Deep Terms in the Spectra of Pb V and Bi VI

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In earlier investigations the Pt I-like isoelectronic sequence was extended to Pb V and Bi VI, establishing terms due to the $5d^96s$, $5d^96p$, and, later, $5d^97s$ and $5d^{10}$ configurations. This paper extends further the previous results by Mack and by the author to include terms assigned as arising from $5d^98s$, $5d^99s$, $5d^97p$ and $5d^98p$ configurations. A total of 69 term values involving 205 lines are listed for Pb V, and 40 terms involving 94 lines for Bi VI. The wave-length measurements for the lines involved are those made by Arvidsson and range from 1400A to 200A, and in more than half the cases the discrepancies are not more than ± 1 cm^{-1}. The absolute values of the $5d^9{}_{5/2}6p_{3/2}$ $J=3$ terms are computed by a Ritz formula.

INDEPENDENT extensions of the Pt I-like isoelectronic sequence to Pb V and Bi VI were made and announced almost simultaneously by Mack[1] and by the author.[2] As the results were not in complete agreement, a more detailed study has been made by Mack[3] and also by the author,[4] including a study of the spectra of Pb IV and Bi V.[5] The results are now almost in agreement, differences being discussed in the comments to Tables I and III. The wave-length region concerned is from 1400A to 200A, the measurements used being those made on a grazing incidence spectrograph at Upsala by Arvidsson.[6]

In Table I the 69 term values assigned to Pb V are given, which involve a total of 205 lines for over half of which the discrepancy is not more than ± 1 cm^{-1}. The wave-lengths of newly assigned lines are given in Table II. Similarly the 40 terms assigned to Bi VI, which involve a total of 94 lines for over three-quarters of which the discrepancy is not more than ± 1 cm^{-1}, are given in Table III. The wave-lengths of newly assigned lines are given in Table IV. The terms assigned as arising from $5d^{10}$, $5d^96s$, $5d^97s$, and $5d^96p$ configurations are as assigned by Mack. By a Ritz formula, the absolute value of the $5d^9{}_{5/2}6p_{3/2}J=3$

[1] A. T. Goble and J. E. Mack, Phys. Rev. **42**, 909 (1932).
[2] G. K. Schoepfle, Phys. Rev. **43**, 374 (1933).
[3] J. E. Mack and M. Fromer, Phys. Rev. **48**, 357 (1935).
[4] G. K. Schoepfle, Phys. Rev. **45**, 747 (1934).
[5] G. K. Schoepfle, Phys. Rev. **47**, 232 (1935).
[6] Gustaf Arvidsson, Ann. d. Physik **12**, 1 (1932).

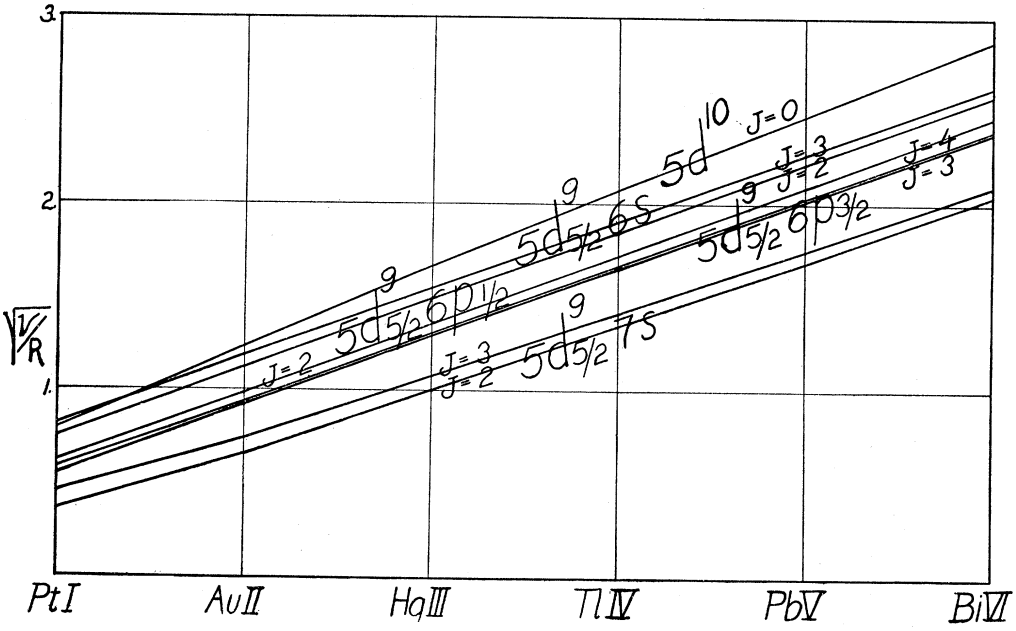

FIG. 1. Moseley diagram.

TABLE I. *Energy levels and transitions in* Pb V.

M indicates lines listed by Mack;[3] a number locates the line in Table II. Terms 327433, 329572, 329935 ($J=4$), 332358, and 332501 are listed by Mack with question marks and assigned as arising from $5d^9_{3/2}6s$. Two of these terms, 329572 and 332501, were independently announced by the author.[4]

Term designation →			$5d^{10}$	$5d^9_{5/2}6s$		$5d^9_{3/2}6s$																		$5d^9_{5/2}7s$			$5d^9_{3/2}7s$			$5d^9_{5/2}8s$			$5d^9_{3/2}8s$		$5d^9_{5/2}9s$
↓	J →		0	3	2	1	2	2	3	3	2	3	2	3	4	3	3	3	2	2	2	2	1	3	2	2	1	2	2	3	2	3	1	2	3
	↓	Term value →	0	110768	114705	132711	135997	141988	283483	297112	299708	317397	326216	326888	327433	328234	329572	329935	331487	331749	332358	332501	335913	338440	339234	341595	360496	361073	450173	452624	452967	473642	476582	476594	546508
$5d^9_{5/2}6p_{1/2}$	2	194803		M	M						45					65	M							M	M.					111		120			129
	3	197131		M	M						46				M	66	M	M			M	M		M	M						117				
	3	199048		1	7				36	40																									
	3	210514		2	8					41					64																				
	2	211487			9				37													85			94		99								
	3	212872		3	10						47			58								86													
	2	213131			11		23							59									87				100	104			118				
	2	215804			12	15	24				48												88												
$5d^9_{3/2}6p_{1/2}$	2	217069		M	M1	M	M			42	49	51										M			M		M	M	107			121			
	3	218043		4						43				60						79															
$5d^9_{3/2}6p_{1/2}$	1	219488	M		M	M	M	31					54														M		108						
$5d^9_{5/2}6p_{3/2}$	4	221069		M											M		M	M						M						112					
	2	223909		M	M	M	M					52	55	61							M	M			M								124	126	
	3	226511		M	M		M	32				53	56	62	M	67	M	M			M	M		M	M							122			
	2	227746				16	25						57							80			89												
$5d^9_{5/2}6p_{3/2}$	1	227835	M			M	M														M	M			M										
	2	232040				17	26											72	74								101								
	2	233830		5		18	27									68				81															
$5d^9_{3/2}6p_{3/2}$	0	237660				M																					M								
	1	239418				19		33												82						96									
$5d^9_{3/2}6p_{3/2}$	3	244661			M		M													83					M			M							
	1	245277	M		M	M	M												75		M2	M	90				M								
	2	247595		M	M	M	M												76	84							M	M						127	
	2	258588			13	20	28	34										73	77																
	1	260674				21	29	35																		97									
	2	350605			14																										119		125		
	3	358771		6					38																					113					
	2	359928				22	30		39																					114					
$5d^9\ 7p$?	2	397410								44	50																							128	130
	3	427026												63		69										98									
	2	427360														70	71		78																
$5d^9\ 8p$?	3	554440																						91					109	115					
	3	571267																						92						116		123			
	2	575919																									102	105							
	3	577526																						93	95										
	2	604560																									103	106	110						

TABLE II. *Newly classified lines of* Pb V.

z indicates the classification according to the state of ionization by Arvidsson.[6] The number in the column labeled "Designation" refers to Table I. b = broad, d = diffuse, a = found in arc.

z	Intensity	λ(vac.)	ν(vac.)	Designation	Discrepancy	z	Intensity	λ(vac.)	ν(vac.)	Designation	Discrepancy
V	2	284.329	351705	129	0	V	2	979.38	102105	3	+1
VI	5	358.636	278834	120	−5	V	1	982.18	101814	115	+2
VI	4	387.870	257818	111	−3	VI	2	983.06	101723	67	0
VI	5	389.745	256578	121	+5	VI	0	988.94	101118	18	−1
	0	390.882	255832	117	−4	V	4	989.15	101097	12	−2
V	1	395.280	252985	126	0	V	0	996.23	100378	62	+1
V	3	395.770	252672	124	−1	V	1	996.73	100328	51	0
V	2	403.217	248005	6	+2	VI	2	997.03	100298	44	0
VI	3	404.644	247131	122	0	VI	2	998.62	101138	63	0
V	1	409.728	244064	103	0	VI	1	1002.55	99745.6	2	−.4
V	3	410.705	243484	106	−3	V	2	1003.01	99699.9	56	+5.1
V	2	416.950	239837	118	+1	III	6	1005.56	99447.1	74	+.1
	0	418.264	239083	93	−3	VI	1b	1006.75	99329.5	17	+.5
V	1	419.650	238294	95	+2	VI	3	1008.82	99125.7	70	−.3
V	2	423.906	235901	14	+1	VI	0	1012.23	98791.8	69	−.2
V	1	428.99	233106	107	+2	VI	0	1015.53	98470.7	57	+.7
V	2	429.51	232823	92	−4	V	1	1015.97	98428.1	11	+2.1
V	2	431.86	231557	112	+2	VI	2	1018.70	98164.3	10	−2.7
V	3	433.487	230687	108	+2	VI	3	1019.74	98064.2	40	+.2
	0	436.10	229305	127	+6		0	1021.26	97918.3	81	−.7
	1	440.11	227216	22	−1		0	1021.51	97894.3	72	−.7
	0	446.56	223934	30	+3	V	4	1022.14	97834.0	27	+1
V	0	462.97	215997	91	−3	VI	1	1022.57	97792.8	71	+4.8
V	1	464.20	215424	102	+1	V	0b	1023.47	97706.8	50	+4.8
IV	7	465.450	214846	105	0	V	3	1024.33	97624.8	123	−.2
	3	647.71	154390	110	+3	VI	3	1026.38	97429.8	33	−.2
	0	670.70	149098	130	0	V	0	1033.23	96783.9	9	+1.9
	0	671.08	149014	99	+5	VI	1	1041.21	96042.1	26	−.9
	4	675.94	147942	104	0	VI	2	1043.04	95873.6	78	+.6
	1	678.58	147367	100	+2	VI	3	1043.70	95813.0	8	+4
	0	695.02	143881	13	−2	IV	4	1052.25	95034.4	16	−.6
V	5	749.46	133429	65	−2	V	0	1059.22	94409.1	68	+5.1
VI	2	762.76	131103	66	0	VI	1	1065.44	93857.9	113	+4.9
VI	1	778.50	128452	101	−4	VI	2	1069.67	93486.8	52	−1.2
VI	2	781.48	127962	21	−1		0	1078.74	92600.7	114	+4.7
VI	3	782.79	127748	94	+1	VI	0	1083.10	92327.6	82	−3.4
	1	793.79	125978	125	+1	VI	4	1089.93	91749.0	25	0
	2	794.41	125880	20	+3		0	1100.25	90888.4	53	+2.4
	5	795.58	124679	29	+2	VI	4	1103.32	90635.5	90	−.5
III	4	812.60	123062	5	0	VI	3d	1132.76	88280.0	1	0
V	1	814.45	122782	87	0	V	3	1148.29	87086.0	83	−2
V	0	815.70	122594	28	+3					M2	+5
VI	4	826.35	121014	85	0	VI	1	1151.63	86883.4	47	−2.6
IV	0	832.57	120110	88	+1		0	1154.71	86601.8	41	+3.8
	1	835.89	119633	86	+4	VI	0	1159.95	86210.6	75	+.6
	0	842.57	118685	35	−1	V	0	1170.56	85429.2	98	−1.8
VI	1	842.86	118644	116	+1	VI	0	1183.18	84518.0	32	−5
VI	1	855.31	116917	64	−2	V	0	1184.34	84435.2	36	+.2
V	7	857.65	116598	34	−2		0?	1185.63	84343.3	7	+.3
	0	877.06	114017	58	+1	V	0	1188.30	84153.8	84	−.2
V	1	879.08	113755	59	−2	IV	0	1191.83	83904.6	48	+.6
V	1	879.45	113707	79	+1	V	0	1192.08	83887.0	76	−5
	0	918.74	108845	60	0	IVa?	6	1203.47	83093.1	15	+.1
IV	2	924.51	108165	89	−2	V	0	1210.07	82639.8	49	+.8
IV	10	932.18	107275	4	0		0	1235.77	80921.2	97	+.2
V	5	936.96	106728	54	0	VI	0	1249.28	80046.1	42	+3.1
V	3	937.16	106705	19	−2		0	1252.99	79809.1	24	+2.1
V	0	953.30	104899	45	−6		0	1258.12	79483.7	128	−.3
V	3	959.08	104267	109	0		0d	1264.72	79068.9	43	−.1
VI	2	960.98	104006	80	+3	V	0	1290.32	77500.2	31	+.2
V	0	971.07	102979	61	0	V	3	1296.43	77134.9	23	+.9
V	0	974.91	102574	46	−3	IVa	6	1308.10	76446.8	39	+3.8
V?	5?	976.93	102362	119	0	V	0	1328.21	75289.3	38	+1.3
				M1	−2	III	6	1371.75	72899.6	77	+.6
V	2	977.46	102306	55	−1	IV	5	1388.97	71995.8	37	−.2
V	1	978.69	102177	96	0		0	1401.56	71349.1	73	+2.1

TABLE III. *Energy levels and transitions in* Bi VI.

M indicates lines listed by Mack;[3] a number locates the line in Table IV. Mack's choice of 298862, $J=0$, is strengthened by the expected transition $5d^9_{5/2}6p_{3/2}-5d^9_{3/2}7s$ designated as 26, apparently overlooked by him.

Term designation	J	Term value	$5d^{10}$	$5d^9_{3/2}6s$	$5d^9_{3/2}6s$		$5d^9_{3/2}6s$			$5d^9_{3/2}7s$	$5d^9_{3/2}7s$				$5d^9_{3/2}8s$	$5d^9_{3/2}8s$		$5d^9_{3/2}9s$	$5d^9_{3/2}10s$
	0	0	0	3	2	1	2	2	2	2	3	2	1	2	1	2	3	2	2	2	3	3
	2	237881		1	3											30						
$5d^9_{3/2}6p_{1/2}$	2	244721		M	M				13		M	M					34				43	46
	3	247165		M	M				14		M				31			37				
	2	250191		2		5		11	15	17					27							
$5d^9_{3/2}6p_{1/2}$	2	270603			M	M		M				M	M	M								
	1	274158	M		M	M		M	16					M	28	32						
	4	277866		M							M						35				44	
$5d^9_{5/2}6p_{3/2}$	2	280930		M	M			M				M										
	1	284036	M		M		8	M		18		M			29	33				40		
	3	284058		M1	M						M	M										
	0	298862				M							26									
$5d^9_{3/2}6p_{3/2}$	3	305272			M		9	M						M					39			
	1	305903	M		M	M		M		19			M							41		
	2	308613		M?	M	M		M2						M?								
	1	315254			4	6																
	2	319159				7	10	12														
$5d^9\,7p?$	3	556721									20	23								42		
	3	562057									21	24									45	
$5d^9\,8p?$	3	744960										25						38				
	3	749193									22						36					

TABLE IV. *Newly classified lines of* Bi VI.

z indicates the classification according to the state of ionization by Arvidsson.[6] The number in the column labeled "Designation" refers to Table III. b = broad, d = diffuse, a = found in arc.

z	Intensity	λ(vac.)	ν(vac.)	Designation	Discrepancy	z	Intensity	λ(vac.)	ν(vac.)	Designation	Discrepancy
	2	189.274	528334	46	0	VI	4	710.32	140782	12	+2
VI	2	214.318	466596	45	+4	VI	5	713.08	140237	6	0
	1	230.710	433445	44	−2	VI	2	723.56	138206	38	−1
VII	2	276.397	361798	34	0	V	10	738.17	135470	21	0
VI	1	277.591	360242	40	0	VI	10b	743.13	134566	24	−8
VI	1	278.095	359589	39	0					M1	+3
VI	1	292.080	342372	30	+1	VI	4	768.44	130134	20	0
VI	3	295.530	338375	41	0					M2	0
VII	0	300.225	333084	31	+3		1	773.76	129239	23	+1
VI	4	304.278	328647	35	+6	V	3	775.43	128961	13	−3
VI	6	306.718	326032	39	0	V	1	777.05	128692	9	−5
VI	5	309.976	322606	22	0	IV	2	790.425	126514	14	−2
VI	2	314.982	317478	25	+1		1	809.82	123484	15	+1
VI	3	326.695	306096	32	−2	V	3	850.66	117556	18	0
VI	3	337.590	296217	33	−1	IV	4	930.65	107452	8	−1
	1	345.479	289453	27	+5		1	993.10	100695	2	−1
IV	8	376.660	265491	28	0	VI	7b	1004.75	99527.2	16	−6.2
IV	8	391.215	255614	29	−1	VI	4	1045.066	95687.7	19	+1.3
V	4	619.13	161517	4	0	IV	2	1131.39	88386.9	1	+.9
	1	651.82	153417	26	−1		0b	1142.11	87557.2	42	−1.2
V	3	660.52	151396	17	−5	IV	4	1188.45	84143.2	3	−.8
	2bd	669.99	149256	45	0	IV	0	1330.19	75177.2	5	+3.2
V	4	693.29	144240	7	−2	V	0	1394.46	71712.3	11	+.3
VI	5	700.90	142674	10	0						
				36	0						

term is computed as 562,600 cm^{-1} for Pb V and as 761,800 cm^{-1} for Bi VI. The ionization potentials are 69.40 volts and 93.97 volts respectively, which values are 1.3 percent and 6.6 percent higher than those obtained by the extrapolation method by Mack. In Fig. 1 a Moseley diagram is given.

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The Pressure Effect on the *C* Band of Strontium Hydride

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At low hydrogen pressures the emission spectrum of the 3808A band of SrH shows a sharp break-off at $R(18)$, while at high pressures the lines extend to $R(49)$. The presence of lines with high K values allows an accurate determination of the constants of the upper state. Analysis shows the presence of an uncoupling term $-0.1415\ (K-1)$ in the upper state. Perturbations due to resonance and predissociation are present. The electronic configurations and probable dissociation energies are considered.

OF the known five band systems which the spectrum of SrH exhibits the *C* system at 3808A is particularly interesting, because its main band, the (0,0), has a line structure that is intense and well defined to a certain point and then abruptly breaks off, leaving no further trace of lines to be found. An analysis of this band has shown it to be a $C^2\Sigma \rightarrow N^2\Sigma$ transition.[1] The only other band observed in the system is a weak (0,1) band, which permitted a sufficiently complete analysis to show the same kind of abrupt breaking-off in rotational structure. This phenomenon has been attributed[1] to predissociation of the upper ("*C*") state due to the influence of a neighboring electronic state (probably the *D* state).

An analogous situation had long been known to exist in the *C* system of CaH.[2] Later Grundström and Hulthén[3] obtained its spectrum with the pressure of the hydrogen surrounding the calcium greatly increased. The bands were no longer predissociated, but were more or less normal in appearance. Bearing in mind the close analogy between the spectrum of CaH and SrH it was thought worth while to investigate the effect of pressure on the SrH *C* band.

[1] W. R. Fredrickson, M. E. Hogan, Jr., and W. W. Watson, Phys. Rev. **48**, 602 (1935).
[2] Mulliken, Phys. Rev. **25**, 509 (1925).
[3] Grundström and Hulthén, Nature **125**, 634 (1930).

Experimental Procedure

The spectrum was obtained from an arc between a copper cathode and a copper cup containing metallic strontium as an anode. The arc burned in an atmosphere of hydrogen at pressures varying from a few mm of Hg to 700 mm of Hg. The cathode was water cooled, and a continuous stream of water was directed on the glass walls of the tube containing the arc. With this arrangement it was possible to operate the arc continuously for two or three hours.

A 120-cm concave grating with a dispersion of 5A/mm in the second order was used in a Rowland mounting. Exposure times were of the order of four hours for second-order plates.

Analysis

When the *C* band is photographed with a hydrogen pressure of a few mm of Hg its rotational structure breaks off at $K'=19$. When the pressure is increased to 400 mm or more the band no longer exhibits this predissociation but displays a fairly normal structure. In addition to the (0,0) very weak traces of the (1,1) and (2,2) bands appear. The assignment of the K values is given in Table I. Combination differences permit these assignments up to $K=28$, beyond which the P branch becomes too weak to observe. For $K>28$ the R lines were fitted to a Fortrat para-