



FIG. 3. Λ -doubling curves for the $E^2\Pi$ state of SrH.

may not be accurate. If it is correct as given, the failure of the curve to return to zero at $J=0$ must be attributed to another perturbation. Because of this possibility of error in the P_1 and R_1 branches at low J values, however, we do not evaluate the usual p_0 and q_0 quantities involved in the Λ -doubling. The other molecular constants, determined from the $\Delta_2 F$ values in the customary manner,² are presented in Table IV.

Satellite branches should be observed in this band. We have located the $^R Q_{21}$ branch at large J values but the other satellite branches cannot be definitely established because of the many weaker lines of the other bands present in this region.

TABLE IV. Rotational constants of the $E^2\Pi \rightarrow N^2\Sigma(0, 0)$ SrH band at 5323A.

$N^2\Sigma$ state: $B_0 = 3.6198$	$D_0 = -1.287 \times 10^{-4}$
$E^2\Pi$ state: $B_0^* - \frac{1}{2} = 3.6388$	$D_0 = -1.03 \times 10^{-4}$
$B_0^* + \frac{1}{2} = 3.8687$	$D_0 = -1.95 \times 10^{-4}$
$A = 117$	

ELECTRONIC STATES OF SrH

In our earlier work¹ on the red bands of SrH we noted that the $A^2\Pi$ and $B^2\Sigma$ states stand to each other in the relation of "pure precession," being undoubtedly $5p\sigma^2 5p\pi^2 \Pi$ and $5p\sigma^2 5p\sigma^2 \Sigma$ respectively. The $N^2\Sigma^+$ normal state is probably $5s\sigma^2 4d\sigma^2 \Sigma$. The E state may be either $5s\sigma^2 4d\pi^2 \Pi$ or $5s\sigma 5p\sigma 5p\pi^2 \Pi$. The D state might then well be $5s\sigma 5p\sigma^2 \Sigma$, and the lack of strong interaction with the E state could be due to the large difference in the B constant of the D state from that of all other states. For our analysis of one of the bands of the D system, with v' as yet unknown, indicates B' to be only 1.91. The lack of strong interaction may also be due to the presence of the $C^2\Sigma$ state above the E state, thus neutralizing in part the effect of the D state.

The D system of SrH as well as the C and B systems of SrD will be discussed in a further paper.

The $3p^3\Sigma \rightarrow 2s^3\Sigma$ Bands of HD and D₂

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The $3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of HD and D₂ which form the most conspicuous regularities in the near infrared are given and the band constants calculated.

IN a previous communication¹ the so-called Fulcher bands ($3p^3\Pi \rightarrow 2s^3\Sigma$) of the isotopes HD and D₂ of the hydrogen molecule were given. There is a band system $3p^3\Sigma \rightarrow 2s^3\Sigma$ chiefly lying in the extreme red and near infrared closely connected with the Fulcher bands. It has the same final state, and the initial states belong to the same complex, i.e., they differ only by the value of the projection Λ of the orbital momentum on the internuclear axis.

¹G. H. Dieke and R. W. Blue, Phys. Rev. 47, 261 (1935).

The present paper contains chiefly the empirical data of the $3p^3\Sigma \rightarrow 2s^3\Sigma$ system. A theoretical discussion of the $3p$ complex is given in the following paper, which will also contain an account of the perturbations in both systems. The general remarks about the production of the spectrum, the wave-length measurements, etc., made in the previous paper¹ apply also to the present investigation.

In the far red and infrared the sensitivity of the photographic plates varies rapidly with the

TABLE I. The $3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of HD.

P BRANCH			R BRANCH			P BRANCH			R BRANCH			P BRANCH			R BRANCH		
J	ν	I	J	ν	I	J	ν	I	J	ν	I	J	ν	I	J	ν	I
0→0						4→3						4→3					
0	—	—	11	664.67	2	4	666.08	9	985.87	5	0	—	—	—	11	950.77	4
1	11 574.34	1		694.49	4	5	574.12	9	961.41	4	1	11 874.62	3		970.71	5	
2	514.36	3		713.90	4	6	472.42	7	925.10	3	2	819.05	1		978.51	5	
3	444.97	3		722.78	4	7	361.56	5			3	752.12	2		974.16	4	
4	366.59	2		721.22	2	8	242.21	3			4	674.32	1		957.75	3	
5	279.73	1		709.06	0	9	114.83	1			5	586.21	0		929.41	2	
1→0						3→1						5→2					
0	—	—	13	465.77	2	0	—	—	14	559.84	7	0	—	—	15	330.13	4
1	13 377.31	4		491.64	10	1	14 477.34	0		580.96	8	1	15 254.16	4		343.93	5
2	315.37	5c		505.20	10	2	415.97	5		590.42	6b	2	192.39	4		341.43	5
3	242.09	5		506.34	10	3	342.07	6		569.03	5	3	115.32	4		322.68	4
4	157.88	6c		495.14	10	4	257.98	4		551.11	6	4	023.30	3		287.72	4
5	063.27	5		471.79	0	5	144.89	5		516.13	5r	5	—	—		coincides with D _α	
6	12 958.84	5		436.34	1	6	037.72	4				6	—	—		169.93	2
7	845.16	4		388.39	0	7	13 916.10	2c				6	—	—			
8	722.88	2c				3→2						5→3					
9	592.63	3				0	—	—	12	459.88	7	0	—	—	13	330.16	2
+D ₂						+D ₂						+D ₂					
1→1						4→1						6→3					
0	—	—	11	262.98	0	1	12 379.33	7		483.05	7	1	13 256.17	3		345.97	2
1	—	—		290.98	1	2	322.13	8		496.62	9	2	198.48	3		347.51	3
2	—	—		308.77	0	3	254.43	9		481.43	6	3	127.41	4		334.78	2
3	—	—		316.41	0	4	178.46	6		471.69	6	4	043.38	4		307.80	2
4	—	—		313.49	00	5	075.59	5		446.90	4	5	12 946.87	5		266.77	1
5	—	—				6	980.54	4				6	—	—		838.43	3
2→0						4→2						6→4					
0	—	—	15	165.34	6	0	—	—	16	050.74	2	0	—	—	14	586.93	4
1	15 078.98	6		187.32	6	1	15 970.62	2		066.61	3	1	14 615.05	3		598.37	5c
2	015.02	7		195.00	8	2	906.81	2		066.24	3	2	455.29	4		593.49	6
3	14 937.79	6		188.37	6	3	827.66	2		049.70	2	3	379.80	4		571.55	7
4	847.70	7		167.47	7r	4	733.67	1		017.18	3bv	4	289.31	4		534.70	5
5	745.23	7		132.56	6	5	625.53	0				5	183.63	2			
6	631.14	5		083.85	5	6	503.70	00				6	065.32	1			
7	505.88	5		021.64	4	4→2						6→4					
8	370.28	3		14 946.35	3	0	—	—	13	950.71	5	0	—	—	12	684.92	4
225.81	1					1	13 872.65	6		968.64	9	1	—	—	1	698.35	3
2→1						+D ₂						+D ₂					
0	—	—	12	962.60	7	2	812.95	7		972.41	9	2	12 559.18	4		697.34	3
1	12 878.32	6		986.71	8	3	740.00	6		962.05	9	3	489.62	5		681.37	3
2	818.64	8		998.65	5	4	654.22	7		937.64	4	4	406.90	5		652.33	3d
3	747.76	9		998.15	4r	5	556.18	4		899.34	4	5	310.38	3			
						6	446.43	2		847.43	1	6	—	—			
						7	325.66	1		781.62	2						
						8	194.85	1									

wave-length. The photographic intensities depend very much on the plate used and the sensitization employed. Relative intensities appear sometimes completely distorted even over a comparatively narrow region. This accounts for almost all the apparent intensity anomalies found in the tables.

The frequencies and intensities of the bands are given in the Tables I for HD and II for D₂. The bands contain a large part of the strongest lines in the infrared and are the most prominent feature in that part of the spectrum. Only those bands which are fairly complete are listed. There are several weaker bands, the position of which can be calculated and of which a number of lines can be found. They, as well as bands with higher values of V' , are left for a later occasion as undoubtedly their identification will be much more certain when the other strong lines in this region have been classified.

The rotational constants were calculated in the

usual way,¹ and they are listed in Table III. The spaces left open are the vibrational levels which are so strongly perturbed that no reliable values can be obtained.

As shown more in detail in the following paper, the B_v values calculated directly from the observations cannot be used for the calculation of the moment of inertia or other constants which have to do with the vibration and rotationless state of the molecule. It is necessary to take into account the influence of the interaction with the $3p^3\Pi$ state. If we correct for this in the way indicated in the following paper the new values for B_v are

	HD	D ₂
B_0	20.257	13.553
B_1	19.259	13.045
B_2	18.236	12.504

This includes the B_v of all those levels which are far enough from any $3p^3\Pi$ level, so that only the regular Λ doubling has to be taken into account.

B_e can then be calculated from $B_v = B_e$.

TABLE III. Rotational constants of the 3p³Σ level.

v	HD		D ₂	
	B _v	D	B _v	D
0	20.077	0.0089	13.475	
1	19.100	87	12.974	0.0042
2	18.095	77	12.440	39
3	+		11.910	39
4	16.044	71	11.367	37
5	15.011	77	+	
6	+		10.201	34
7			+	
8			8.920	27
9			8.024	39

-α(V+1/2). In evaluating these constants the B₀ value of D₂ which is less reliable than the others was disregarded.

We find then

	HD	D ₂
B _e	20.766	13.856
α	1.010	0.541
I _e	1.3319 · 10 ⁻⁴⁰	1.9961 · 10 ⁻⁴⁰
r _e	1.09662 · 10 ⁻⁸	1.09649 · 10 ⁻⁸
	average r ₀ = 1.09655 · 10 ⁻⁸ .	

The ratio of the B_e values is 0.6672 which compares well with the theoretical value 0.6671. The ratio 0.534 of the α is lower than the theoretical value 0.544, but the accuracy with which the α can be determined in this case is hardly better than this agreement.

If the constants would be calculated in the same way from the observed B_v without the correction, the ratio of the B_e values would be 0.6692 which is considerably different from the theoretical value 0.6671.

With the rotational energy of initial and final states known, the origins of all the bands can be calculated and they are given in the Tables IV and V. The values marked with a + are the origins of those bands which have strong perturbations. They are obtained only from the P(1) line as the J'=0 level cannot be perturbed.² As they are calculated from one line only they are less accurate than the other values.

The constants in the formula for the vibrational energy

$$\omega v - xv^2 + yv^3 - zv^4 + \dots (v = V + 1/2)$$

² G. H. Dieke, Phys. Rev. 47, 870 (1935).

TABLE IV. Zero lines of the 3p³Σ→2s³Σ bands of HD.

V' \ V''	0	1	2	3
0	11 624.55			
1	13 427.56	11 224.80		
2	15 129.24	12 926.46		
3		14 525.41 ⁺	12 525.41 ⁺	
4		16 018.66	13 918.64	11 918.67
5		17 400.16	15 300.16	13 300.18
6				14 521.32

TABLE V. Zero lines of the 3p³Σ→2s³Σ bands of D₂

V' \ V''	0	1	2	3	4	5
0	11 649.14					
1	13 137.49					
2	14 558.24	12 743.35				
3	15 911.16	14 096.23	12 350.41			
4		15 380.22	13 634.40	11 956.15		
5			14 847.31 ⁺	13 169.12 ⁺		
6			15 985.94	14 307.64	12 695.57	
7				15 366.35 ⁺	13 754.23 ⁺	12 207.29 ⁺
8				16 336.30	14 724.19	13 177.25
9					15 591.37	14 044.37

are

	ω	x	y	z	ν _e
H ₂	2196.13	65.80	-0.433		11 838.91
HD	1905.17	51.70	0.522	-0.091	11 825.68
D ₂	1556.64	34.51	0.287	0.04	11 813.40
D ₂ : HD	0.81706	0.6675	0.550	-0.44	—
ρ ⁿ	.81675	0.6671	0.544	0.445	—

The values for H₂ are obtained from the formula given by Richardson and Das.³ They cannot be compared directly with the constants for HD and D₂ as they were calculated in a different way from less complete data.

The ratio of the constants for D₂ and HD, which is given in the fourth row, is again approximately equal to the theoretical ρⁿ values calculated from the mass ratios. The remarks about the agreement in the Fulcher bands¹ apply also here. In another paper² it was shown that the agreement cannot be expected to be better, and that if a higher accuracy is desired, various corrections must be applied. In that paper also the shifts between the origins ν_e of the band systems were discussed.

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³ O. W. Richardson and K. Das, Proc. Roy. Soc. A122, 688 (1929).