	6089.4	16418	1	0	h_0
$5F_{2\frac{1}{2}} - 6G$	6081.5	16439	40	0	$x\ h_0$
$5F_{3\frac{1}{2}} - 6G$	6075.8	16454	40	0	$x\ h_0$
$8P_{\frac{1}{2}} - 11S_{\frac{1}{2}}$		16497 (calc.)			(*b*)
$p^2\,{}^4P_{\frac{1}{2}} - 7P_{\frac{1}{2}}$	6041.4	16548	8*d*	0	$h_{7'}$
$7D_{2\frac{1}{2}} - 8F_{3\frac{1}{2}}$	6009.7	16635	9	1	h_{13}
$7D_{2\frac{1}{2}} - 8F_{2\frac{1}{2}}$	6007.5	16641	2	1	
$7P_{1\frac{1}{2}} - 7D_{1\frac{1}{2}}$	5876.7	17011	10	1	$xxx\ h_0\ Z$ (*c*)
$8P_{\frac{1}{2}} - 10D_{1\frac{1}{2}}$	5767.9	17333	10	−1	h_0
$7D_{2\frac{1}{2}} - 11P_{1\frac{1}{2}}$	5713.8	17496	4	0	
$7D_{1\frac{1}{2}} - 8F_{2\frac{1}{2}}$	5660.1	17663	2	−1	
$7S_{\frac{1}{2}} - 7P_{1\frac{1}{2}}$	5608.8	17824	10	0	$x\ h_8\ Z$
$7P_{1\frac{1}{2}} - 7D_{2\frac{1}{2}}$	5544.6	18031	10	1	$h_{14}\ Z$ (*d*)
$8P_{1\frac{1}{2}} - 11D_{1\frac{1}{2}}$	5483 ?	18230?	000		
$8P_{1\frac{1}{2}} - 11D_{2\frac{1}{2}}$	5472.4	18268	7	1	$xxx\ h_0$
$p^2\,{}^4P_{2\frac{1}{2}} - 5F_{3\frac{1}{2}}$	5372.1	18608	10	1	$xx\ h_1\ Z$
$p^2\,{}^4P_{2\frac{1}{2}} - 5F_{2\frac{1}{2}}$	5367.3	18624	10	0	$xx\ h_1$
$8P_{\frac{1}{2}} - 12S_{\frac{1}{2}}$	5308.2	18834	3	1	h_0
$7D_{2\frac{1}{2}} - 9F_{3\frac{1}{2}}$	5306.8	18839	6	2	h_{13}
$8P_{1\frac{1}{2}} - 13S_{\frac{1}{2}}$	5191.4	19257	1	1	
$p^2\,{}^4P_{\frac{1}{2}} - 7P_{1\frac{1}{2}}$	5163.8	19360	7	1	$h_{7'}$ (*e*)
$8P_{\frac{1}{2}} - 11D_{1\frac{1}{2}}$	5155.8	19390	7	−1	h_0
$p^2\,{}^2D_{2\frac{1}{2}} - 7F_{3\frac{1}{2}}$	5111.9	19557	10	0	h_6
$p^2\,{}^2D_{2\frac{1}{2}} - 7F_{2\frac{1}{2}}$	5109.6	19566	3	0	h_6
$8P_{1\frac{1}{2}} - 12D_{1\frac{1}{2}}$		19647 (calc.)			(*f*)
$8P_{1\frac{1}{2}} - 12D_{2\frac{1}{2}}$	5081.2	19675	3	−1	h_0
$5F_{2\frac{1}{2}} - 7G$	5074.6	19700	10	1	$x\ h_0$
$5F_{3\frac{1}{2}} - 7G$	5070.7	19716	10	0	$x\ h_0$
$p^2\,{}^2D_{1\frac{1}{2}} - 6F_{2\frac{1}{2}}$	5049.3	19799	9	−1	h_7
$7P_{\frac{1}{2}} - 7D_{1\frac{1}{2}}$	5042.5	19825	50	0	$xxx\ h_0\ Z$
$7D_{1\frac{1}{2}} - 9F_{2\frac{1}{2}}$	5032.2	19866	6	0	
$7D_{1\frac{1}{2}} - 12P_{\frac{1}{2}}$	4924.9	20299	1	2	
$8S_{\frac{1}{2}} - 10P_{\frac{1}{2}}$	4920.4	20318	1	2	
$7D_{2\frac{1}{2}} - 10F_{3\frac{1}{2}}$	4912.7	20350	3	−1	h_{13}
$8P_{\frac{1}{2}} - 13S_{\frac{1}{2}}$	4895.6	20421	2	−2	
$8P_{1\frac{1}{2}} - 13D_{1\frac{1}{2}}$	4838.6	20661	0	0	
$8S_{\frac{1}{2}} - 10P_{1\frac{1}{2}}$	4836.3	20671	6	0	
$8P_{1\frac{1}{2}} - 13D_{2\frac{1}{2}}$	4833.7	20682	5	0	h_0
$8P_{\frac{1}{2}} - 12D_{1\frac{1}{2}}$	4804.5	20808	8	0	h_0
$p^2\,{}^2D_{2\frac{1}{2}} - 10P_{1\frac{1}{2}}$	4788.1	20879	6	0	h_6
$p^2\,{}^2D_{1\frac{1}{2}} - 9P_{\frac{1}{2}}$	4684.9	21339	5	0	h_7
$7D_{1\frac{1}{2}} - 10F_{2\frac{1}{2}}$	4677.8	21372	7	1	
$8P_{1\frac{1}{2}} - 14D_{1\frac{1}{2}}$	4668.9	21412	0	0	
$7D_{2\frac{1}{2}} - 11F_{3\frac{1}{2}}$	4666.5	21423	1	1	
$8P_{1\frac{1}{2}} - 14D_{2\frac{1}{2}}$	4665.5	21428	5	0	h_0
$5F_{2\frac{1}{2}} - 8G$	4582.3	21817	10	0	$x\ h_0$
$8P_{\frac{1}{2}} - 13D_{1\frac{1}{2}}$	4581.3	21822	4	0	h_0
$5F_{3\frac{1}{2}} - 8G$	4579.1	21832	10	0	$x\ h_0$
$p^2\,{}^2D_{1\frac{1}{2}} - 9P_{1\frac{1}{2}}$	4557.2	21937	2	0	h_7
$8P_{1\frac{1}{2}} - 15D_{2\frac{1}{2}}$	4544.8	21997	4	0	h_0
$7D_{2\frac{1}{2}} - 12F_{3\frac{1}{2}}$	4499.6	22218	0	−2	
$p^2\,{}^4P_{2\frac{1}{2}} - 8P_{1\frac{1}{2}}$	4476.3	22334	3	−1	h_1
$8P_{1\frac{1}{2}} - 16D_{2\frac{1}{2}}$	4454.9	22441	1	0	h_0
$7D_{1\frac{1}{2}} - 11F_{2\frac{1}{2}}$	4453.8	22446	3	0	
$8P_{\frac{1}{2}} - 14D_{1\frac{1}{2}}$	4428.7	22574	2	−1	h_0
$6D_{1\frac{1}{2}} - 5F_{2\frac{1}{2}}$	4386.4	22791	20	−2	$x\ h_4\ Z$
$8P_{1\frac{1}{2}} - 17D_{2\frac{1}{2}}$	4386.0	22793	2	0	
$p^2\,{}^2D_{2\frac{1}{2}} - 8F_{3\frac{1}{2}}$	4352.7	22968	10	0	h_6
$p^2\,{}^2D_{2\frac{1}{2}} - 8F_{2\frac{1}{2}}$	4351.5	22974	3	0	
$8P_{1\frac{1}{2}} - 18D_{2\frac{1}{2}}$	4332.2	23077	0	0	
$8P_{\frac{1}{2}} - 15D_{1\frac{1}{2}}$	4319.2	23146	1	0	h_0
$7D_{1\frac{1}{2}} - 12F_{2\frac{1}{2}}$	4302.1	23238	1	0	
$5F_{2\frac{1}{2}} - 9G$	4296.6	23268	6	0	$x\ h_0$
$5F_{3\frac{1}{2}} - 9G$	4293.8	23283	7	0	$x\ h_0$
$8P_{1\frac{1}{2}} - 19D_{2\frac{1}{2}}$	4288.9	23310	00	0	
$8S_{\frac{1}{2}} - 11P_{\frac{1}{2}}$	4272.5	23399	3	−1	(*g*)
$6D_{2\frac{1}{2}} - 5F_{3\frac{1}{2}}$	4245.1	23550	20	0	$x\ h_2\ Z$
$6D_{2\frac{1}{2}} - 5F_{2\frac{1}{2}}$	4242.5	23565	9	0	$x\ h_2\ Z$
$8P_{\frac{1}{2}} - 16D_{1\frac{1}{2}}$	4237.6	23591	0	0	h_0
$8S_{\frac{1}{2}} - 11P_{1\frac{1}{2}}$	4232.4	23620	2	0	
$p^2\,{}^2D_{2\frac{1}{2}} - 11P_{1\frac{1}{2}}$	4195.5	23828	3	0	h_6
$7D_{1\frac{1}{2}} - 13F_{2\frac{1}{2}}$	4193.7	23838	00	0	
$8P_{\frac{1}{2}} - 17D_{1\frac{1}{2}}$	4175.0	23945	00	0	
$7P_{1\frac{1}{2}} - 9S_{\frac{1}{2}}$	4152.8	24073	10	1	$x\ h_9\ Z$
$5F_{2\frac{1}{2}} - 10G$	4113.4	24304	4	0	$x\ h_0$
$5F_{3\frac{1}{2}} - 10G$	4110.8	24319	5	0	$x\ h_0$
$5F_{2\frac{1}{2}} - 11G$	3987.6	25070	2	1	$x\ h_0$
$5F_{3\frac{1}{2}} - 11G$	3985.2	25086	2	0	$x\ h_0$
$p^2\,{}^2D_{2\frac{1}{2}} - 9F_{3\frac{1}{2}}$	3971.3	25174	4	−1	h_6
$p^2\,{}^2D_{1\frac{1}{2}} - 7F_{2\frac{1}{2}}$	3927.3	25456	6	−1	h_7
$5F_{2\frac{1}{2}} - 12G$	3896.9	25654	0	0	
$5F_{3\frac{1}{2}} - 12G$	3894.6	25669	1	0	
$p^2\,{}^2D_{2\frac{1}{2}} - 12P_{1\frac{1}{2}}$	3880.5	25763	0	0	
$5F_{2\frac{1}{2}} - 13G$	3829.2	26108	0	0	
$7P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	3827.2	26121	3	1	$h_{10}\ Z$
$p^2\,{}^4P_{1\frac{1}{2}} - 5F_{2\frac{1}{2}}$	3785.9	26406	10	−1	$xx\ h_3\ Z$
$p^2\,{}^2D_{1\frac{1}{2}} - 10P_{\frac{1}{2}}$	3784.0	26419	2	−2	
$6D_{1\frac{1}{2}} - 8P_{1\frac{1}{2}}$	3772.9	26497	00	1	
$p^2\,{}^2D_{2\frac{1}{2}} - 10F_{3\frac{1}{2}}$	3746.9	26681	4	0	h_6
$p^2\,{}^2D_{1\frac{1}{2}} - 10P_{1\frac{1}{2}}$	3734.8	26767	2	1	
$7P_{\frac{1}{2}} - 9S_{\frac{1}{2}}$	3718.2	26887	7	0	$x\ h_9\ Z$
$7P_{1\frac{1}{2}} - 8D_{2\frac{1}{2}}$	3714.0	26918	10	0	$h_0\ Z$
$7P_{1\frac{1}{2}} - p^2\,{}^2S_{\frac{1}{2}}$	3699.2	27025	2	0	h_{21}
$p^2\,{}^2D_{2\frac{1}{2}} - 13P_{1\frac{1}{2}}$	3689.0	27100	0	0	(*i*)
$6D_{2\frac{1}{2}} - 8P_{1\frac{1}{2}}$	3665.6	27273	4	1	h_2
$7P_{1\frac{1}{2}} - p^2\,{}^2P_{1\frac{1}{2}}$	3649.0	27397	3	0	h_{11}
$p^2\,{}^2D_{2\frac{1}{2}} - 11F_{3\frac{1}{2}}$	3601.8	27756	3	0	h_6
$p^2\,{}^2D_{2\frac{1}{2}} - 12F_{3\frac{1}{2}}$	3501.9	28548	2	0	h_6
$p^2\,{}^2D_{1\frac{1}{2}} - 8F_{2\frac{1}{2}}$	3463.6	28863	6	0	h_7
$7P_{\frac{1}{2}} - 8D_{1\frac{1}{2}}$	3455.0	28935	8	0	$h_{10}\ Z$
$p^2\,{}^4P_{1\frac{1}{2}} - 8P_{\frac{1}{2}}$	3453.0	28952	0	1	
$p^2\,{}^4P_{2\frac{1}{2}} - 6F_{3\frac{1}{2}}$	3451.7	28963	9	0	$xx\ h_1\ Z$
$p^2\,{}^4P_{2\frac{1}{2}} - 6F_{2\frac{1}{2}}$	3450.0	28976	2	0	$xx\ h_1$
$p^2\,{}^2D_{2\frac{1}{2}} - 13F_{3\frac{1}{2}}$	3429.6	29149	1	0	
$p^2\,{}^2D_{1\frac{1}{2}} - 11P_{\frac{1}{2}}$	3389.4	29495	2	0	h_7
$p^2\,{}^2D_{2\frac{1}{2}} - 14F_{3\frac{1}{2}}$	3375.6	29616	00	0	
$7P_{\frac{1}{2}} - p^2\,{}^2S_{\frac{1}{2}}$	3350.5	29838	00	0	
$7P_{\frac{1}{2}} - p^2\,{}^2P_{1\frac{1}{2}}$	3309.2	30210	6	0	h_{11}
$7P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	3261.0	30656	6	2	h_0
$p^2\,{}^2D_{1\frac{1}{2}} - 9F_{2\frac{1}{2}}$	3217.9	31067	3	0	h_7
$p^2\,{}^4P_{2\frac{1}{2}} - 9P_{1\frac{1}{2}}$	3213.0	31114	00	1	
$p^2\,{}^2D_{1\frac{1}{2}} - 12P_{\frac{1}{2}}$	3173.5	31502	0	0	
$7P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$	3125.6	31985	6	0	h_0
$7P_{1\frac{1}{2}} - 9D_{2\frac{1}{2}}$	3117.7	32064	10	0	h_0
$p^2\,{}^2D_{1\frac{1}{2}} - 10F_{2\frac{1}{2}}$	3068.5?	32574?	2		h_7 (*j*)
$p^2\,{}^2D_{1\frac{1}{2}} - 13P_{\frac{1}{2}}$	3039.9	32886	00	−2	
$6D_{1\frac{1}{2}} - 6F_{2\frac{1}{2}}$	3016.4	33142	10	−1	$x\ h_4\ Z$
$7P_{\frac{1}{2}} - 10S_{\frac{1}{2}}$	2986.9	33470	4	1	h_0
$p^2\,{}^2D_{1\frac{1}{2}} - 11F_{2\frac{1}{2}}$	2971.1	33647	0	0	
$p^2\,{}^2D_{1\frac{1}{2}} - 14P_{\frac{1}{2}}$	2951.3	33873	00	2	
$6D_{2\frac{1}{2}} - 6F_{3\frac{1}{2}}$	2948.5	33905	10	−1	$x\ h_2\ Z$
$6D_{2\frac{1}{2}} - 6F_{2\frac{1}{2}}$	2947.5	33918	2	−1	$x\ h_2$
$7P_{1\frac{1}{2}} - 11S_{\frac{1}{2}}$	2914.5	34302	3	0	h_0
$p^2\,{}^4P_{2\frac{1}{2}} - 7F_{3\frac{1}{2}}$	2887.3	34624	3	0	$xx\ h_1$
$7P_{\frac{1}{2}} - 9D_{1\frac{1}{2}}$	2873.0	34797	4	1	h_0
$7P_{1\frac{1}{2}} - 10D_{1\frac{1}{2}}$	2845.2	35136	1	1	h_0
$7P_{1\frac{1}{2}} - 10D_{2\frac{1}{2}}$	2840.6	35194	6	1	h_0
$7S_{\frac{1}{2}} - 8P_{\frac{1}{2}}$	2805.9	35628	00	1	
$6D_{2\frac{1}{2}} - 9P_{1\frac{1}{2}}$	2772.7	36055	1	1	h_2
$7P_{1\frac{1}{2}} - 12S_{\frac{1}{2}}$	2728.4	36641	00	−1	xxx

TABLE I.—*Continued.*

Classification	$\lambda(A)$	$\nu(\mathrm{cm}^{-1})$	Intensity	$\Delta\nu$	Notes
$p^2\,{}^4P_{1\frac12} - 6F_{2\frac12}$	2719.8	36758	4	−1	*xx* h_3 *Z*
$7S_{\frac12} - 8P_{1\frac12}$	2717.5	36789	4	1	h_{20} *Z*
$7P_{\frac12} - 11S_{\frac12}$	2693.6	37114	0	1	
$7P_{1\frac12} - 11D_{2\frac12}$	2684.9	37235	2	0	h_0
$7P_{\frac12} - 10D_{1\frac12}$	2634.3	37950	4	0	h_0
$p^2\,{}^4P_{2\frac12} - 8F_{3\frac12}$	2628.3	38036	3	−1	
$p^2\,{}^4P_{\frac12} - 8P_{1\frac12}$	2608.4	38326	2	1	
$7P_{1\frac12} - 12D_{2\frac12}$	2587.2	38640	0	0	*xxx* h_0
$6D_{1\frac12} - 7F_{2\frac12}$	2576.6	38799	8	−1	*x* h_4
$6D_{2\frac12} - 7F_{3\frac12}$	2526.7	39566	8	−1	*x* h_2 *Z*
$7P_{1\frac12} - 13D_{2\frac12}$	2521.1	39653	0	−5	h_0
$7P_{\frac12} - 11D_{1\frac12}$	2498.9	40005	2	2	h_0
$6D_{2\frac12} - 10P_{1\frac12}$	2445.1	40885	1	2	
$p^2\,{}^4P_{1\frac12} - 7F_{2\frac12}$	2356.9	42414	1	0	*xx* h_3
$7P_{\frac12} - 13D_{1\frac12}$	2355.3	42444	0	−4	
$6D_{2\frac12} - 8F_{3\frac12}$	2326.2	42976	1	0	*x* h_2
$6D_{2\frac12} - 11P_{1\frac12}$	2280.8	43831	0	5	
$6P_{1\frac12} - 7S_{\frac12}$	2203.5	45368	2	−1	*x Z*

From here on λ vac is given.

Classification	Wave-length (A_{vac})	Wave No. (cm^{-1})	Inten-sity	$\Delta\nu$	Notes	ν Arvid.	In-ten. Arv.	$\Delta\nu$ Arv.
$6P_{1\frac12} - p^2\,{}^4P_{1\frac12}$	1921.66	52038	7	5				
$6P_{1\frac12} - 6D_{2\frac12}$	1822.03	54884	10	−1				
$6P_{1\frac12} - 6D_{1\frac12}$	1796.68	55658	10	1	*x*			
$6P_{\frac12} - p^2\,{}^4P_{\frac12}$	1726.75	57912	20	−1				
$6P_{\frac12} - 7S_{\frac12}$	1682.15	59447	10	1	*x*			
$6P_{1\frac12} - p^2\,{}^4P_{2\frac12}$	1671.53	59825	10	−1	*xx*			
$6P_{\frac12} - p^2\,{}^4P_{1\frac12}$	1512.42	66119	10	5				
$6P_{1\frac12} - p^2\,{}^2D_{1\frac12}$	1449.35	68996	3	6				
$6P_{\frac12} - 6D_{1\frac12}$	1433.96	69737	10	3	*x*	69740	8	0
$6P_{1\frac12} - p^2\,{}^2P_{\frac12}$	1348.37	74164	10	3		74168	4	−1
$6P_{1\frac12} - p^2\,{}^2D_{2\frac12}$	1335.20	74895	10	−4	C?	74890	8	1
$6P_{1\frac12} - 8S_{\frac12}$	1331.65	75095	10	4	Hg?	75097	1	2
$6P_{1\frac12} - 7D_{2\frac12}$	1231.20	81222	10	1		81223	9	0

Classification	Wave-length (A_{vac})	Wave No. (cm^{-1})	Inten-sity	$\Delta\nu$	Notes	ν Arvid.	In-ten. Arv.	$\Delta\nu$ Arv.
$6P_{\frac12} - p^2\,{}^2D_{1\frac12}$	1203.63	83082	10	1		83083	4	0
$6P_{1\frac12} - 9S_{\frac12}$	1145.91	87267	4	−2				
$6P_{\frac12} - p^2\,{}^2P_{\frac12}$	1133.14	88250	10	−2		88248	7	0
$6P_{\frac12} - 8S_{\frac12}$	1121.36	89177	10	3		89180	0	0
$6P_{1\frac12} - 8D_{1\frac12}$	1119.57	89320	10	−7		89314	4*d*	−1
$6P_{1\frac12} - 8D_{2\frac12}$	1109.84	90103	10	6		90110	1	−1
$6P_{1\frac12} - p^2\,{}^2S_{\frac12}$	1108.43	90218	10	−2		90217	4	−1
$6P_{1\frac12} - p^2\,{}^2P_{1\frac12}$	1103.94	90585	10	3		90590	5*d*	−2
$6P_{1\frac12} - 10S_{\frac12}$	1065.58	93846	9	3				
$6P_{\frac12} - 7D_{1\frac12}$	1060.66	94281	10	3		94285	4	−1
$6P_{1\frac12} - 9D_{1\frac12}$	1050.77	95168	10	8				
$6P_{1\frac12} - 9D_{2\frac12}$	1049.82	95254	10	1				
$6P_{1\frac12} - 11S_{\frac12}$		97489	(calc.)		*k*			
$6P_{1\frac12} - 10D$	1016.61	98366	10		*m*			
$6P_{1\frac12} - 12S_{\frac12}$	1001.81	99819	6	12				
$6P_{1\frac12} - 11D$	995.89	100413	10		*m*			
$6P_{\frac12} - 9S_{\frac12}$	986.71	101347	10	−1	*x*			
$6P_{1\frac12} - 12D$	982.17	101815	8		*m*			
$6P_{1\frac12} - 14S_{\frac12}$	975.35	102527	1	7				
$6P_{1\frac12} - 13D$	972.56	102823	9		*m* H?			
$6P_{\frac12} - 8D_{1\frac12}$	967.23	103388	10	6		103389	0	5
$6P_{1\frac12} - 14D$	965.36	103588	3		*m*			
$6P_{1\frac12} - 15D$	960.21	104144	2		*m*			
$6P_{\frac12} - p^2\,{}^2S_{\frac12}$	958.76	104301	2	−4				
$6P_{1\frac12} - 16D$	955.91	104612	1		*m*			
$6P_{1\frac12} - 17D$	952.92	104941	1		*m*			
$6P_{\frac12} - 10S_{\frac12}$	926.44	107940	5	−10				
$6P_{\frac12} - 9D_{1\frac12}$		109257	(calc.)		*n*			
$6P_{\frac12} - 11S_{\frac12}$	896.30	111570	3	4				
$6P_{\frac12} - 10D_{1\frac12}$	889.68	112400	8	9				
$6P_{\frac12} - 12S_{\frac12}$	877.96	113900	2	12				
$6P_{\frac12} - 11D_{1\frac12}$	873.71	114455	6	11				
$6P_{\frac12} - 13S_{\frac12}$	865.97	115477	1	19				
$6P_{\frac12} - 12D_{1\frac12}$	863.00	115875	3	10				
$6P_{\frac12} - 13D_{1\frac12}$	855.57	116881	3	18				
$6P_{\frac12} - 14D_{1\frac12}$	849.88	117664	2*d*	−14				
$6P_{\frac12} - 15D_{1\frac12}$	846.04	118198	2	25				
$6P_{\frac12} - 16D_{1\frac12}$	842.81	118651	1	17				
$6P_{\frac12} - 17D_{1\frac12}$	840.25	119012	00	12				

Notes and notation, Table I:

$\Delta\nu = \nu_{\mathrm{Predicted}} - \nu_{\mathrm{Experimental}}$.

x—line classified previously by Gieseler.[9]

xx—line classified by Gieseler, but with different assignment of the levels involved.

xxx—line classified erroneously by Gieseler.

h_0—hyperfine structure observed by Rose: line single.

$h_{1,\,2,\,\ldots}$—hyperfine structure observed by Rose, similar to other lines marked $h_{1,\,2,\,\ldots}$.

(a) This line may cover the line $sp^2\,{}^2P_{\frac12} - 9p\,{}^2P_{\frac12}$.

(b) This line may be covered by a Pb I line.

(c) The absence of hyperfine structure in this line is inconsistent with its previous classification by Gieseler as $sp^2\,{}^4P_{\frac12} - 7p\,{}^2P_{1\frac12}$, since the level from sp^2 would be expected to show structure.

(d) Murakawa suggested on the basis of hyperfine structure that this line was a transition from $6s^27p\,{}^2P_{1\frac12}$ to an unknown level with $J = 2\frac12$ which he called $6s6p^2\,{}^4P_{2\frac12}$; this level was located independently in the present work, and is differently assigned.

(e) This line was classified by Gieseler as Pb I; its hyperfine structure is definitely inconsistent with that classification, but agrees with the present one.

(f) This line may be covered by a Pb I line.

(g) Smith[11] classified a line at 4272.63A with intensity 5 as Pb III ($6s7s\,{}^1S_0 - 6s7p\,{}^1P_1$).

(i) Smith[11] classified a line at 3689.32A, intensity 5, as Pb III ($6s7s\,{}^3S_1 - 6s7p\,{}^1P_1$).

(j) This value of ν is questionable; however, Rose observed a line at this point which had the correct hyperfine structure for the transition here ascribed to it.

(k) This line may be covered by a H line (λ1025.78).

(m) Unresolved doublet.

(n) This line may be covered by a Hg line (λ915.83).

made, with satisfactory general agreement. Comparison with the isoelectronic spectra Tl I and Bi III may be made by use of the regular and irregular doublet laws, as well as the similarity of relative positions of the sp^2 levels. The values of the screening constant s in the regular doublet law formula

$$\Delta\nu = f(l)(Z-s)^4/n^3$$

are given in Table III, where the agreement is as satisfactory as could be expected for heavy atoms and in view of the existing perturbations. The agreement of the observed levels with the irregular doublet law is shown in Fig. 1. The principal deviations occur in differences involving the $6d\,{}^2D$ terms, which are shown below to be considerably perturbed by neighboring sp^2 levels. In Fig. 2 the sp^2 levels of Pb II and Bi III are plotted together, with scales so adjusted that the separation of the extreme levels is equal. The

TABLE II. *Term values and effective quantum numbers in Pb II*—(Terms underlined are those previously found by Gieseler.[9])

	$n=5$	6	7	8	9	10	11	12	13	14	15	16	17	18	19
$^2S_{\frac{1}{2}}$			61795	32063	19897	13313	9669	7331	5747	4628					
			2.665	3.700	4.697	5.742	6.738	7.738	8.740	9.739					
$^2P_{\frac{1}{2}}$		121243	46784	26166	16821	11743	8665	6658	5276	4285					
		1.903	3.063	4.096	5.108	6.114	7.118	8.120	9.121	10.121					
$\Delta\nu$		14081	2813	1161	598	351	222	150	105						
$^2P_{1\frac{1}{2}}$		107162	43971	25005	16223	11392	8443	6508	5171						
		2.024	3.160	4.190	5.201	6.207	7.211	8.213	9.214						
$^2D_{1\frac{1}{2}}$		51503	26959	17849	11986	8834	6777	5358	4344	3593	3020	2575	2221		
		2.920	4.035	4.959	6.051	7.049	8.048	9.051	10.052	11.053	12.056	13.056	14.057		
$\Delta\nu$		−776	1020	796	79	58	41	27	21	16	12	11	9		
$^2D_{2\frac{1}{2}}$		52279	25939	17053	11907	8776	6736	5331	4323	3577	3008	2564	2212	1928	1695
		2.898	4.114	5.074	6.072	7.072	8.073	9.074	10.077	11.078	12.080	13.084	14.087	15.089	16.092
$^2F_{2\frac{1}{2}}$	28714	18362	12705	9297	7093	5586	4513	3721	3121						
	3.910	4.890	5.878	6.871	7.867	8.864	9.862	10.86	11.86						
$\Delta\nu$	−15	−13	−9	−6	−5	−4	−2	−2	−1						
$^2F_{3\frac{1}{2}}$	28729	18375	12714	9303	7098	5590	4515	3723	3122	2655					
	3.909	4.888	5.876	6.869	7.864	8.862	9.860	10.858	11.858	12.858					
$^2G_{3\frac{1}{2},4\frac{1}{2}}$	17684	12275	9013	6897	5446	4410	3643	3060	2606	2247	1957				
	4.982	5.980	6.979	7.978	8.978	9.98	10.98	11.98	12.98	13.98	14.98				

$6s6p^2$	$^4P_{\frac{1}{2}}$	63332	$^2D_{1\frac{1}{2}}$	38160	$^2P_{\frac{1}{2}}$	32995	$^2S_{\frac{1}{2}}$	16946
	$^4P_{1\frac{1}{2}}$	55119	$^2D_{2\frac{1}{2}}$	32271	$^2P_{1\frac{1}{2}}$	16574		
	$^4P_{2\frac{1}{2}}$	47338						

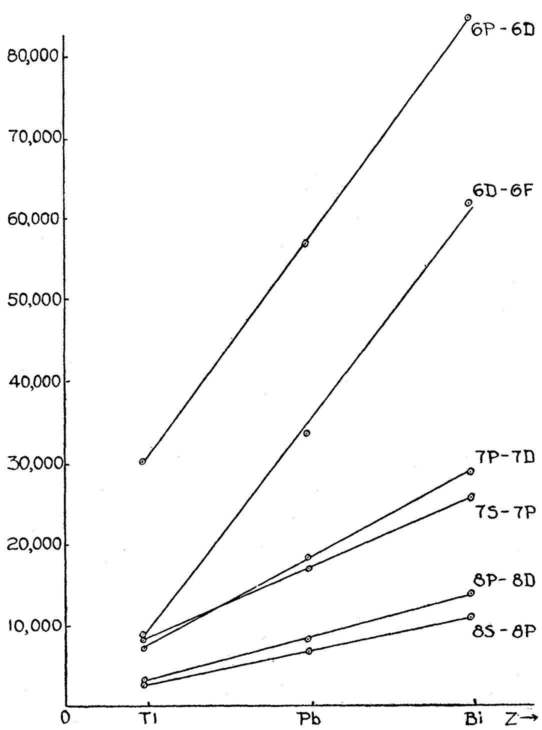

FIG. 1. Irregular doublet law.

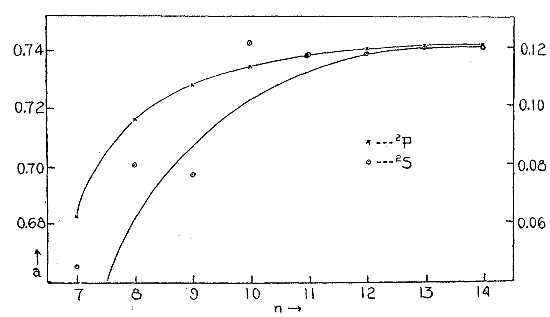

FIG. 2. Irregularities in ^2S series as shown by values of $a\ (\equiv n^*-m)$ *vs.* n.

TABLE III. *Regular doublet law. Values of s from* $\Delta\nu=f(l)(Z-s)^4/n^3$.

	6P	7P	8P	9P	
Tl I	53.422	62.467	64.984	66.408	
	−3.443	−4.463	−4.253	−4.114	
Pb II	49.979	58.004	60.731	62.294	
	−2.278	−2.897	−2.739		
Bi III	47.701	55.107	57.992		
	6D	**7D**	**8D**	**9D**	**10D**
Tl I	(inverted)	70.262	70.852	71.255	71.470
Pb II		56.587	56.511	66.341	66.367
Bi III		60.615	62.025		

general agreement is evident; particular deviations are discussed below as due to perturbations.

Substantiations and Perturbations

The Zeeman pattern observations by Green and Loring[15] were used to check the present classification. A recalculation from the observed patterns was necessary, since the present classification changes Gieseler's assignment of several levels and includes several lines which were unclassified when their patterns were observed. Table IV is a revision of Table III of reference 15,

Table IV. *g-values for even levels of Pb II.*

λ	$7S_{\frac{1}{2}}$	$^4P_{1\frac{1}{2}}$	$6D_{2\frac{1}{2}}$	$6D_{1\frac{1}{2}}$	$^4P_{2\frac{1}{2}}$	$7D_{1\frac{1}{2}}$	$7D_{2\frac{1}{2}}$	$9S_{\frac{1}{2}}$	$8D_{1\frac{1}{2}}$	$8D_{2\frac{1}{2}}$
2203	2.02									
2719*		0.55								
2948			1.29							
3016				0.89						
3452					1.41					
3455									1.07	
3714										1.16
3718								1.93		
3786		1.65								
3827									(.51 fr σ; .92 fr π)	
4153								1.98		
4242			1.29							
4245			1.35							
4386				.86						
5042						0.81				
5372					1.67					
5545							1.18			
5609	2.00									
5876						.78				
6660	2.02									
Ave.	2.01	1.65	1.31	.87	1.54	.80	1.18	1.96	.99	1.16
Theor.	2.00	1.73	1.20	.80	1.60	.80	1.20	2.00	.80	1.20

* There appears to be a confusion between λ2719.8 and λ2717.5. Green and Loring remark that λ2717.5 appears to have a pattern similar to λ3786, thus appropriate to the $6F_{2\frac{1}{2}}-sp^2\,{}^4P_{1\frac{1}{2}}$ transition to which λ2719.8 is assigned. (This assignment is required by the frequency difference in the two levels and by the hyperfine structure of λ2719.8.) However, the Zeeman pattern given by them for λ2719 leads to inconsistent results for the *g*-value of $7S_{\frac{1}{2}}$ if attributed to λ2717.5.

and gives the *g*-values for the various even levels, calculated from the unresolved patterns by the method of Shenstone and Blair,[16] assuming in each line that the odd level involved has the appropriate theoretical (i.e., unperturbed) *g*-value. Comparison with the theoretical *g*-values for the even levels shows good agreement. The effect of the mutual perturbation between the two levels $sp^2\,{}^4P_{1\frac{1}{2}}$ and $6d\,{}^2D_{1\frac{1}{2}}$, and between $6d\,{}^2D_{2\frac{1}{2}}$ and $sp^2\,{}^4P_{2\frac{1}{2}}$, is shown by the tendency to share *g*-values, thus decreasing the *g*-values of the sp^2 levels approximately as much as the *6d* level values are increased. Further evidences of these perturbations exist in the hyperfine structure of the levels, and in their positions, as discussed below.

Hyperfine structure data made available by Dr. J. L. Rose were used as a guide to assigning the sp^2 levels and as a further indication of perturbations existing between various even levels. Levels from sp^2 should show a larger separation in the components of the Pb 207 isotope (due principally to the increased interaction of the single *s* electron with the nucleus); and the isotope shift for Pb 206 and 208 should be different for the sp^2 levels as compared with the normal s^2x levels. Inspection of the data in Dr. Rose's article immediately following shows that the sp^2 levels as assigned do have consistently larger hyperfine structure separations. These separations also substantiate the perturbations expected between such even terms as have equal *J*-values and are located in proximity to each other. Such perturbations would cause a sharing of the larger separations of the sp^2 levels with those from the normal s^2s and s^2d configurations. This sharing is shown by the fact that the sum of the isotope shifts for $sp^2\,{}^4P_{1\frac{1}{2}}$ and $6d\,{}^2D_{1\frac{1}{2}}$ is approximately equal to the sum of the shifts for $sp^2\,{}^4P_{2\frac{1}{2}}$ and $6d\,{}^2D_{2\frac{1}{2}}$. A similar effect on the hyperfine structure appears in the $8d\,{}^2D$ terms. Since $7d\,{}^2D_{1\frac{1}{2}}$ is single and $7d\,{}^2D_{2\frac{1}{2}}$ shows only a small structure (perhaps due to interaction with $sp^2\,{}^2D_{2\frac{1}{2}}$), the $8d\,{}^2D$ terms would be expected to show vanishingly small structure. The separation observed in the $8d\,{}^2D_{1\frac{1}{2}}$ level is thus due to the effect of the neighboring level $sp^2\,{}^2P_{1\frac{1}{2}}$, while the absence of such separation in the $8d\,{}^2D_{2\frac{1}{2}}$ level is in complete agreement with the absence of any neighboring term with $J=2\frac{1}{2}$.

Since the odd terms in the Pb II spectrum include only the ^2P and ^2F series from $6s^2mx$, no perturbations should occur, on account of the inequality of *J*-values for adjacent levels. This absence of perturbations is evident in the regularity of the effective quantum numbers of these series in Table II. On the other hand, the even terms show a mixing of the levels from sp^2 with the $6s^2ms$ and $6s^2md$ configurations. The

[15] Green and Loring, Phys. Rev. **43**, 459 (1933).
[16] Shenstone and Blair, Phil. Mag. **8**, 765 (1929).

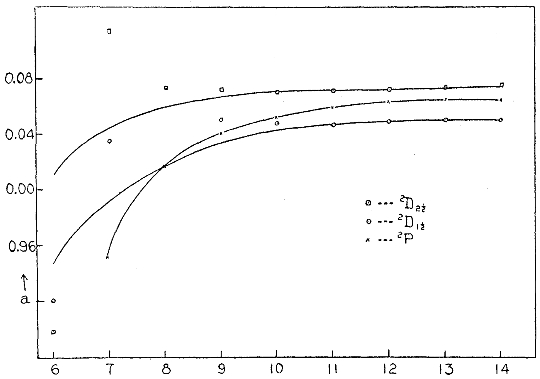

FIG. 3. Irregularities in ^2D series as shown by values of a $(\equiv n^* - m)$ *vs.* n.

resulting mutual perturbations are particularly evident in the locations of the series members, and may be explained very satisfactorily, though qualitatively, by the concepts of Langer[17] and Shenstone and Russell.[18] They find that the perturbation between two interacting levels is a mutual repulsion whose magnitude depends on the overlapping of the wave functions of the two levels, and hence should increase with increasing proximity of the levels. If the quantum number discrepancy a of the Rydberg series formula be plotted against the total quantum number n (Fig. 2), the higher $6s^2ms$ series members are evidently regular; at $n=11$ and 10 an increasing deviation is apparent, due to repulsion by the $sp^2\,{}^2S_{\frac{1}{2}}$ level; at $n=9$ the effect of this perturbation is reversed in direction, causing the value of a to be smaller than normal. The value of a for the $8s$ term is too large, agreeing with the expected effect of the neighboring $sp^2\,{}^2P_{\frac{1}{2}}$ level. And finally, the $7s$ value of a is also too large, due to the effect of $sp^2\,{}^4P_{\frac{1}{2}}$.

Similarly explainable effects are found in the case of the ^2D series, for which the effective quantum number discrepancy is plotted against n in Fig. 3. Again the higher members are regular, but in the $^2D_{1\frac{1}{2}}$ terms at $n=10$ and 9 there appears a deviation due to the presence of the $sp^2\,{}^2P_{1\frac{1}{2}}$ level. This in turn causes a reversed effect upon $8d\,{}^2D_{1\frac{1}{2}}$, decreasing the effective quantum number below its normal value. The $7d\,{}^2D_{1\frac{1}{2}}$ level is

[17] Langer, Phys. Rev. **35**, 649 (1930).
[18] Shenstone and Russell, Phys. Rev. **39**, 415 (1932).

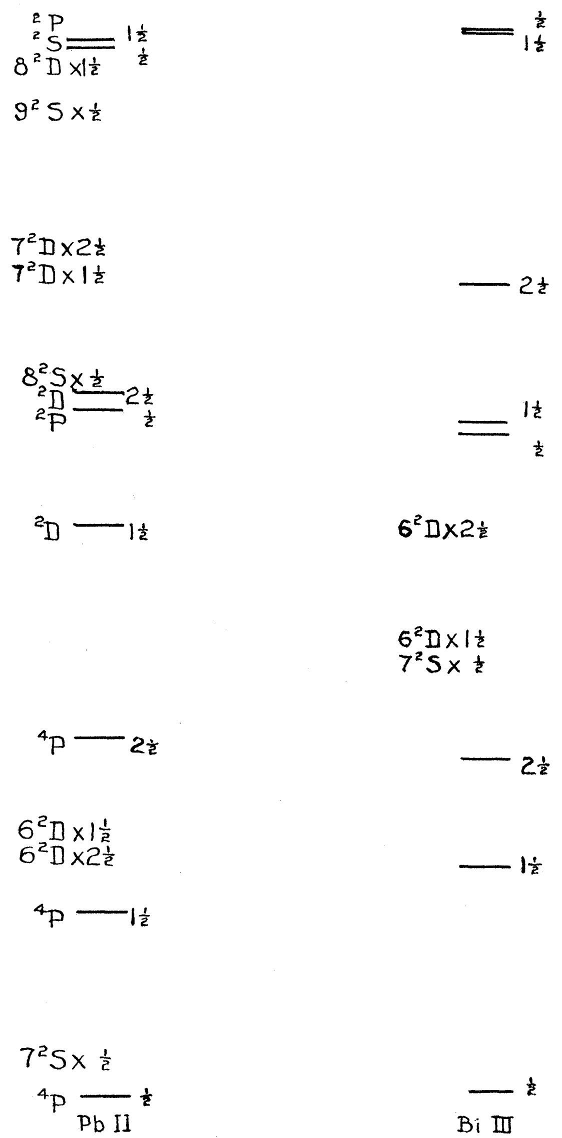

FIG. 4. sp^2 levels from Pb II and Bi III. (The x's indicate the location of terms of the normal (s^2nx) series.)

affected by both $sp^2\,{}^2P_{1\frac{1}{2}}$ and $sp^2\,{}^2D_{1\frac{1}{2}}$, so a prediction of the net effect is not immediately possible; this is also true of the $6d\,{}^2D_{1\frac{1}{2}}$, affected by $sp^2\,{}^2D_{1\frac{1}{2}}$ and $sp^2\,{}^4P_{1\frac{1}{2}}$. In the case of the $^2D_{2\frac{1}{2}}$ series the deviations of the terms $n=10$, 9, 8 and 7 are due to repulsion by the $sp^2\,{}^2D_{2\frac{1}{2}}$ level; the relative magnitudes and directions of these displacements are in accord with expectation. Further, the $6d\,{}^2D_{2\frac{1}{2}}$ term is displaced in the direction of smaller effective quantum number by the proximity of $sp^2\,{}^4P_{2\frac{1}{2}}$. These perturbation effects explain very satisfactorily the inversion of the $6d\,{}^2D$ and the abnormally large separations of the $7d$ and $8d$ doublets as observed.

The effect of the perturbations on the sp^2 levels is not so readily discussed, since the unperturbed arrangement is not so well known. Referring to Fig. 4, however, the larger separation of the ${}^4P_{1\frac{1}{2}}-{}^4P_{2\frac{1}{2}}$ levels in Pb II may well be due to the presence of the $6d\,{}^2D$ terms, both of which would tend to increase the separation. In Bi III[19] the effect does not occur, since the $6d$ doublet lies above the ${}^4P$ group. The difference in location of the $sp^2\,{}^2D_{2\frac{1}{2}}$ levels in the two spectra may be explained by the downward effect of the $7d\,{}^2D_{2\frac{1}{2}}$ term in Pb II and the upward effect of $6d\,{}^2D_{2\frac{1}{2}}$ in Bi III. The perturbations existing in the sp^2 levels with $J=\frac{1}{2}$ and $1\frac{1}{2}$ appear too complicated to admit of present interpretation on a qualitative basis.

The friendly cooperation of Dr. Rose by the loan of plates and the communication of unpublished hyperfine structure data is gladly acknowledged.

[19] McLay and Crawford, Proc. Roy. Soc. **A143**, 540 (1934).

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Hyperfine Structure of Singly Ionized Lead

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Some one hundred and thirty lines of Pb II were observed with Lummer-Gehrcke plates and Fabry-Perot interferometers from 2300 to 10,000A. The isotope shifts between Pb^{208} and Pb^{206}, and the h.f.s. splitting of Pb^{207} were computed from the h.f.s. measurements of these lines for all of the levels of Pb II, classified by Earls and Sawyer, with the exception of $6s^26p^2P_{1/2,\,3/2}$ and $6s6p^2\,{}^2P_{1/2}$. Parameters were obtained for equations derived by Breit and Wills for finding the h.f.s. constants, a', a'', a''', and $a(s)$, of the $6s6p^2$ configuration in intermediate coupling.

NUCLEAR spins for the three more abundant isotopes, Pb^{208}, Pb^{206} and Pb^{207}, of ordinary lead were found from h.f.s. measurements of spectral lines by several investigators[1, 2, 3] to be $I=0$ for Pb^{208} and Pb^{206}, and $I=\frac{1}{2}$ for Pb^{207}. Most of the lines observed were those of Pb I. The h.f.s. of a few of the more intense lines of Pb II was measured from which the isotope shift and Pb^{207} splitting was found for several levels. In the present work an attempt was made to increase the intensity of the Pb II radiation from a hollow cathode tube in order to observe the h.f.s. of the weaker lines. The Paschen-Schüler type tube with a hollow iron cathode (2.5 cm diameter×7.5 cm), supported in the center of a brass tube (10 cm diameter×25 cm) serving as the anode, and the conditions of excitation, with the exception of the He pressure were similar to those used in the investigation of the h.f.s. of PbI[3]. It was found that a He pressure of about 1.0 cm of Hg and currents from 50 to 500 ma would produce a Pb II spectrum much more intense than that of Pb I. With these currents and no cooling of the cathode all of the h.f.s. components of Pb II were very sharp and it was possible to operate the tube with a current as high as 500 ma for several weeks continuously before a few grams of lead, previously placed in the cathode, were completely carried over as a fine powder to the anode. Any increase of current above 500 ma caused very little increase in the intensity of the Pb II spectrum, but a very small increase of current at this point showed a large gain in the radiation due to Pb I. At about 600 ma the more intense lines of both spectra seemed to be of about the same intensity and with larger currents the arc lines were decidedly the stronger. A large number of new lines always appeared with the above He pressure which had

[1] H. Kopfermann, Zeits. f. Physik **75**, 363 (1932).
[2] H. Schüler and E. G. Jones, Zeits. f. Physik **75**, 563 (1932).
[3] J. L. Rose and L. P. Granath, Phys. Rev. **40**, 760 (1932).