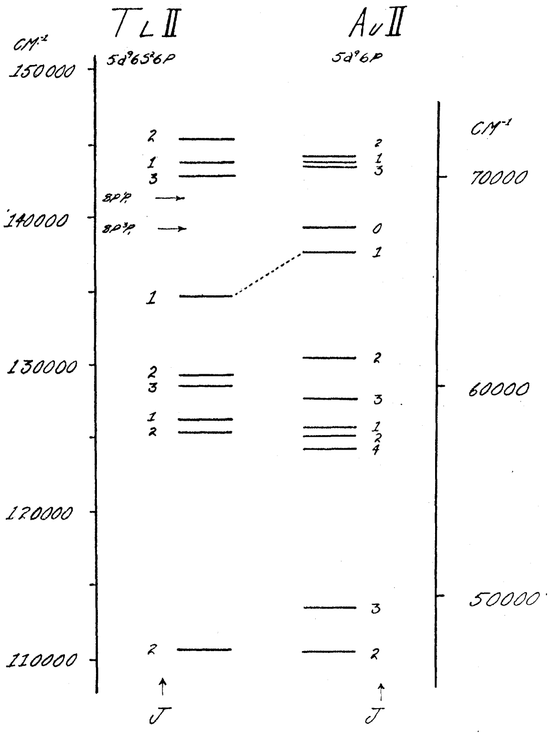

FIG. 3. A comparison of the configurations $5d^96s^26p$ of Tl II and $5d^96p$ of Au II. The arrows show the positions of $6s8p\ ^{3,1}P_1$ which probably cause the large shift in the middle $J=1$ level. Three of the Tl levels are still unlocated.

causing the two terms to share their properties—each being partly ^1F and partly ^3F. With the newly found $6g$ configuration the ratio of h.f.s. to multiplet separation is even larger. The $5f$–$6g$ transitions indicate the presence of two $6g$ levels, separated by about 6 cm^{-1}. These are probably the two hyperfine structure components, the multiplet structure being too small to observe. A similar case of h.f.s. larger than multiplet structure has been found in Al II.[12] Structure could not be observed in $5g$ since the transitions fall in a region of low dispersion.

6. REMAINING LINES

In the entire spectrum there now remain only five unclassified lines of intensity greater than 1, these being also included in Table II. Besides these five our plates showed one important line (2210.75A; 45,219 cm^{-1}; int. 10) which must belong to the arc spectrum. There seems no possible place for it in the Tl II system; furthermore it has been previously observed as reversed in the arc by Kayser and Runge.[13] An arc line of this frequency, and reversed, can only be a transition ending on the ground state. The initial level is thus established as a new even term in Tl I (with $J=\frac{1}{2}$ or $1\frac{1}{2}$), at an absolute value of 4045 cm^{-1}, and probably belongs to the $6s6p^2$ configuration expected in that region.

We wish to express our appreciation to Dr. S. A. Goudsmit for his interest in the work and to Dr. McLay for the location of the levels previously mentioned.

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[12] Paschen, Preuss. Akad. Wiss. Berlin, Ber. **32**, 502 (1932).

[13] Kayser, *Handbuch der Spektroscopie*, Vol. 6, p. 709.

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Strontium Deuteride and Hydride Spectra

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The analyses of the B and C band systems of SrD and of a portion of the D system of SrH are presented. $B_e^*=1.9427$ for SrD and 3.8788 for SrH for the normal $^2\Sigma$ state. The ratio of these, 0.50635, shows about the expected departure from equality with the ratio $\rho^2=0.50603$ of the reduced masses. The spin doubling of this SrD state is regular, $\gamma_0=+0.0613$ being almost exactly in the ratio ρ^2 with the value for SrH. The spin doubling of the $B\,^2\Sigma$ state of SrD departs markedly from the usual linear variation with $K+\frac{1}{2}$. Multiple perturbations occur in the (0,0) C band of SrD, and there is a sharp cut-off of the branches at $K'=29$. For this $C\,^2\Sigma$ state $B_0\cong 1.95$, but exact analysis is hindered by the lack of any unperturbed lines. Two bands $(v',2)$ and $(v',3)$, with a common upper state, of the $D\,^2\Sigma\rightarrow N\,^2\Sigma$ "many-lined" SrH system have been analyzed. In this D state, for which $B_v=1.913$, large irregular perturbations occur. Electronic configurations are discussed.

INTRODUCTION

We have recently described[1] three new band systems of the SrH molecule in the visible and near ultraviolet regions of the spectrum, supplementing the previous analysis[2] of the (0,0) bands of the $B\,^2\Sigma \rightarrow N\,^2\Sigma$ system at 7020A and the $A\,^2\Pi \rightarrow N\,^2\Sigma$ system at 7508A. Of the newly discovered systems we were able to present fairly complete quantum analyses of the abbreviated and strongly perturbed (0,0) and (0,1) $C\,^2\Sigma \rightarrow N\,^2\Sigma$ bands at 3808A and 3984A, respectively, as well as of the (0,0) $E\,^2\Pi \rightarrow N\,^2\Sigma$ band at 5323A. Very probably, however, the upper state of the latter system does not correspond to the upper state of the $E\,^2\Pi \rightarrow N\,^2\Sigma$ bands of CaH at 4900A,[3] and so should be dubbed $F\,^2\Pi$. We give the argument for this change below.

The present report is concerned with the deuteride modification of the B and C systems and with a partial analysis of the complicated "many-lined" D system of SrH. The experimental procedure was similar to that described in the earlier papers. Heavy hydrogen was obtained by vacuum distillation of the vapor of 99 percent heavy water onto metallic calcium. To minimize contamination of the spectrograms with SrH band lines, light from the first few minutes of burning of the arc between a water-cooled copper cathode and an anode of metallic strontium was not used. The gas was then pumped out of the arc chamber, fresh deuterium was admitted to about 7 cm of Hg pressure, and the exposure begun. From time to time during the exposure additional deuterium gas was added because of the consumption of gas in the arc. The few SrH lines occurring on the plates are so faint that they offer no hindrance in the measurement and analysis of the SrD bands. The dispersion for these spectrograms varies from 2.2A per mm for the B bands at 7000A to 2.5A per mm for the C band at 3800A.

THE B SYSTEM OF SrD

The analysis of the (0,0) and (1,1) $B\,^2\Sigma \rightarrow N\,^2\Sigma$ bands of SrD has been carried out both to provide lower state combination differences as an aid in analyzing the strongly perturbed (0,0) C band (cf. below) and also for the comparison of constants of the SrH and SrD molecules in connection with isotope effect theory. For this second purpose we have had to provide also the analysis of the (1,1) SrH B band to go with the data for the (0,0) SrH band given in reference 2. In Table I are listed the assignments of frequencies for the (1,1) SrH band, in Table II those for the (0,0) and (1,1) SrD bands. The values of all of the constants of the rotational energy term formula for these states are assembled in Table V. A new calculation of B_0^* for the normal state of SrH yields the value 3.6344, replacing the less accurate value given in reference 2.

In comparing the constants of the two isotopic molecules it should be remembered that all the B's as determined by application of the usual rotational energy formulas are really B^* values,

TABLE I. *Assignment of frequencies in the (1,1) $B\,^2\Sigma \rightarrow N\,^2\Sigma$ band of SrH* (cm^{-1} units).

$J''+\frac{1}{2}$	P_1	R_1	P_2	R_2
1		14377.91		14393.18
2		83.82		403.90
3	14356.63	89.28	14358.61	14.62
4	48.60	96.41	54.80	25.88
5	40.60	403.90	51.28	37.11
6	32.60	11.14	48.05	48.85
7	25.77	18.73	45.29	60.63
8	19.06	26.73	43.00	72.73
9	12.34	35.25	40.60	85.07
10	06.51	43.72	38.60	97.82
11	00.85	52.71	37.21	510.65
12	295.62	62.06	35.99	23.59
13	90.90	71.66	35.13	37.01
14	86.37	81.60	34.20	50.17
15	82.28	91.77	33.80	63.48
16	76.68	502.34	34.20	76.38
17	75.49	13.05	34.20	
18	72.70	24.20	34.00	
19	70.30		35.13	
20	67.92	47.35	35.99	
21	66.08	58.70	37.21	
22	64.65	70.63	38.60	
23	63.56	82.71	40.60	
24	62.89	95.02	42.00	
25	62.33	607.50	43.72	
26	62.33	20.14	45.29	
27	62.89	32.82	47.13	
28	64.65	45.68	49.25	
29	66.08	58.56	51.28	
30	67.92	71.50	53.80	
31	70.30	84.47	57.01	
32	72.50	97.55	60.24	
33	74.89	711.04	63.75	
34	78.03			

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[1] W. R. Fredrickson, M. E. Hogan, Jr. and W. W. Watson, Phys. Rev. **48**, 602 (1935).

[2] W. W. Watson and W. R. Fredrickson, Phys. Rev. **39**, 765 (1932).

[3] W. W. Watson and R. L. Weber, Phys. Rev. **48**, 732 (1935).

TABLE II. *Assignment of frequencies in the B* $^2\Sigma \rightarrow N\ ^2\Sigma$ *system of SrD.*

$J''+\frac{1}{2}$	(0,0) BAND				(1,1) BAND			
	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2
1		14346.79						
2		49.51						
3	14335.69	52.77				14368.61		
4	31.43	56.00		14370.59		71.77		
5	27.12	59.36		76.42		75.14		
6	22.97	62.99	14330.16	82.29		78.71		
7	18.81	66.87	28.74			82.29	14345.06	
8	14.96	70.59	27.12	94.34		86.04	43.54	14409.70
9	11.35	74.58	25.72	400.50		89.99	42.12	
10	07.97	78.71	24.43	06.71		93.95	40.85	21.77
11	04.63	83.06	23.34	13.25	14320.83	98.16	39.61	27.89
12	01.52	87.52	22.34	19.94	17.88	402.58	38.68	34.58
13	298.56	92.17	21.47	26.60	14.96	06.90	37.88	
14	95.65	96.94	20.83	33.43	12.19	11.59	37.18	47.79
15	93.03	401.83	20.33	40.34	09.52	16.41	36.67	54.57
16	90.62	06.90	19.98	47.54	07.04	21.32	36.16	61.33
17	88.36	12.08	19.79	54.57	04.63	26.33	35.89	68.32
18	86.21	17.43	19.79	61.77	02.54	31.50	35.69	75.34
19	84.25	22.88	19.79	69.26	00.68	36.83	35.69	82.49
20	82.50	28.52	19.98	76.78	298.67	42.36	35.69	89.67
21.	80.87	34.27	20.33	84.42	97.02	47.79	35.89	97.02
22	79.44	40.15	20.83	92.00	95.65	53.53	36.16	504.26
23	78.09	46.14	21.47	99.78	94.22	59.34	36.67	
24	76.95	52.28	22.15	507.58	93.03	65.26	37.18	19.42
25	76.01	58.53	22.97	15.50	92.07	71.31	37.88	26.92
26	75.26	64.87	23.93	23.39	91.19	77.48	38.68	34.28
27	74.64	71.31	24.98	31.45	90.62	83.75	39.61	
28	74.22	77.90	26.19	39.46	89.99	90.09		
29	73.81	84.59	27.43	47.42	89.48	96.56		
30	73.81	91.43	28.74	55.34	89.19	503.10		
31	73.81	98.32	30.16	63.48	89.19	09.77		
32	74.22	505.31	31.43		89.19	16.51		
33	74.64	12.42	33.40		89.48	23.39		
34	75.26	19.57			89.99	30.29		
35	76.01	26.92			90.62	37.03		
36	76.95	34.28			91.19	44.22		
37	77.93	41.66			92.07	51.33		
38	79.03	49.16			93.03	58.56		
39	80.33	56.78			94.22	65.80		
40	81.74	64.38			95.24	73.06		
41	83.25	72.18			96.61	80.45		
42	84.95	79.94			98.00	87.80		
43	86.76	87.80			99.49	95.20		
44	88.68	95.67			301.17	602.71		
45	90.62	603.65			02.83	10.22		

differing from true B_v and B_e values for several reasons. Accurate calculation of the corrections to these B_e^*'s to obtain true B_e values, which should be in the ratio of the reduced masses for the two isotopes, is impossible for these states.[4] Comparison of some of the observed energy constants for the two molecules, however, is of some interest. By using atomic weights 87.63, 1.0081 and 2.0148 for Sr, H and D, respectively, the ratio ρ^2 of the reduced masses of SrH and SrD is 0.50603, $\rho = 0.71136$ and $\rho^3 = 0.35997$. The ratio of the B_e^* values for the $N\ ^2\Sigma$ states of the two molecules is 0.50635, which is larger than ρ^2 by about the expected amount as judged by the results for the hydrogen isotope effect for other molecules. For the B states the B_e^*'s have a ratio 0.50085, the large deviation from ρ^2 in the opposite sense reflecting the large "pure precession" interaction with the neighboring $A\ ^2\Pi$ state. If one corrects these B^*'s by addition of the Λ-doubling constants q_0 of the $^2\Pi$ state[5] ($q_0 = -0.398$ for SrH and -0.102 for SrD), the resulting $B_e = 3.4808$ for SrH and 1.8407 for SrD have the large ratio 0.52882. The excess of this figure over the ρ^2 value would seem to indicate

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[4] For a discussion of the relative magnitude of these corrections for some hydride molecules, cf. W. W. Watson, Phys. Rev. **49**, 70 (1936).

[5] For similar calculations for CaH/CaD, cf. W. W. Watson, Phys. Rev. **47**, 27 (1935).

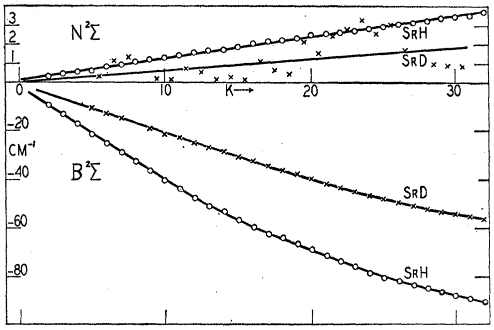

FIG. 1. Comparison of spin doubling in the $N\,^2\Sigma$ and $B\,^2\Sigma$ states for SrH and SrD. The relatively large spread of the values about their mean for the $N\,^2\Sigma$ state of SrD is due to the necessary indirect computation with the aid of the relation $\Delta\nu_{12}(K)=\frac{1}{2}[\Delta_2T_1(K+\frac{1}{2})-\Delta_2T_2(K-\frac{1}{2})](K+\frac{1}{2})$.

strong alteration of the effective potential function for this state because of the perturbing influence of the numerous other near-lying states of the SrH molecule.

The quantity α of the relation $B_v=B_e[1-\alpha(v+\frac{1}{2})]$ should, according to the simple isotope theory, vary as ρ^3. Any change in this variation due to the fact that α is determined from the experimental B^* values should to a first order be negligible. We find that for the $N\,^2\Sigma$ state $\alpha=0.0814$ for SrH. Multiplication by ρ^3 gives 0.0293, as compared to the observed value 0.0292 for SrD. The ratio of the spin doubling constants γ of the relation $\Delta\nu_{12}(K)=\gamma(K+\frac{1}{2})$ for the two molecules should be ρ^2 according to the theory of spin doubling. For the normal state of SrH this linear variation of $\Delta\nu_{12}(K)$ with $K+\frac{1}{2}$ does exist, with $\gamma_0=+0.122$. $\rho^2\times0.122=0.062$, which is almost exactly the observed value $+0.061$ for the $v''=0$ level of SrD. In the $B\,^2\Sigma$ state, however, neither molecule exhibits this ordinary spin doubling. In Fig. 1 the course of the doubling in these states is plotted as a function of K. The slopes of these curves for the B state are large, negative and decrease markedly with increasing molecular rotation. The large, negative γ_0 values reflect the pure precession interaction with the $A\,^2\Pi$ state just below this B state, and the rapid change in slope must be due to the perturbing influence of other close SrH levels. For the B state of SrD $\gamma_0=-2.01$ for $K<10$, while at $K=30$ this slope has dropped to -1.14. This anomalous behavior of the spin doubling for SrD is in contrast with the normal linear variation in the corresponding state of CaD.[5]

THE C SYSTEM OF SrD

As is to be expected from the closer spacing of the rotational levels and the probable near equality of the frequencies of vibration in the two electronic states of each molecule, the (0,0) $C\,^2\Sigma\rightarrow N\,^2\Sigma$ band of SrD has even more perturbations than has the corresponding SrH band[1] and is found at almost exactly the same wave-length. In fact there are no unperturbed lines in this SrD band, which makes the determination of the exact magnitude of the perturbations and the rotational energy constants of the C state rather difficult. We list in Table III the frequencies, intensities and quantum assignments of all the observed lines in this band. Fig. 2 is a comparison of microphotometer traces of these

TABLE III. *Assignment of frequencies in the* $C\,^2\Sigma\rightarrow N\,^2\Sigma$ (0,0) *band of SrD* (cm⁻¹ units). Numbers in brackets are estimated intensities.

K''	R	P
0	26291.02(0)	
1	94.44(1)	
2	93.69(1)	26280.05(2)
3	96.10(3)	76.06(2)
4	300.80(2)	68.07(1)
5	05.39(1) 06.18(2)	62.66(1)
6	11.69(2)	60.22(3b)
7	17.21(2)	58.38(12)
8	22.68(2)	56.38(7)
9	26.43(1)	54.83(7b)
10	44.74(1)	52.87(4)
11	48.53(2)	49.20(1)
12	54.89(3)	60.22(3b)
13	61.92(2) 62.25(2)	56.38(7)
14	69.48(2)	56.38(7)
15	26375.54(2)	26256.38(7)
16	93.83(2)	56.38(7)
17	98.57(4)	54.83(7b)
18	406.69(2) 07.85(2)	65.74(4b)
19	14.53(1) 15.81(1)	63.63(3)
20	27.01(1) 29.06(1)	64.58(1) 65.74(4b)
21	36.40(2) 37.05(2)	65.74(4b) 66.67(2)
22	46.11(2) 47.07(2)	71.13(2) 73.04(4)
23	57.10(2) 57.44(2)	73.04(4) 74.18(2)
24	67.36(1) 67.97(1)	76.06(2) 77.18(2)
25	74.69(1) 76.58(1)	80.05(2) 80.55(2)
26	90.92(2b) 91.78(1)	83.61(2) 84.24(2)
27	500.40(2)	84.24(2) 86.13(1b)
28	16.18(2) 16.78(1)	93.69(1)

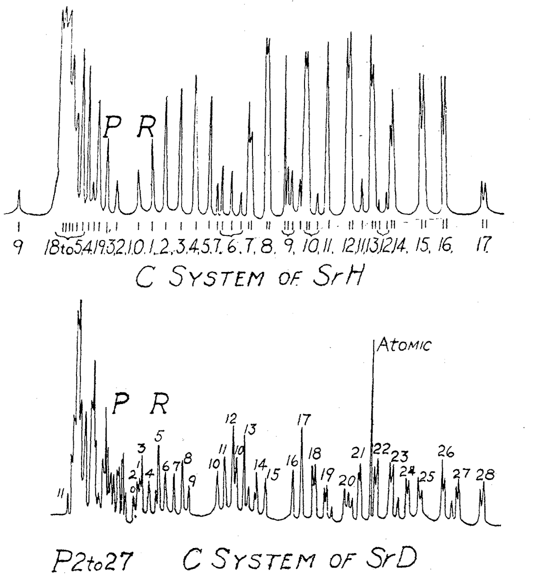

FIG. 2. Microphotometer traces of the $C\,^2\Sigma \rightarrow N\,^2\Sigma$ (0,0) bands of SrH and SrD.

(0,0) *C* bands of SrH and SrD. The (0,1) SrD band does not occur with appreciable intensity on our spectrograms.

Even though all the lines are perturbed, some violently, producing a confusion of lines in the region of the *P* branch, assignments of *K* values may be made with the aid of lower state combination differences known from the analysis of the *B* bands. As in the SrH band, doubling of some of the lines occurs in an irregular manner. We estimate from the $\Delta_2 T'(K)$ values, none of which are undisturbed by perturbations however, that $B_0^* \leqq 1.95$ for this *C* state. The sharp cut-off of the branches of the band at $K' = 29$ comes at closely the same energy as the corresponding cessation at $K' = 19$ in the SrH band. In view of the fact that this breaking-off of the band very probably represents predissociation into the continuum of the less stable $D\,^2\Sigma$ state, the multiplicity of the perturbations is somewhat puzzling. Levels of still another state, such as the $E\,^2\Pi$ or indicated $F\,^2\Pi$ must also be situated so as to perturb these *C* levels.

THE *D* SYSTEM OF SrH

The *D* system of SrH is a complicated, "many-lined" spectrum extending from 5000A to 6700A and containing few regularities. There are no evident series of doublets as in the corresponding CaH *D* system,[6] probably due both to the larger spin doubling in SrH and to the greater number of perturbations. We have analyzed two bands in this complex, the (v',2) and (v',3) bands, which have a common upper state but with v' unknown.

TABLE IV. *Assignment of frequencies in (v',2) and (v',3) $D\,^2\Sigma \rightarrow N\,^2\Sigma$ bands having a common upper state.*

	(v',2) BAND				(v',3) BAND			
$J''+\frac{1}{2}$	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2
1				18446.21		17341.39		17342.20
2	18435.31	18446.21	18425.26	43.94	17330.95	42.22	17320.95	40.12
3	25.26	43.94	11.50	37.51	20.95	40.12	08.35	35.09
4	11.50	37.51	395.20	29.63	08.35	35.09	292.71	27.18
5	395.20	29.63	76.02	18.12	292.71	27.18	74.13	16.29
6	76.02	18.12	53.98	03.91	74.13	16.29	52.69	at.
7	53.98	03.71	27.93	386.27	52.69	02.45	28.29	286.59
8	27.93	385.56	299.48	66.10	28.29	285.83	00.93	67.71
9	00.16	65.86	69.03	43.28	00.93	66.51	172.06	46.24
10	268.02	40.84	35.14	17.76	171.14	44.48	39.84	22.49
11	33.69	15.31	198.84	290.33	38.44	19.86	05.17	196.67
12	196.68	286.95	59.62	60.70	03.26	193.46	068.14	69.22
13	57.25	56.81	18.85	30.16	065.58	65.14	29.32	40.63
14	15.31	26.72	076.26	198.84	25.84	37.24	16988.80	11.64
15	071.93	198.84	32.26	63.70	16984.56	11.64	47.21	078.65
16		68.46	17987.88	38.16	43.63	083.60	05.39	56.33
17	17986.71	39.51	41.17	23.44	05.39	58.16	859.24	41.51
18	44.11	17.12	03.06	07.50	864.58	37.37	24.84	29.67
19	03.06	098.72			26.58	22.19	797.73	996.92
20	869.44	60.60			793.02	16984.48	73.32	66.00
21					65.45	61.55	28.24	40.66
22					29.68	37.59	685.39	13.43
23					680.67	12.70	48.52	895.78
24					44.58	883.47		

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[6] B. Grundström, Zeits. f. Physik **75**, 302 (1932).

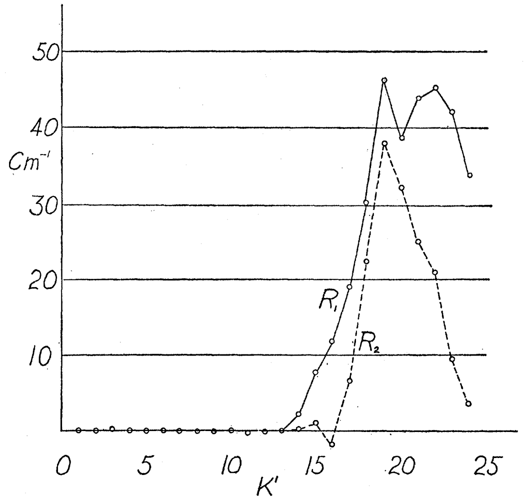

FIG. 3. Deviations of the observed R_1 and R_2-branch lines of the $(v',3)$ SrH D band at $\nu = 17,341$ from positions computed with fourth-degree least-squares equations fitting the first 13 lines in each branch. Positive deviation indicates observed frequency to be larger than the calculated frequency.

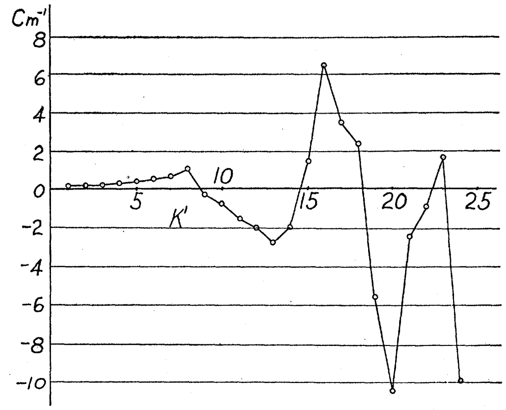

FIG. 4. Spin doubling in the upper state of the $\nu = 17,341$ $(v',3)$ SrH D band.

Table IV contains the assignment of frequencies in these bands. The B'' values as determined from the lower state combination differences agree well with those predicted for $v=2$ and 3 of the $N\,{}^2\Sigma$ state from the known values of B_0^*, B_1^* and α. Upper state combinations involving unperturbed levels of low K value yield a $B_v^* = 1.913$. This is much lower than the B's for any of the other SrH levels, indicating that this $D\,{}^2\Sigma$ state has a large equilibrium r value and is less stable.

The peculiar nature of the perturbations in these D levels is illustrated in Figs. 3 and 4. For the first of these diagrams fourth degree equations were developed by the method of least squares to fit the first 13 lines of the R_1 and R_2 branches of the $(v',3)$ band. The deviations of all the remaining R-branch lines from the frequencies calculated by means of these equations were then plotted. Positive deviations indicate that the observed frequencies are larger than the calculated ones. Fig. 4 gives the course of the spin doubling for this $D\,{}^2\Sigma$ state as a function of K. Somewhat similar but less marked irregularities exist in the $D\,{}^2\Sigma$ levels of CaH.[6]

TABLE V. *Rotational constants for SrH and SrD.*

	$N\,{}^2\Sigma$			$B\,{}^2\Sigma$	
	SrH	SrD		SrH	SrD
B_0^*	3.6344	1.8463	B_0^*	3.8323	1.9252
B_1^*	3.5530	1.8171	B_1^*	3.7393	1.8903
B_2^*	3.471		α	0.0930	0.0349
B_3^*	3.390		B_e^*	3.8788	1.9427
α	0.0814	0.0292	D_0	-1.722×10^{-4}	-4.02×10^{-5}
B_e^*	3.6751	1.8609	D_1	-1.732×10^{-4}	-3.81×10^{-5}
D_0	-1.348×10^{-4}	-3.47×10^{-5}	$\gamma_0(K<10)$	-3.81	-2.008
D_1	-1.293×10^{-4}	-3.64×10^{-5}			
γ_0	$+0.122$	$+0.0613$			
				$C\,{}^2\Sigma$	
			B_0^*	3.930	1.95
				$D(v)\,{}^2\Sigma$	
			B_v	1.913	

DISSOCIATION PRODUCTS

Because the ${}^2\Pi\rightarrow{}^2\Sigma$ SrH system at 5323A was thought to correspond with the 4900A E system of CaH, we labeled its upper state $E\,{}^2\Pi$.[1] Now the only possible electron configurations for these Π states are $\ldots ns\sigma np\sigma np\pi$ or $\ldots ns\sigma^2(n-1)d\pi$, since $\ldots ns\sigma^2 np\pi$ is known definitely to give the $A\,{}^2\Pi$ states. The $E\,{}^2\Pi$ state of CaH has been shown[3] to have a coupling constant $A=9.3$, fairly close to the value $A=7$ of the $3\,{}^3D$ level of the Ca atom. We found that for the upper ${}^2\Pi$ state of the 5323A bands of SrH, however, $A=117$, whereas for Sr $4\,{}^3D$ A is but 32. Apparently, then, the $E\,{}^2\Pi$ state of CaH is $\ldots 4s\sigma^2 3d\pi$, while this ${}^2\Pi$ state of SrH is $\ldots 5s\sigma 5p\sigma 5p\pi\,{}^2\Pi$. We shall therefore refer to this as the $F\,{}^2\Pi$ state of SrH. Among the large number of lines near 5800A in the SrH spectrum we can trace some of the outline of a ${}^2\Pi\rightarrow{}^2\Sigma$ band which could not have a very large doubling in its ${}^2\Pi$ state. This is very possibly the $E\,{}^2\Pi$ state of SrH. Analysis of this band is unfortunately made very difficult by the considerable overlapping of fine structure from other SrH bands.