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The Spectrum of Lead Hydride

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From a lead arc in a hydrogen atmosphere at four to five atmospheres pressure, a "many-lined" spectrum in the region 5000–7000A due to PbH has been produced. Practically all of the lines have been assigned to ten bands constituting a $^2\Sigma \rightarrow ^2\Sigma$ transition between an upper state of low stability and a stable ground state ($\omega_e = 1565.2$, $B_e = 4.972$). Strong interaction with other states is evidenced by a very large spin-doubling ($\gamma = 6.17$) in the lower state and in the upper state by an unorthodox variation of $B_v{}^*$ with v, irregular spin doubling, a prominent failure of the Mecke rule and a sharp cut-off of levels at about $\frac{1}{3}$ volt above $K' = 0$, $v' = 0$.

The source ordinarily used in obtaining the emission spectra of metallic hydrides is an arc between electrodes of the metal burning in a hydrogen atmosphere at a pressure of but a few centimeters of Hg. A lead arc under these conditions, however, displays no characteristic hydride spectrum. But since the elements Tl and Bi which flank Pb in the periodic table both have interesting hydride spectra,[1, 2] it was thought that with some different experimental source a spectrum of PbH could be produced. Grundström and Valberg found that Tl too showed no hydride spectra in low pressure sources, but they were successful in producing TlH bands either in thermal emission in an electric furnace or in a high pressure arc providing the hydrogen pressure was above 50 cm of Hg. Of these two sources the arc in hydrogen at four atmospheres pressure was much more intense.

With a similar lead arc in hydrogen at four to five atmospheres pressure, I have found a band spectrum of the many-lined type in the region from 5000 to 7000A which from all indications is to be assigned to the PbH molecule. The analysis of this spectrum shows that the upper of the two electronic states involved is of low stability and has its equilibrium point at a considerably larger internuclear distance than that of the lower state. Now Farkas[3] and Olsson[4] have shown that the emission from an arc at high gas pressure is principally thermal radiation. At low pressure, the excitation being by electron impacts, this higher electronic state is not populated, since during electron impact excitation the internuclear distance in the molecule cannot change. But if at the high pressures approximate thermodynamic equilibrium exists, with much interchange between this upper electronic state and other repulsion states, the population of molecules in this state is built up to such an extent that the transitions to the lower ground state, even though improbable according to the Franck-Condon principle, give rise to a band system of fair intensity.

Experimental

A vertical arc was maintained between a fixed water-cooled copper cathode and an adjustable anode made of a thin-walled iron cup filled with "test lead." The source of potential was a 1000-volt d.c. generator delivering a current of 0.8 ampere. At hydrogen pressures of four to five atmospheres the PbH spectrum was emitted with fair intensity and the band lines were not too much pressure-broadened. Higher pressures were not used because of the diminution of the effective resolution on the spectrograms caused by this broadening of the lines, as well as the increased difficulty in making the arc run steadily. The PbH spectrum extends from 5000A on into the infra-red, but good spectrograms were obtained only of the range 5000–6800A with Eastman F-I plates. The second order of the 21-foot grating in a stigmatic mounting was used; the average dispersion was 2.24A per mm. Exposure times of about eight hours were necessary.

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[1] TlH: B. Grundström and P. Valberg, Zeits. f. Physik **108**, 326 (1938).
[2] BiH: A. Heimer, Zeits. f. Physik **95**, 328 (1935).
[3] L. Farkas, Zeits. f. Physik **70**, 733 (1931).
[4] E. Olsson, Zeits. f. Physik **104**, 402 (1937).

In the whole of the visible spectrum the only atomic lines other than those of Pb I and Pb II produced by this source are those of H, Na and faintly the Tl resonance line at 5350A. Since NaH and TlH may be ruled out, PbH is the indicated emitter of this spectrum. Also the quantum analysis given below yields very reasonable lower state values of the constants B_e and ω_e in comparison with those known for TlH and BiH. About one thousand PbH band lines of measurable intensity were recorded between 5000A and 6800A. The considerable overlapping of the bands, the lack of band heads, and the large spin doubling all contributed to make the spectrum of the "many-lined" type. A very large majority of these lines has been assigned to the ten bands tabulated below; the whole constitutes a single electronic transition of the $^2\Sigma\rightarrow{}^2\Sigma$ type. Since the line breadths decrease somewhat the accuracy of measurement, wave numbers are given to only one decimal place.

Analysis of the Spectrum

There are four branches in each band, strongly degraded to the red and with large second differences ($\sim$5 cm^{-1}) between successive rotational lines. This at once indicates a multiplicity of two, which is to be expected for the neutral PbH molecule, and an upper electronic state with a much lower vibrational frequency and much larger moment of inertia than for the lower state. From the rough equality in intensity of the four branches in some of the bands which are free of any partial fusions of branches, from the number of missing lines at the origin and the lack of any apparent spin-orbit doubling, $^2\Sigma\rightarrow{}^2\Sigma$ would seem to be the best choice of electronic transition involved. Quantum assignments based on the usual combination differences are presented in Table I.

Although the four branches are of approximately equal intensity in those bands with $v''=1$ and 2, throughout the spectrum, and especially in the bands of the $v''=0$ progression, the R_1 and P_2 branches seem to be somewhat more intense than the R_2 and P_1 branches. Transitions such as $^2\Pi$ (case a)$\leftrightarrows{}^2\Pi$ (case b) should have sub-bands with two strong and two weaker satellite branches, but this spectrum cannot be of this type since there is no evidence for another set of sub-bands and no internal combinations such as $^SR_{21}(J-1)-{}^QP_{21}(J+1)=R_1(J-1)-P_1(J+1)$ exist. I therefore assume that the eye estimates of intensities are rather inaccurate (for they are considerably influenced by the many partial fusions of the pressure-broadened lines which occur particularly in the 2,0 and 3,0 bands), and that the equality in intensity of the branches for the higher K values characteristic of $^2\Sigma\rightarrow{}^2\Sigma$ bands is nearly enough established.

From the combination differences the rotational energy term constants have been computed in the customary semi-graphical manner. These constants are assembled in Table II. The value $B_e''=4.972$ is to be compared with the values 4.806 and 5.136 for TlH and BiH, respectively. In the upper electronic state the B_v's do not decrease in the usual manner regularly with increasing v. The B_v' values first increase and then decrease as v' increases, this despite the fact that the values of $\Delta G(v'+\frac{1}{2})$ decrease steadily with increase in v' (cf. Table III). By way of possible explanation of this abnormality it should be pointed out that these experimental B's are really B^*'s which may differ very appreciably from the true B_v values[5] if there is strong quantum mechanical interaction with near-lying $^2\Pi$ states. As further evidence for the existence of other electronic states of PbH close to this upper $^2\Sigma$ state there may be mentioned the large and irregularly varying values of γ in this state, the existence of perturbations in several of its rotational levels, the marked failure of the Mecke rule for this $^2\Sigma$ state, and the sharp cut-off of all its energy levels at a height of about $\frac{1}{3}$ volt above $K'=0$, $v'=0$. Each of these facts merits a brief discussion.

In the lower electronic state the constant γ of the spin doubling relation $\Delta\nu_{12}(K)=\gamma(K+\frac{1}{2})$ is of record size, 6.17 for $v''=0$, but there is no departure from the normal linear variation of the doubling with $K+\frac{1}{2}$ except for some decrease at the highest K values. In the upper $^2\Sigma$ state, however, the γ's are smaller—3.05, 2.65, 2.28 and 1.49 for $v'=0,1,2$ and 3, respectively, at $K'=14$—vary irregularly at certain rotational

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[5] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

TABLE I. *Assignments of lines in the* $^2\Sigma-{}^2\Sigma$ *system of* PbH. *cm*$^{-1}$ *units. d denotes fused lines.*

	0,0				1,0				2,0				3,0				4,0			
K''	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2
0										18874.1				19305.3						
1						18433.6*d*				873.1				303.3						
2			17962.7*d*			428.8	18412.3			867.5				297.0						
3		17970.8*d*	946.6			419.1	396.4		18814.8	857.5	18836.2			285.9	19266.7*d*					
4		955.5	925.6			405.2	376.0		791.2*d*	843.5	815.9		19220.8*d*	270.2	246.1					
5	17875.4*d*	936.2	899.9			387.0	351.5		762.2*d*	824.5	791.2*d*		190.4*d*	250.0	220.8*d*					
6	841.6	912.3	869.6		18291.3	364.3	322.5	18391.4	728.9*d*	801.3	762.2*d*		155.7*d*	225.0	190.4*d*					
7	803.2	883.8	834.8		253.9	337.2	289.2	367.6*d*	691.1*d*	773.6	728.9*d*		116.2*d*	195.1	155.7*d*	19231.3			19551.8	
8	759.8	850.8	795.4		211.8	305.6	251.2*d*	340.9	648.6*d*	741.4	691.1*d*		072.0*d*	160.6	116.2*d*			19544.4	509.6	
9	712.2	812.9	751.3	17846.5	165.4	269.4	209.2	308.9*d*	601.8*d*	704.6*d*	648.6*d*		0.230*d*	121.1	072.0*d*	166.9		500.3	462.1	
10	659.8	770.1	702.4	807.1	114.7	228.5	162.3	271.5	550.4*d*	663.3	601.8*d*	18711.0	18969.3*d*	076.7	023.0*d*			450.7	409.3	
11	602.6	722.5*d*	648.9	762.7	059.3	182.8*d*	111.0	229.8*d*	494.3*d*	617.1	550.4*d*	668.8	910.8*d*	027.2	18969.3*d*	082.6		395.3	351.2	
12	541.0	670.0	590.6	713.8	17999.4	132.3	054.6*d*	182.8*d*	433.3*d*	566.1	494.3*d*	622.2		18972.6	910.8*d*	032.8		333.9	287.6	
13	474.8	612.5	527.5	659.8*d*	934.9	076.9	17994.1	131.1	367.6*d*	510.0	433.3*d*	570.2		912.8	847.4	18977.5		266.7*d*	218.6	
14	403.4	550.0	459.3	599.8	865.7*d*	016.4	928.4	073.8	299.3	449.1	367.6*d*	512.8	706.1	847.4*d*	778.4	916.8		192.7	143.6	
15	326.8*d*	482.6	386.2		791.5	17950.9	857.9	011.5	224.8	382.6	297.1	450.1*d*	627.7	776.7	704.6*d*	850.5		112.3	062.6	
16	246.1	409.9	308.2		712.7	880.1	782.4	17944.1	144.9*d*	310.9	221.4	382.6*d*	543.8	699.9	625.3	778.4*d*		024.5	18975.6	
17		332.3	225.2			804.0	701.8	871.1	060.8	233.7	140.6	308.9*d*	454.6	617.1	540.7	669.9*d*		18929.3	882.0	
18		249.6	137.1		539.6	722.5*d*	615.8	792.8	17970.8	150.8	054.6*d*	229.8*d*	359.5	527.9	450.1	615.4		825.6	781.6	
19			044.3		445.6		524.9	708.8	875.4	060.8	17962.7*d*	144.9*d*	258.8	431.9	353.7	523.8		714.3	673.7	
20			16946.1		346.2	542.9	428.6		774.5	17966.9	865.7*d*	054.6*d*	151.5	328.8	251.2*d*	425.4			557.9	
21					241.6	444.5	326.8*d*		667.0	865.7*d*	762.7*d*	17955.5*d*	038.0	218.1	141.9	319.5				
22					131.6	340.4	219.6	423.1	555.5	758.1	653.9*d*		17917.4	099.1	025.9	206.0				
23					015.6*d*	230.5	107.1		437.3	643.8	539.1	741.3	789.4	17970.8	17902.6					
24						114.9	16988.9		312.4*d*	522.4	417.8		653.9*d*	832.1	771.7					
25						16993.3			181.2	393.6	290.3	499.4	508.4							
26						865.3			043.3	257.0*d*	156.3*d*									
27											015.6									
28											16867.9*d*									
29											712.0									

	0,1				1,1				2,1				0,2				1,2			
0														15038.5*d*						
1		16483.4				16931.5*d*								038.5*d*						
2	16448.8	478.4*d*				926.8	16910.5*d*						15005.4	034.1*d*	15016.4	15038.5*d*				
3	429.1*d*	469.1	16445.3			918.2	894.7						14986.5	026.0*d*	001.2	034.1*d*				
4	405.7	455.9	425.0		16854.1	905.6	875.5			17343.6			963.8	013.9*d*	14982.1	026.0*d*		15475.0		
5	377.8	438.0*d*	400.7		826.9*d*	888.6*d*	852.2		17264.5	326.8*d*			937.3	14997.8*d*	959.2	013.9*d*		463.7	15432.2*d*	
6	345.5	416.1	372.1	16438.0*d*	795.3	867.9	824.9		232.9	304.8			906.8	977.6	932.0*d*	14997.8*d*	15386.3	448.5	410.6	15468.9
7	308.9	389.8	339.2	414.9	759.8	843.1	793.4	16872.5	197.3	279.4		17312.4	872.4*d*	953.4	901.1	976.9	356.6	429.5	384.9	453.6
8	268.2	359.1	301.9	387.8*d*	720.1	813.8	757.9*d*	847.3*d*	157.3	249.6		286.6	834.2	925.1	866.0*d*	951.7	323.3	406.6	355.4	434.6
9	223.1	323.8*d*	260.3	355.5	676.4	780.3	718.1	817.5	113.0*d*	215.5	17156.3	257.0	791.9	892.5	827.0	922.2	286.1	379.8	322.0	411.5
10	174.0	284.1	214.3	319.1	628.6	742.4	674.1	783.6	064.4	177.1	113.0*d*	222.6	745.5	855.8	783.7	888.5	245.1	349.0	284.8	384.2
11	120.1	239.8	163.8	277.8	576.5	700.1	625.8	744.5	012.3*d*	134.2	065.1	183.6		814.8	736.4	850.2	200.4	314.1	243.6	352.7
12	061.9	190.9	108.7	231.9	520.1	652.9*d*	573.1	701.0	16955.1*d*	086.7	012.3*d*	140.1		769.5		807.7	151.6	275.0	198.3	317.0
13	15999.4*d*	137.3	049.2	181.2	459.7	601.5	515.9	652.9*d*	893.6*d*	034.6	16955.1*d*	091.8				760.8	098.8		148.9	276.8
14	932.2	078.8	15985.1	125.6	394.4	545.2	454.2	599.6	828.0	16977.6	893.6*d*	038.7				709.1	042.0	184.0	095.5	
15	860.6		916.3	065.1	324.8	484.0	387.8*d*	541.6	757.9*d*	915.7	826.9*d*	16980.5					14981.1	131.9	037.7	183.2
16	784.1*d*	15947.8*d*	842.8	15999.4*d*	250.6	418.0	316.8	478.4*d*	682.9	848.6	755.8	917.0					915.9	075.2	14975.5	129.4
17	703.5*d*	875.2	764.7	929.7	171.7	346.9	240.9	410.4	603.4	776.5	679.8	847.3*d*					846.4	013.9*d*	909.0	070.8
18	617.8*d*	796.3	681.5	854.5	087.9	270.7	160.2	337.0	518.7	698.9	598.6	774.1					772.8	14947.8	837.9	007.4
19	527.8	714.0	593.8	775.0	15999.4*d*	189.3	074.5	258.4	429.1*d*	614.6	512.3	694.2						876.8	762.3	14939.1
20	431.6	626.3	501.5	688.0	905.9	102.4	15983.8	174.4	334.2	526.4	420.7	608.5						801.0		866.0*d*
21	332.1	533.7	404.7	598.3	807.4		888.0	085.0	232.7	431.4	323.8*d*	516.9								787.6
22	227.6	436.0	300.7	503.1	703.5*d*	15912.7	787.1	15990.2	127.7	330.2	221.2									704.1
23	118.3	333.3	194.1	402.8	594.8	809.5	680.9	889.8		222.6	112.7	315.0								
24	004.1	225.6	082.4	297.5	480.8	700.7	569.5	784.1*d*	15898.4	108.2	15998.4	204.5								
25	14885.0	112.7	14965.7	187.2	361.4	586.2	452.8	672.3	774.4	15986.6	877.9	087.0								
26		14995.0	844.2		236.5	466.4	330.6*d*	555.1	643.9	857.8	751.2	15962.6								
27		872.4*d*			106.2	339.1	203.1	432.2*d*	506.7	721.2	617.8*d*	830.8								
28		744.6			14970.7		070.4	304.0	362.2	575.8	477.8	691.2								
29					828.2		14932.0*d*		210.1*d*	420.6	330.6*d*	543.5								
30							788.6		049.8		175.7									
31											012.5									

TABLE II. *Constants of the energy terms for* PbH. *cm*$^{-1}$ *units.*

CONSTANT	$^2\Sigma'$	$^2\Sigma''$
B_0*	2.660	4.899
B_1*	2.766	4.754
B_2*	2.770	4.609
B_3*	2.646	
B_e*		4.972
α		0.145
r_0	2.507*A*	1.848*A*
D_0	-4.07×10^{-4}	-2.01×10^{-4}
ω_e	455.6	1565.2
$\chi\omega$	4.0	30.3
ν_e	18530.3	

TABLE III. PbH *band origins.*

v'	$v''=0$		1		2
0	17982.0	*1505.3*	16476.7	*1444.3*	15032.4
	445.9		*448.2*		*448.4*
1	18427.9	*1503.0*	16924.9	*1444.1*	15480.8
	439.8		*437.0*		
2	18867.7	*1505.8*	17361.9		
	431.2				
3	19298.9				
	(*401*)				
4	19700				

levels and tend to maximum values at intermediate K values. For $v'=2$, for example, the spin doubling drops to zero and reverses sign at $K=29$. Peculiar variations in the spin doubling such as these have been noted before for upper $^2\Sigma$ levels of CaH, CdH, and HgH, for each of which interaction with near-lying $^2\Pi$ levels is known to be responsible.

Perturbations occur in $v'=0$ at $J=19\frac{1}{2}$ for the T_1 terms and at $J=20\frac{1}{2}$ for the T_2 terms, in $v'=1$ at $J=28\frac{1}{2}$ and in $v'=2$ at $J'=20\frac{1}{2}$. The perturbations are not large, but the fact that there are several indicates the presence of one or more Σ or Π states at about this same energy interval above the ground state.

The array of band origins is given in Table III. If the Mecke rule that the ratio of the ω values in the two electronic states should be about the same as that of the B values held, one would expect upper state vibrational intervals of about 800 cm^{-1}. There are several arguments against placing just alternate v' levels in any one electronic state or considering each v' level as a different electronic state. This upper $^2\Sigma$ state must then represent a strong violation of the Mecke rule. A similar failure of this rule occurs in the $D\ ^2\Sigma$ state of CaH.

There is a rather sharp cut-off in the rotational series in the 4,0 band at $K'=20$ and no 5,0 band seems to exist. This $K'=20$ level lies about 2700 cm^{-1} above $K=0$ of the $v'=0$ level. In the 2,1 and 3,0 bands the branches drop sharply to zero intensity at $K'=30$ and 24, respectively. These levels lie about 2850 to 2900 cm^{-1} above $K=0$, $v'=0$. There is thus an instability of the levels of this state above about $\frac{1}{3}$ of a volt. Apparently no tendency exists for the stabilization by the high pressure of still higher levels as happens in certain CaH and AlH states. There is also evidence from the course of the $\Delta_2F'(J)$ difference at the higher J levels for the setting in of a considerable centrifugal expansion of the molecule, for these differences actually reach a maximum and begin to decrease with increasing K in the $v'=2$ and 3 levels.

DISCUSSION

Probably both of these PbH states are formed from a Pb atom in its lowest $6p^2$ configuration plus the H electron promoted to a seven-quantum orbit. They could, for example, be $6p\sigma^27s\sigma$ and $6p\pi^27s\sigma$. The lower of these two $^2\Sigma$ states may well be the ground state of PbH. Configuration theory would predict a number of Σ, Π, Δ and Φ states, both doublets and quartets, from these same electrons, and it would indeed be surprising if the stable states investigated here did not show signs of strong interaction with other near-lying electronic states. The large size of the spin doubling in the ground $^2\Sigma$ state would indicate the possible existence of a low $^2\Pi$ state with the same configuration as for this $^2\Sigma$ state except that one $6p\sigma$ electron has become $6p\pi$. Search of the photographic infra-red might reveal bands involving such a state as well as furnish data on higher levels of the ground state which has an unusually large anharmonic term in its vibrational level scheme.

The arc in gases under high pressure would seem to be a source that should be further exploited. Data on a large number of new molecular energy states perhaps may thus be easily produced.