5. Results and Comparison with Theory

The f values for $\lambda=1.54$A are shown in column 7 of Table II. These are obtained from the F values by multiplying the corresponding values shown in columns 3 and 4. Column 8 shows experimental values of $f_{0.44}-f_{1.54}$. Experimental values of $f_{0.71}-f_{1.54}$ are shown in column 9. The theoretical values of $f_{0.71}-f_{1.54}$ are shown in column 10. For these it is necessary to include the $\eta_1^{(0)}$ term and there is a slight dependence on angle. However, the variation is smaller than the experimental error and so the average of the values shown in column 9 is compared with that of column 10 thus

$$\left.\begin{aligned}\Delta f'_{\text{exp}}&=2.40\\ \Delta f'_{\text{theo}}&=2.45\end{aligned}\right]\text{0.71A to 1.54A.}$$

The theoretical value of $f_{0.44}-f_{1.54}$ is 2.45 and is practically constant with the angle. A comparison with the experiment is shown thus

$$\left.\begin{aligned}\Delta f'_{\text{exp}}&=2.57\\ \Delta f'_{\text{theo}}&=2.49\end{aligned}\right]\text{0.44A to 1.54A.}$$

This is a clear verification of the validity of Hönl's theory. It also gives one considerable faith in the f values of zinc as given by these four experiments and in the M values as given by Jauncey and Bruce. Table III lists the average of the experimental f values of the four experiments corrected for the change in structure factor due to the nearness of the K absorption edge.

Table III. *Structure factors for zinc.*

$(\sin\frac{1}{2}\phi)/\lambda$	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
f for $\psi=0°$	27.0	23.5	20.2	17.0	14.4	12.5	9.5	7.3
f for $\psi=90°$	28.4	25.9	21.5	18.2	14.9			

It is interesting to note that the f values for $(\sin\frac{1}{2}\phi)/\lambda=0.2$ for $\psi=0°$ and 90° differ by 2.4 electrons which is greater than 2. By reference to James and Brindley's paper[19] on the calculation of quantum-mechanical f values, it is seen that at this value of $(\sin\frac{1}{2}\phi)/\lambda$ the scattering for the two valence electrons is negligibly small, and so this variation of 2.4 electrons cannot be due to the valence electrons as stated in a previous paper.[17] The electron asymmetry thus extends deeper into the atom than the valence electrons.

The author wishes to thank Professor G. E. M. Jauncey for his encouragement and guidance in this work.

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[19] James and Brindley, Phil. Mag. **7**, 81 (1931).

MAY 15, 1938 PHYSICAL REVIEW VOLUME 53

The Band Spectra of SrCl and SrH

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(Received March 30, 1938)

The spectra of SrCl and SrH are observed in absorption. The SrCl analysis given by Parker is confirmed. Measurement of the relative intensities of corresponding bands of the electronic doublet $^2\Pi\rightarrow{}^2\Sigma$ indicates that $^2\Sigma$ is the ground state. Rotational analyses of several bands of the C and D systems of SrH lead to values of B_e of 4.008 and 1.925 for the C and D states, respectively. Vibrational analyses of the two systems give $\omega_e=1206.2$, $x_e\omega_e=17.0$ for the $X\,^2\Sigma$ state; $\omega_e=1347$, $x_e\omega_e=23.5$ for the $C\,^2\Sigma$ state and $\omega_e=1014.1$ and $x_e\omega_e=15.4$ for the $D\,^2\Sigma$ state. The perturbations in the C and D states are discussed in terms of the interactions of the C, D, and E states.

Introduction

A total of five band systems of the SrH molecule have been reported in a series of papers by Watson and Fredrickson[1–4] and their co-workers. All but one of these systems have a strong (0,0) band, together with a weak (0,1)

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* Sterling Fellow.

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

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

[3] W. W. Watson, W. R. Fredrickson and M. E. Hogan, Jr., Phys. Rev. **49**, 150 (1936).

[4] R. F. Humphreys and W. R. Fredrickson, Phys. Rev. **50**, 542 (1936).

band, and very weak (1,1) and (2,2) bands. The exception to this is the D system, $D^2\Sigma \rightarrow X\,^2\Sigma$. Watson, Fredrickson and Hogan[3] report two bands of this system, corresponding to transitions from a common state of unknown v' value to the ground state vibrational levels for which v'' equals 2 and 3. No other bands of this system have been reported. The D state differs from the other states of the SrH molecule in that the B constant has a value of about 1.9, while the B constants for the other states vary from 3.3 to 3.9. This same difference is found in the case of the corresponding states of CaH as reported by Grundström.[5] It is interesting to note that in the D system of CaH the bands of the $v'=0$ and $v''=0$ progressions are more prominent than are the corresponding bands of the other systems, and that the (0,0) band is absent. It is also observed that the vibrational frequency for the D state is appreciably less than that in the ground state.

The present investigation was undertaken primarily for the purpose of extending the analysis of the D system of SrH. Since the work on SrH just discussed was done in emission it was felt that it would be profitable to attempt the problem in absorption. During the course of the experimental work it became evident that some interesting information was being obtained about the C system of SrH, and about the band systems of the SrCl molecule. These latter bands were observed because of the presence of some chloride as an impurity in the material used for the core of the furnace in the earlier part of the work. Indeed the red bands were extremely strong and were well developed at relatively low furnace temperatures.

A high temperature vacuum furnace which was constructed for such spectroscopic investigations was used for the study of the absorption spectra to be considered. The furnace will be described in another article.

In order to obtain the spectrograms, light from a tungsten filament lamp operated considerably over its rated voltage was passed through the core tube of the furnace and focused on the slit of the spectrograph by means of a suitable optical system. For the study of the SrH and SrCl bands, strontium metal was distributed along the core tube and the furnace filled with hydrogen to a pressure of about 70 cm of mercury. In the case of the SrCl bands, zirconium oxide cores were used and the furnace heated to a temperature of 800° to 1000°C. The chlorine came mainly from the core because the chloride bands were much weaker when graphite cores were used. Temperatures of the order of 1600° to 2000°C were found necessary for the observation of the D system of SrH. Graphite cores were used in this case.

The spectra were photographed in the second order of a 21-foot grating in a stigmatic mounting. The dispersion was about 2.5A per mm. Eastman II-O and I-F plates were used in the regions below and above 5000A, respectively. Exposure times of the order of 2 to 5 minutes were ample. It was thus possible to obtain an exposure before the strontium metal all diffused out of the core.

Strontium Chloride

Two band systems of strontium chloride have been observed in emission by Hedfeld[6] and by Parker,[7] and in absorption by Walters and Barratt.[8] The latter apparently used rather low dispersion. According to the analyses of Hedfeld and of Parker the red system is due to a transition of the type $^2\Pi \rightarrow {}^2\Sigma$. It was not possible to tell from the emission data which of the two states involved was the ground state.

Both band systems previously reported are present on our spectrograms. Our data confirm the analyses already published, and extend some of the sequences to higher members. It is of interest that sequences extending as far as the (12,12) band are observed in absorption at temperatures of about 1500°C. Since the vibrational frequency for the ground state of SrCl is 300 cm^{-1}, an appreciable number of molecules are excited to levels up to about 3500 cm^{-1} above the level $v''=0$.

If the ground state of SrCl is $^2\Pi$, with the electronic interval of 607 cm^{-1} which is observed, the relative intensities of corresponding bands of the two members of the doublet observed in

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

[6] K. Hedfeld, Zeits. f. Physik **68**, 610 (1931)

[7] A. E. Parker, Phys. Rev. **47**, 349 (1935).

[8] O. H. Walters and S. Barratt, Proc. Roy. Soc. **A118**, 120 (1928).

absorption can be calculated from the Boltzmann factor for the temperature used. For a temperature of 800°C the ratio of intensities is about 0.5 to 1. A spectrogram taken at a temperature which was certainly not greater than 800°C has been photometered in order to determine the relative intensities of the two members of the electronic doublet. The Q heads of the $\Delta v=0$ sequences were compared. Within the limits of accuracy the intensities were equal. This indicates that the ground state is $^2\Sigma$. It should be pointed out that even though the plate used for this comparison was not calibrated the result should be reasonably accurate. The galvanometer deflections produced by the background and by the absorption band heads, when compared with the clear plate and total blackness deflections, indicated that the blackenings involved fell on the straight line portion of the plate calibration curve. At any rate conditions were such that a true intensity ratio of 0.5 to 1 could hardly give equal blackenings. The result that the ground state is $^2\Sigma$ is in agreement with the work of Jenkins and Harvey[9] who report the ground states of CaF and SrF and BaF to be $^2\Sigma$.

STRONTIUM HYDRIDE

A. The *C* system

The (0,0) and (0,1) bands of the $C\,^2\Sigma \leftrightarrows X\,^2\Sigma$ band system which have been reported by Fredrickson, Hogan and Watson[2] and by Humphreys and Fredrickson[4] are present on the absorption spectrograms taken with the furnace at a temperature of about 1500°C. These bands do not show the predissociation cut off at $K'=19$ which was reported for the emission bands excited at low hydrogen pressures. This is in agreement with the work of Humphreys and Fredrickson,[4] who extended the R branch of the (0,0) band to members as high as $K''=49$ by operating a strontium arc in hydrogen at pressures above 400 mm of mercury. It is of interest that the band lines obtained in absorption are relatively sharp from the origin to $K''=18$, beyond which point they are somewhat diffuse.

In addition to the (0,0) and (0,1) bands, the (1,0), (1,1) and (2,2) bands are present on the absorption spectrograms. The (0,0) band is much more intense than the others. The (1,0) band was not observed in emission by the authors mentioned. It, of course, lies far beyond the predissociation limit at $K'=19$ in the (0,0) band. Like the high K value lines of the (0,0) band, the lines of the (1,0) band are diffuse. The assignment of frequencies in the (1,0) band is given in Table I. This analysis was made with the help of the lower state combination differences given by Watson and Fredrickson.[1] The weakness of this band and the presence of perturbations make the assignments somewhat doubtful in some cases. The (1,1) and (2,2) bands are very weak but the positions of the heads are reasonably certain.

The rotational and vibrational constants of the C state are given in Tables V and VI, respectively. The B_1' value was obtained from an analysis of the (1,0) band, and the B_0' value is that given by Humphreys and Fredrickson.[4] The vibrational constants are obtained from the vibrational array for the C system which is given in Table II. This array was constructed from head data. The lower state frequencies found from this array are in good agreement with those found from the D system which is discussed in the following.

TABLE I. *Assignment of frequencies in the* $C\,^2\Sigma \leftarrow X\,^2\Sigma$ *(1,0) band of* SrH.

K''	R	P	K''	R	P
0	27619.5		12	45.0	49.9
1	27.2	27604.3	13	58.0	49.9
2	35.4	597.7	14	70.8	49.9
3	43.7	91.0	15	85.1	49.9
4	54.1	84.7	16	96.8 99.4 801.5	49.9
5	60.6	78.5			
6	67.2	73.3	17	19.9	49.9
7	74.8	66.1	18	31.1	49.9
8	85.5	59.5	19	44.2	57.8
9	96.1 708.5	49.9	20	59.4 61.5	
10	08.5 20.6	49.9	21		
11	28.0 32.7	49.9 57.8	22	91.2	57.8 59.5

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[9] F. A. Jenkins and A. Harvey, Phys. Rev. **39**, 922 (1931).

TABLE II. *Wave numbers of the band-heads of the* $C\,^2\Sigma \leftarrow X\,^2\Sigma$ *system of* SrH.

v' \ v''	0	1	2
0	26251	25080	
1	27550	26380	
2			26495

B. The *D* system

Bands attributed to the *D* system were found throughout the region from 4000 to 5600A, with the strongest ones between 4080 and 4480A. No bands were observed between 4480 and 4720A because of the extreme breadth of the strontium resonance line at 4607A. The band lines from 4720 to 5000A were all weak. The band $(v',2)$ reported by Watson, Fredrickson and Hogan[3] was present. The region of the $(v',3)$ band was not photographed.

With the aid of the known lower state combination differences, and the combination differences for the level of unknown v', six bands have been analyzed.

The bands at 19580 and 20752 have upper state combination differences equal to those reported for the $(v',2)$ and $(v',3)$ bands, and lower state combination differences which correspond to values of 1 and 0 respectively for v''. The band at 20561 cm^{-1} gives a value of 1 for v'' and upper state combination differences slightly lower than those of the two already discussed. The bands at 22686, 23611, and 24500 cm^{-1}, which incidentally are the strongest observed, all indicate that $v''=0$, and that the upper state combination differences decrease uniformly in going from one band to the next. The wave numbers 20752, 22686, 23611, 24500 and the change in B' indicate that these bands for which $v''=0$ belong to the $v''=0$ progression with one member missing. The missing member falls in the region of the strontium resonance line. It is also evident that the bands 20752, 19580, 18442 $(v',2)$, and 17338 $(v',3)$ form a v' progression. It is probable that this is the $v'=0$ progression.

The rotational quantum assignments of the six bands discussed are given in Table III. The vibrational array for the *D* system, using origin

TABLE III. *Assignment of frequencies in the* $D\,^2\Sigma \leftarrow N\,^2\Sigma$ *band system of* SrH.

(0,0) BAND		
K''	R	P
0		
1		
2	20754.0	
3		
4	37.4	
5	24.6	20681.1
6	06.4	56.1
7	685.0	30.3
8	63.0	597.4
9	34.1	62.2
	31.9	
10	05.1	25.9
11	572.1	482.1
	70.3	79.4
12	44.3	42.7
	38.4	38.9
13	506.3	394.0
	496.6	86.9
14	69.7	49.8
		44.5
15	31.1	298.9
	27.8	88.3

(3,0) BAND		
K''	R	P
0	23614.6	
1	14.6	23604.0
2	11.0	593.1
3	04.0	79.1
4	593.1	60.1
5	79.1	38.6
6	61.5	13.5
7	40.3	485.0
8	15.5	52.8
9	488.5	18.1
	87.0	17.1
10	57.5	379.0
	55.7	77.4
11	24.0	37.1
	21.3	35.5
12	388.1	292.5
	84.4	90.1
13	49.9	44.8
	45.6	41.7
14	10.6	194.6
	08.2	90.6
15	271.1	42.7
		38.0
16	32.6	089.7
		87.5
17	03.0	36.2
18	181.4	22983.9
	73.5	
19	61.2	40.8
	57.4	
20		906.2
		898.1
21		73.0
		68.1

(4,0) BAND		
K''	R	P
0	24504.8	
1	04.8	24493.6
2	00.7	82.4
3	493.6	67.8
4	82.4	49.3
5	67.8	27.2
6	49.3	02.3
7	27.2	373.1
8	02.3	40.6
9	373.1	04.1
10	40.6	265.1
11	04.1	22.2
		21.1
12	268.3	176.1
	65.1	74.3
13	28.2	26.7
	23.9	24.5
14	181.0	074.9
	76.1	71.6
15	44.4	20.9
	41.3	16.1
16	08.9	23959.7
	04.8	57.1
17	082.4	09.3
	78.8	06.2
18	62.0	859.5
	52.1	57.1
19	20.9	19.1
	11.6	17.4
20	23993.0	786.0
	80.1	76.6

(2,0) BAND		
K''	R	P
0		
1	22689.7	
2	86.5	
3	80.0	22653.6
4		36.3
5	55.9	14.8
6	38.7	589.9
7	18.4	61.6
	17.6	
8	595.1	30.2
	93.7	29.1
9	68.3	496.1
	66.0	94.6
10	38.8	58.1
	35.9	56.5
11	06.5	17.1
	03.0	15.0
12	467.5	373.6
	63.1	70.4
13	36.4	27.4
	32.5	23.4
14	03.5	
	02.5	
15	373.6	
	70.4	

(0,1) BAND		
K''	R	P
0		
1		
2	19581.7	
3	75.3	19551.1
4	66.2	31.7
5	53.8	11.1
6	38.0	488.0
7	19.8	62.5
	18.7	
8	497.1	
9	71.6	
	68.9	
10		
11	17.7	322.5
	14.0	20.2

(1,1) BAND		
K''	R	P
0	20565.6	
1	65.6	20554.6
2	62.6	44.3
3	56.9	30.2
4	47.4	13.3
5	33.5	493.7
6	17.6	69.7
7	01.5	42.7
8	479.4	13.3
	77.3	
9	54.2	380.9
	52.5	78.3
10	27.8	44.5
	24.3	42.3
11	398.0	07.1
	94.0	04.0
12		266.3
	63.8	62.5
13	34.2	23.1
	18.8	18.5
14	301.4	178.6
		73.2
15	262.5	31.8
	57.2	16.8
16	37.8	085.3
	35.7	84.5
17	06.7	
	06.2	

TABLE IV. *Wave numbers of the band-origins of the* $D\,^2\Sigma \leftarrow X\,^2\Sigma$ *system of* SrH.

v' \ v''	0	1	2	3
0	20751.4	19580.0	18441.8	17337.5
1		20561.8		
2	22686.4			
3	23611.0			
4	24500.5			

data, is shown in Table IV. The rotational and vibrational constants of the $D\,^2\Sigma$ and $X\,^2\Sigma$ states are given in Tables V and VI.

The origins of the bands of the D system are given by the following formula:

$$\nu = 20847.6 + \{1014.1(v'+\tfrac{1}{2}) - 15.4(v'+\tfrac{1}{2})^2\} - \{1206.2(v''+\tfrac{1}{2}) - 17.0(v''+\tfrac{1}{2})^2\}.$$

A comparison of the intensity distributions in the case of emission and absorption is of interest. The strongest bands observed in emission by Watson, Fredrickson and Hogan[3] were those analyzed and now called the (0,2) and (0,3) bands. The strongest bands observed in absorption are the (3,0) and (4,0), followed in the order of decreasing intensity by (2,0), (1,1), (0,1), (0,0) and (0,2), the latter three being about equal. This indicates that the distribution may be represented by a broad Condon parabola. In the case of the absorption bands the (0,2) and (0,3) bands are weakened by the Boltzmann factor, since the vibrational energies of states for $v''=2$ and 3 are 2310 and 3404 cm^{-1} above the $v''=0$ state. This effect is not present in emission. This intensity distribution is similar to that found by Grundström[5] for the D system of CaH.

The Mecke rule, which states that B_e/ω_e is constant for all states of a molecule, is violated by the D state of SrH, as it is for the D state of CaH. The ratio B_e/ω_e equals 1.9×10^{-3} for the D state, 3.1×10^{-3} for the ground state and 2.9×10^{-3} for the C state.

Most of the bands of the C and D systems show perturbations after the first few members of a band. The (1,0) band of the C system shows perturbations similar to those reported for the (0,0) band by Humphreys and Fredrickson.[4] It was not possible to trace these perturbations in detail because the band was not extended to high enough values of K. The (0,0), (1,1), (2,0), (3,0), and (4,0) bands of the D system all show perturbations of the type illustrated by Watson, Fredrickson and Hogan[3] in the case of the (0,3) band (called (v',3) in their paper). At a K' value of 10 to 15 the observed frequencies suddenly deviate by a marked amount from the frequencies calculated from a fourth power equation which fits the observed values up to the K' in question. The deviations in some cases reach values of 50 to 100 cm^{-1}. The values of K' at which the perturbations begin are different in the different bands, but all fall in the range 10 to 15. The states which interact with the C and D states to cause these perturbations, and the predissociation in the C state will be discussed after the dissociation products and the heats of dissociation are considered.

DISCUSSION

In order to obtain some idea of the probable products of dissociation to be associated with each molecular state, approximate values of the heats of dissociation for the X, C, and D states were determined by the method of Rydberg. The values of the vibrational constants found for these states were used in this determination. Since the vibrational constants for the $A\,^2\Pi$, $B\,^2\Sigma$, and $E\,^2\Pi$ states of SrH are not known it was not possible to calculate the heats of

TABLE V. *Rotational constants of the* $C\,^2\Sigma$ *and* $D\,^2\Sigma$ *states of* SrH.

$C\,^2\Sigma$	$D\,^2\Sigma$	$D\,^2\Sigma$
$B_0=3.942$	$B_0=1.914$	$B_4=1.816$
$B_1=3.810$	$B_1=1.890$	$\alpha=0.024$
$\alpha=0.132$	$B_2=1.865$	$B_e=1.925$
$B_e=4.008$	$B_3=1.841$	$D=-0.3\times10^{-4}$
$D=-1.4\times10^{-4}$		

TABLE VI. *Vibrational constants of the* $X\,^2\Sigma$, $C\,^2\Sigma$, *and* $D\,^2\Sigma$ *states of* SrH.

$X\,^2\Sigma$ (FROM ORIGIN DATA)	$C\,^2\Sigma$ (FROM HEAD DATA)	$D\,^2\Sigma$ (FROM ORIGIN DATA)
$\omega_e=1206.2$	$\omega_e=1347$	$\omega_e=1014.1$
$x_e\omega_e=17.0$	$x_e\omega_e=23.5$	$x_e\omega_e=15.4$

dissociation for those states. However, some idea of the values was obtained from the probable dissociation products, once the results for the X, C, and D states were used to make a correlation with the known atomic states. The heats of dissociation are given in Table VII.

The potential energy curves for the X, C, and D states, obtained by using the Morse function, are shown in Fig. 1. The states of the Sr atom into which the molecules dissociate from the various molecular states are shown at the right of the figure. Potential curves for the A, B, and E states are also shown. They were obtained from the known positions of the minima and the probable dissociation limits.

It is seen that the D state is the only known state which can cause the predissociation in the C state. This determines the heat of dissociation of the D state, because the dissociation limit must be lower than the predissociation cut off in the C state. The value of the dissociation energy thus found for the D state is lower than that found from the vibrational constants by the Rydberg method. It thus seems reasonable to assume that the values given by the Rydberg method are high rather than low for the X and C states. By taking a value of the dissociation energy of the ground state somewhat lower than that calculated, it is possible to correlate the dissociation limits with the atomic terms as shown in Fig. 1. The probable configurations and dissociation products are given in Table VII. It should be pointed out in this connection that if the dissociation energy of the ground state is higher rather than lower than the value calculated from the molecular constants, the ^3P state of the atom could be the dissociation limit of the D state. In this case the A, B, D, and perhaps the E states would all approach the ^3P term as a dissociation limit. It seems reasonable however to take the correlation given because the dissociation energy in the D state is considerably lower than that calculated by the Rydberg method.

TABLE VII. *Probable configurations and dissociation products of the* SrH *molecule.*

STATE	PROBABLE CONFIGURATION	DISSOCIATION PRODUCTS	DISSOCIATION ENERGY (cm^{-1})
$X\ ^2\Sigma$	$5s\sigma^2 4d\sigma$	Sr, ^1S+H, ^2S	10,000
$A\ ^2\Pi$	$5s\sigma^2 5p\pi$	Sr, ^3P+H, ^2S	11,000
$B\ ^2\Sigma$	$5s\sigma^2 5p\sigma$	Sr, ^3P+H, ^2S	10,000
$E\ ^2\Pi$	$5s\sigma^2 4d\pi$?	Sr, ^3D+H, ^2S	9,500?
$D\ ^2\Sigma$	$5s\sigma 5p\sigma 4d\sigma$	Sr, ^3D+H, ^2S	7,500
$C\ ^2\Sigma$	$5s\sigma^2 6s\sigma$	Sr, ^3S+H, ^2S	12,500

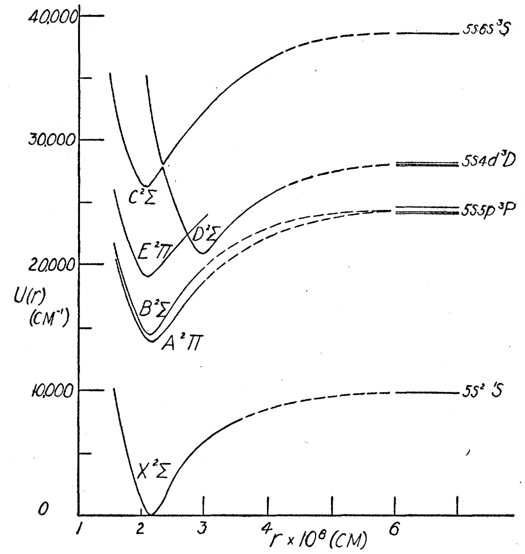

FIG. 1. Potential energy curves for SrH.

From the relative positions of the potential energy curves shown it is seen that the levels of the D state are perturbed probably by levels of the E state. The curves of the C and D states do not actually cross, because levels of the same Λ value cannot do so. In view of the indicated shapes of the C and D curves, they merge in the manner shown. This merging of the curves occurs in the region of predissociation of the C state. The predissociation is to be accounted for by this interaction of the C and D states, together with the relative positions of the point of merging and the dissociation limit of the D state.

In conclusion the authors wish to express their appreciation to Professor W. W. Watson for many stimulating discussions of this work.