

Absorption Spectra of SH and SD Produced by Flash Photolysis of H2S and D2S

D. A. Ramsay

Citation: J. Chem. Phys. **20**, 1920 (1952); doi: 10.1063/1.1700339 View online: http://dx.doi.org/10.1063/1.1700339 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v20/i12 Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about_the_journal Top downloads: http://jcp.aip.org/features/most_downloaded Information for Authors: http://jcp.aip.org/authors

ADVERTISEMENT



Absorption Spectra of SH and SD Produced by Flash Photolysis of H_2S and D_2S

D. A. RAMSAY

Division of Physics, National Research Council, Ottawa, Canada

(Received April 2, 1952)

 H_2S and D_2S were irradiated in a flash photolysis apparatus, and the absorption spectra of the products were photographed within 1 millisecond of the photolysis flash using the second order of a 21 ft grating spectrograph. The (0, 0) and (1, 0) bands of SH and SD were observed and analyzed. The following molecular constants for SH were obtained: ${}^{2}\Sigma^{+}$ state: $B_{e'} = 8.538_{1}$ cm⁻¹, $\alpha_{e'} = 0.509_{1}$ cm⁻¹, $r_{e'} = 1.421_{5}$ A, $\nu_{00} = 30,662.4_{2}$ cm⁻¹, $\Delta G_{2'} = 1784.6_{3}$ cm⁻¹, $\gamma_{0} = 0.313$ cm⁻¹. ²II state: $B_{0''} = 9.461_{1}$ cm⁻¹, $r_{0''} = 1.350_{3}$ A, $A = -376.9_{6}$ cm⁻¹. The rotational lines of the (1, 0) SH band were observed to be diffuse, indicating a predissociation in the first vibrational level of the ${}^{2}\Sigma^{+}$ state. This establishes an upper limit of 92.7 kcal and a lower limit of 66.3 kcal for the ground state dissociation energy of SH.

INTRODUCTION

HE ${}^{2}\Sigma \leftarrow {}^{2}\Pi$ band system of SH with band heads at 3236.6A and 3279.1A was first observed by Lewis and White¹ in absorption in a pulsed radiofrequency discharge through H₂S, after several unsuccessful attempts by earlier workers to obtain this band system in emission. A rotational analysis of the ${}^{2}\Sigma \leftarrow {}^{2}\Pi_{\frac{3}{2}}$ sub-band was carried out and the 2II state was shown to be inverted. Gaydon and Whittingham² obtained band heads of the same band in emission in the spectra of coal gas flames to which H₂S had been added, and Dyne and Style³ obtained similar band heads in fluorescence by irradiating H₂S with vacuum ultraviolet radiation. Leach⁴ observed about 50 lines of this band in emission using a Schüler-type discharge tube containing H_2S and evaluated constants for the $^2\Sigma$ and $^2\Pi$ states. More recently he has reported⁵ three new bands for SD in emission. Porter⁶ obtained the band at 3236.6A in absorption by the flash photolysis of H_2S and observed another similar band at 3060A. By obtaining the corresponding bands for SD he was able to show that the 3236.6A band was the (0, 0) and the 3060 band the (1, 0) band for SH. At the same time we⁷ were engaged on an independent investigation of the flash photolysis of H_2S and D_2S using higher resolving power than Porter and have carried out analyses of the (0, 0) and (1, 0) bands of SH and SD. The values for the molecular constants obtained are more accurate than those determined in earlier investigations.^{1,4} The rotational



FIG. 1 Flash photolysis apparatus.

- ⁵ S. Leach, Disc. Faraday Soc. No. 9, p. 81 (1950).
 ⁶ G. Porter, Disc. Faraday Soc. No. 9, p. 60 (1950).

lines of the (1, 0) band of SH were observed to be diffuse while those of the (0, 0) band were sharp, establishing with certainty a predissociation in the first vibrational level of the ${}^{2}\Sigma$ state.

EXPERIMENTAL

1. Description of Apparatus

The flash photolysis apparatus was similar in many aspects to the one described earlier by Porter.8 A quartz absorption tube T was mounted parallel to a quartz flash tube P known as the photolysis flash tube (see Fig. 1). The gas to be photolyzed was introduced into T and subjected to a light flash of high intensity and short duration ($\sim 10^{-3}$ sec) by discharging a bank of large condensers through P. To increase the amount of photodecomposition both tubes were surrounded by two hemicylinders coated with magnesium oxide.^{9,10}

The absorption spectrum of the photolysis products was observed by mounting a second quartz flash tube S—known as the "source" tube—on the axis of T, and focusing it by means of quartz lenses L_1 and L_2 on to the slit of a 21 ft concave grating spectrograph. The source tube contained a central 3-mm quartz capillary and under suitable conditions (see below) emitted an almost pure continuum. The photolysis and source flashes were initiated by means of high voltage pulses from two spark coils applied to external trigger electrodes wrapped round the middle of the flash tubes, the time delay between the flashes being controlled by means of a thyratron circuit (see Fig. 2). The details of the apparatus were as follows:

Quartz absorption tube: 1-meter long, 5-cm diameter, fitted with quartz windows.

Photolysis flash tube: 1-meter long, 1-cm diameter, $\frac{3}{8}$ -in. diameter tungsten electrodes, filled with xenon to 70-mm pressure, dissipates 4800 joules (600 μ f at 4000 v) per flash, duration of flash 1.5×10^{-3} sec.

¹ M. N. Lewis and J. U. White, Phys. Rev. 55, 894 (1939).

² A. G. Gaydon and G. Whittingham, Proc. Roy. Soc. (London) A189, 313 (1947).

^a P. J. Dyne and D. W. G. Style, Nature **167**, 899 (1951). ⁴ S. Leach, Compt. rend. **230**, 2181 (1950).

⁷G. Herzberg and D. A. Ramsay, Disc. Faraday Soc. No. 9, p. 80 (1950).

 ⁸ G. Porter, Proc. Roy. Soc. (London) A200, 284 (1950).
 ⁹ A. C. Menzies and J. Skinner, J. Sci. Instr. 26, 299 (1949).

¹⁰ The diffuse reflectance of magnesium oxide has been recently measured by W. E. K. Middleton and C. L. Sanders, J. Opt. Soc. Am. 41, 419 (1951) and found to be between 95 percent and 98 percent for the spectral region 2400A to 8000A.

Source flash tube: Approximately 5-in. long with a central quartz capillary 2-in. long and 3-mm internal diameter, tungsten electrodes, filled with xenon to 150-mm pressure, dissipates 80 joules (10 μ f at 4000 v) per flash, duration of flash 3×10^{-4} secs.

Details of the charging circuits and timing mechanism are given in Fig. 2. The condensers C_1 , C_2 , C_3 , and C_4 were charged, and the firing sequence started by closing the control switch S_3 . The condenser C_4 discharged through the primary of the spark coil SC_1 and triggered the photolysis flash. As the condenser C_1 discharged through the photolysis flash tube P, the negative potential on the grid of the thyratron M_3 decreased until at a certain potential the thyratron fired. This discharged the condenser C_3 through the spark coil SC_2 and triggered the source flash. The time delay between the photolysis and source flashes was determined by the constants of the circuits and could be varied from 0-5 milliseconds by means of the variable condenser C_5 . The time delay was measured by means of a photocell coupled to the vertical plates of a cathode-ray oscilloscope and was found to be reproducible to better than 0.1 millisecond.

2. Flash Tube Performance¹¹

It was found that if sufficient care was taken in outgassing the walls of the tube and the electrodes before filling with xenon, the photolysis flash tube could be flashed repeatedly at intervals of approximately 10 sec and had a lifetime of a few thousand flashes. The radiation emitted consisted mainly of xenon lines with very little continuum.

The radiation from the source tube consisted mainly of continuum with a few emission and absorption lines. The ratio of continuum to line emission could be increased by (a) increasing the capacity of the condensers, (b) increasing the voltage applied, (c) reducing the diameter of the quartz capillary. With the source tube used and a dissipation of 80 joules per flash, an almost pure continuum was obtained extending from 9000 to 2000A with virtually no emission lines and only a few silicon absorption lines. The quality of the continuum was found to be very sensitive to the internal diameter of the quartz capillary and deteriorated slowly with repeated flashing due to the gradual enlargement of the quartz capillary. After several thousand flashes when the internal diameter had increased with approximately 3 to 5 mm it became necessary to renew the quartz capillary.

3. Absorption Spectra of SH and SD

The H_2S was obtained from commercial cylinders while the D_2S was prepared by dropping 99.6 percent



PHOTOLYSIS FLASH TUBE,

FIG. 2. R_1 , R_2 charging resistors, R_3 , R_4 discharging resistors. Electrical circuit diagram.

 D_2O on to Al_2S_3 which had previously been heated to red heat to remove any H_2S . Both gases were purified by distilling twice from a dry ice trap to one at liquid air temperature.

Initial experiments were carried out varying (a) the pressure of H_2S or D_2S , and (b) the time interval between the photolysis and the source flashes to determine the conditions for the optimum concentration of SH and SD radicals. Eastman Kodak 103a0 plates were used with a wide slit (0.1 mm) so that exposures could be obtained with the 21-ft grating in a single flash. With pressures of H_2S from 1 to 10-mm Hg the (0, 0) SH band was obtained together with the ${}^{3}\Sigma - {}^{3}\Sigma$ absorption system of S₂ extending from 3300A to the H₂S absorption limit near 2450A. The S_2 bands were not very troublesome in the region of the (0, 0) SH band but were sufficiently intense to obscure most of the (1, 0) SH band. With higher pressures of H₂S (100-500mm Hg) the S₂ bands were considerably reduced in intensity and the (1,0) SH band was clearly visible. Under these conditions however the (0, 0) SH band appeared to be less intense. Similar results were obtained by adding an excess inert gas. Thus when H₂S at 10-mm pressure was photolyzed in the presence of 200-mm helium, the S_2 bands were again reduced in intensity and the (1, 0) SH band was readily observed. The (0, 0) SH band also was somewhat reduced in intensity. Variation of the time interval between the photolysis and source flashes indicated that the optimum concentration of SH radicals occurred, as might be expected, when the source flash immediately followed the photolysis flash, though weak spectra could be observed even 5 milliseconds after the photolysis flash.

Final plates were taken with a resolving power of $\sim 100,000$. Five flashes were required using Eastman Kodak 103a0 plates. For the (0, 0) SH and SD bands, 10-mm pressure of H₂S or D₂S was used while for the (1, 0) bands 200-mm helium was added. The H₂S or D₂S was renewed between flashes, and the quartz absorption tube was flamed at the end of each exposure to remove the thin deposit of sulfur. A spectrogram of the (0, 0) SH band is shown in Fig. 3.

The rotational lines of the SD bands and the (0, 0) SH band were observed to be sharp while those of the

¹¹ Further discussions of flash tubes and their characteristics have been given by P. M. Murphy and H. E. Edgerton, J. Appl. Phys. **12**, 848 (1941); G. Porter (see references 6 and 8); G. D. Hoyt and W. W. MacCormick, J. Opt. Soc. Am. **40**, 658 (1950).



FIG. 3. The (0, 0) band of SH in absorption. The R_2 head is at 3236.6A and the Q_2 head is at 3279.3A.

(1, 0) SH band were found to be distinctly diffuse. Vacuum wave numbers were obtained in the usual manner¹² and are listed in Tables I-IV. The wave numbers are accurate to about 0.03 cm⁻¹ for the sharp lines and 0.15 cm⁻¹ for the diffuse lines.

ROTATIONAL ANALYSIS

For a ${}^{2}\Sigma - {}^{2}\Pi_{i}$ (a) transition¹³ a total of twelve branches is predicted by theory and are designated $P_1, Q_1, R_1, {}^{o}P_{21}, {}^{R}Q_{21}, {}^{S}R_{21}$ for the ${}^{2}\Sigma - {}^{2}\Pi_{\frac{3}{2}}$ sub-band and $P_2, Q_2, R_2, {}^{o}P_{12}, {}^{P}Q_{12}, {}^{Q}R_{12}$ for the ${}^{2}\Sigma - {}^{2}\Pi_{\frac{1}{2}}$ sub-band. In the present investigation all twelve branches have been identified for the (0, 0) bands of SH and SD while only the stronger branches have been identified for the (1,0) bands (Tables I-IV). The principal branches were picked out by inspection and the other branches identified by means of combination relations.¹⁴

1. Determination of Accurate Molecular Constants

A. The $^{2}\Sigma$ State

The rotational term values for a ${}^{2}\Sigma$ state are given by 15

$$F_1(K) = B_v K(K+1) - D_v K^2(K+1)^2 - \frac{1}{2}\gamma K, \qquad (1)$$

$$F_2(K) = B_v K(K+1) - D_v K^2(K+1)^2 - \frac{1}{2}\gamma(K+1), \quad (2)$$

where $F_1(K)$ refers to components with $J = K + \frac{1}{2}$ and $F_2(K)$ refers to those with $J = K - \frac{1}{2}$. B_v and D_v are effective rotational constants and γ is the spin doubling constant. When the initial and final states are in the relation of pure precession¹⁶

$$B_{\nu} = B_{v_{\text{true}}} - \frac{2B^2_{v_{\text{true}}}l(l+1)}{\nu(\Pi, \Sigma)},$$
(3)

where $B_{v_{\text{true}}}$ is the true rotational constant; $\nu(\Pi, \Sigma)$ is the separation of the Π from the Σ state, and l=1 for a II state.

(a) Determination of γ .—The spin doubling in the ${}^{2}\Sigma$ state was determined from the combination relations¹⁴

$$R_{1}(J) - {}^{R}Q_{21}(J) = Q_{1}(J+1) - {}^{Q}P_{21}(J+1) = {}^{Q}R_{12}(J) - Q_{2}(J) = {}^{P}Q_{12}(J+1) - P_{2}(J+1) = \gamma(J+1)$$
(4)

and found to be a linear function of J (see Fig. 4). The best values of γ obtained are given in Table V.

(b) Determination of B_{v}' and D_{v}' .—It is readily shown from Eqs. (1) and (2) that

$$\Delta_2 F_1'(J) = (4B_v' - 6D_v')J - 8D_v'J^3 + \gamma, \tag{5}$$

$$\Delta_2 F_2'(J) = (4B_v' - 6D_v')(J+1) - 8D_v'(J+1)^3 - \gamma. \quad (6)$$

The quantities $\Delta_2 F_1'(J)$ and $\Delta_2 F_2'(J)$ were obtained from the combination relations¹⁴

$$\Delta_2 F_1'(J) = R_1(J) - P_1(J) = {}^{Q}R_{12}(J) - {}^{O}P_{12}(J), \quad (7)$$

$$\Delta_2 F_2'(J) = R_2(J) - P_2(J) = {}^{S}R_{21}(J) - {}^{Q}P_{21}(J).$$
(8)

¹³ G. Herzberg, Spectra of Diatomic Molecules (D. Van Nos-

trand Company Inc., New York, 1950), p. 258. ¹⁴ See W. Jevons, "Report on the Band-Spectra of Diatomic Molecules" (The Physical Society, London, 1932), p. 164, for an energy level diagram of a ${}^{2}\Sigma - {}^{2}\Pi_{i}$ transition and pps. 172–3 for combination relations in a ${}^{2}\Sigma - {}^{2}\Pi_{i}$ band.

¹⁵ See reference 13, p. 222.
 ¹⁶ J. H. Van Vleck, Phys. Rev. 33, 467 (1929).

¹² M. I. T. wavelength tables were used for the Fe lines, and Kayser's Schwingungszahlen were used for the vacuum corrections.

TABLE I. Vacuum wave numbers and assignments of the rotational lines of the (0, 0) SH band.

J	<i>P</i> ₁	Q1	R1	<i>QP</i> ²¹	<i>R</i> Q21	\$ _{R21}	P 2	Q 2	R_2	0 _{P12}	P _{Q12}	Q _{R12}
$\begin{array}{c} 0.5\\ 1.5\\ 2.5\\ 3.5\\ 4.5\\ 5.5\\ 6.5\\ 7.5\\ 9.5\\ 10.5\\ 11.5\\ 12.5\\ 13.5\\ 14.5\\ \end{array}$	30,832,68 30,803,45* 30,771,96 30,703,79 30,666,87 30,526,89 30,586,99 30,544,17 30,499,22 30,452,03* 30,403,05	30,849,42 30,836,54 30,821,67* 30,786,26* 30,786,26* 30,742,79 30,717,94 30,690,96 30,630,14 30,659,92 30,521,19	$\begin{array}{c} 30,882.71\\ 30,886.57^{\rm s}\\ 30,886.01^{\rm s}\\ 30,885.01^{\rm s}\\ 30,885.30^{\rm s}\\ 30,885.30^{\rm s}\\ 30,881.06\\ 30,874.47\\ 30,865.69\\ 30,854.66\\ 30,841.27\\ 30,825.37\\ 30,807.05\\ 30,786.26^{\rm s}\\ \end{array}$	30.848.95 30.835.76 30.820.62 30.803.45¥ 30.784.53 30.763.54 30.740.42 30.715.164 30.687.94 30.658.21*	30,881.95 30,885.30¤ 30,886.57* 30,886.12* 30,883.39 30,878.67 30,871.93* 30,862.69 30,851.38 30,831.67* 30,803.45*	30,931.39 30,951.16 30,968.89 30,984.57 30,998.13 30,009.43 31,025.09 ^a 31,025.09 ^a 31,025.09 ^a 31,029.37 31,031.08 31,030.03	30,451,39 30,435,75* 30,417,44 30,372,38 30,345,73 30,345,73 30,345,73 30,249,14 30,211,39 30,170,83 30,127,48	$\begin{array}{c} 30,480.88\\ 30,484.89\\ 30,485,94a\\ 30,484.50\\ 30,479.92\\ 30,472.61\\ 30,472.61\\ 30,442.35\\ 30,472.51\\ 30,449.25\\ 30,433.15\\ 30,414.17\\ 30,392.23\\ 30,367.30\\ \end{array}$	$\begin{array}{c} 30,513.57\\ 30,553.87\\ 30,551.17\\ 30,565.76\\ 30,577.34\\ 30,585.79\\ 30,591.62\\ 30,594.27\\ 30,593.96\\ 30,590.45\\ 30,590.45\\ 30,583.93\\ 30,574.30\\ \end{array}$	30,435.75 30,404,14 30,369,84 30,332,80 30,250,52 30,205,40 30,157,53 30,106,86	$\begin{array}{c} 30,464.38\\ 30,451.88^{*}\\ 30,436.60\\ 30,418.55\\ 30,3769\\ 30,374.10\\ 30,347.76\\ 30,318.63\\ 30,286.72\\ 30,252.17\\ 30,214.62\\ 30,174.42\\ 30,131.35\\ \end{array}$	$\begin{array}{c} 30,481.38^{\rm a}\\ 30,485.94^{\rm a}\\ 30,487.22\\ 30,485.94^{\rm a}\\ 30,474.67\\ 30,474.67\\ 30,454.66\\ 30,451.88^{\rm a}\\ 30,436.10\\ \end{array}$

^a Denotes blended line.

The rotational constants were obtained by plotting

$$rac{\Delta_2 F_2'(J) - \gamma}{J}$$
 and $rac{\Delta_2 F_2'(J-1) + \gamma}{J}$

against J^2 . The best straight line was determined by the method of least squares, each point being given a weight of J^2 . The values of B_{ν}' and D_{ν}' obtained are given in Table V.

(c) Determination of ΔG_{1} and α .—The quantities ΔG_{i} and α' were obtained from combination relations between corresponding lines of the (0, 0) and (1, 0)bands.¹⁷ It is readily shown that

$$Q_1^{1,0}(J) - Q_1^{0,0}(J) = \Delta G_{\frac{1}{2}}' - (B_0' - B_1')(J - \frac{1}{2})(J + \frac{1}{2}), \quad (9)$$

neglecting terms involving $(D_0' - D_1')$ and $(\gamma_0 - \gamma_1)$. Similar relations may be obtained for the other branches of the (0, 0) and (1, 0) bands. By plotting all these combination differences against $(J-\frac{1}{2})$ $(J+\frac{1}{2})$ the best values of $\Delta G_{\frac{1}{2}}'$ and $(B_0' - B_1') = \alpha'$ were obtained (see Table V).

(d) Determination of B_e' , I_e' and r_e' .—From the B_0' and α' values obtained above, values of $B_{e'}$, $I_{e'}$, and r_e' were calculated¹⁸ (see Table V). The r_e' values agree to 0.001_{0} A which is the order of agreement found for hydrides and deuterides.¹⁹ It should be noted however that these r_e' values are still effective values, and the agreement is slightly improved if true values are calculated using Eq. (3). The values obtained are

for SH
$$r_{e_{true}} = 1.422_2 \text{A}$$
, for SD $r_{e_{true}} = 1.422_9 \text{A}$.

B. The $^{2}\Pi$ State

Two general expressions have been derived for the rotational term values of the components of a ²II state. In the first, due to Hill and Van Vleck^{20, 21} the centrifugal distortion term has been assumed to be the same as for Hund's case (b). The term values are given by

$$F_{1}(J) = B_{v} \Big[(J + \frac{1}{2})^{2} - \Lambda^{2} - \frac{1}{2} \{ 4(J + \frac{1}{2})^{2} + V(Y - 4)\Lambda^{2} \}^{\frac{1}{2}} \Big] \\ - D_{v}J^{4} \pm \varphi_{1}(J),$$

$$F_{2}(J) = B_{v} \Big[(J + \frac{1}{2})^{2} - \Lambda^{2} + \frac{1}{2} \{ 4(J + \frac{1}{2})^{2} + V(Y - 4)\Lambda^{2} \}^{\frac{1}{2}} \Big] \\ - D_{v}(J + 1)^{4} \pm \varphi_{2}(J), \quad (10)$$

where $Y = A/B_v$, A is the spin-coupling constant and $\varphi_i(J)$ denotes the expressions for the Λ -doubling. Terms for which $\varphi_i(J)$ are positive are denoted F_{1d} , F_{2d} while those for which $\varphi_i(J)$ are negative are denoted $F_{1c}, F_{2c}.$

TABLE II. Vacuum wave numbers and assignments of the rotational lines of the (1, 0) SH band.

J	P_1	Q_1	R_1	<i>R</i> Q21	Q_2	P_2
0.5 1.5 2.5 3.5 4.5 5.5 6.5 7.5 8.5	32,617.72 ^a 32,586.98 32,553.73 32,517.16 32,478.37 32,436.09 32,390.93	32,633.04 32,617.72 ^a 32,579.39 ^a 32,579.34 32,555.73 32,528.85 32,465.76	32,664.18ª 32,664.18ª 32,662.80ª 32,657.25 32,648.73	32,663.53ª 32,663.53ª 32,660.83ª	32,264.54* 32,266.50* 32,264.54* 32,258.90 32,249.42 32,235.88 32,218.50	32,234.95

Denotes blended line.

¹⁷ See G. Herzberg, reference 13, p. 188. ¹⁸ The formula $B_e = \frac{27.98_{30} \times 10^{-40}}{T_e}$ (G. Herzberg, reference 13, p. 106) was employed. Reduced masses were calculated from the I. isotopic data given by J. Mattauch and A. Flammersfeld, Z. Naturforsch. (Tübingen) (1949), and the following values obtained: Isotopic data given by J. Mattation and A. Frammersteid, Z. Naturnovsci $\mu_{BH} = 0.97732_{24}$ at. wt units, $\mu_{BD} = 1.895323_{01}$ at. wt units. ¹⁹ G. Herzberg, reference 13, pp. 501–581. ²⁰ E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928). ²¹ See also R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

TABLE III. Vacuum wave numbers for the (0, 0) SD band.

J	<i>P</i> ₁	<i>Q</i> 1	R ₁	$Q_{P_{21}}$	RQ21	^S R ₂₁	P_2	Q2	<i>R</i> ₂	0 _{P12}	PQ12	<i>QR</i> ₁₂
0.5 1.5 2.5 3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5 12.5 13.5 14.5	30,948.24* 30,932.78 30,916.24 30,880.00 30,860.30 30,839.46* 30,817.68 30,794.77 30,770.79 30,745.75 30,719.48 30,692.13	30,957,19* 30,950,10 30,942,12 30,933,06 30,923,01 30,911,85 30,899,56 30,886,19 30,871,73 30,856,12 30,839,46* 30,821,54 30,802,51 30,782,25	30,974.27* 30,976.00* 30,976.03 30,976.03 30,974.63 30,971.97 30,968.22 30,968.22 30,968.23 30,957.19 30,949.66* 30,941.58*	30,956.80 ^a 30,949.66 ^a 30,941.58 ^a 30,922.08 30,910.78 30,8898.39 30,884.85 30,870.22 30,854.43 30,837.56 30,819.45	30,973,92a 30,975,33a 30,976,00a 30,975,33a 30,973,62 30,970,69 30,966,80 30,966,80 30,966,80 30,955,55 30,948,24a 30,939,69	$\begin{array}{c} 30,999,47\\ 31,009,73\\ 31,018,80\\ 31,026,66\\ 31,033,45a\\ 31,033,45a\\ 31,034,58\\ 31,043,80\\ 31,044,98\\ 31,044,98\\ 31,049,20\\ 31,050,07\\ \end{array}$	30,569,80 30,562,25 30,552,87 30,542,40 30,530,77 30,517,72 30,503,44 30,487,79 30,470,85 30,452,46 30,4322,88 30,411,81 *	$\begin{array}{c} 30,584.73^a\\ 30,586.98^a\\ 30,586.98^a\\ 30,587.66^a\\ 30,586.04\\ 30,586.04\\ 30,586.05\\ 30,578.66\\ 30,572.96\\ 30,572.96\\ 30,555.93\\ 30,557.52\\ 30,557.52\\ 30,557.52\\ 30,547.71\\ 30,536.52\\ 30,523.92 \end{array}$	30,601.15 30,612.15 30,621.90# 30,630.02 30,636.69 30,642.08 30,644.13 30,648.73# 30,649.73#	30,545.37 30,528.20 30,509.44 30,489.19ª 30,468.31 30,445.76	$\begin{array}{c} 30,576.14\\ 30,559.80\\ 30,552.25\\ 30,553.31\\ 30,543.15\\ 30,531.61\\ 30,518.78\\ 30,504.61\\ 30,489.19\\ 30,472.38\\ 30,472.38\\ 30,454.21\\ 30,434.83\\ 30,413.93 \end{array}$	30,584.73* 30,587.66* 30,588.46* 30,588.46* 30,586.98 30,579.89 30,579.89 30,577.33* 30,559.47*

a Denotes blended line.

In the second expression, due to Almy and Horsfall,²² a more detailed treatment of the centrifugal distortion term has been considered. The formulas developed are considerably more complicated than the Hill and Van Vleck expressions, but give a somewhat better representation of the term values and slight modifications in the molecular constants (see below).

(a) Determination of B_{v}'' and D_{v}'' .—It may be shown from (10) that

$$\frac{\Delta_2 F_1''(J) + \Delta_2 F_2''(J)}{4J + 2} = (2B_{\nu}'' - 7D_{\nu}'') - 4D_{\nu}''(J + \frac{1}{2})^2. \quad (11)$$

The LHS involves the mean of the four second differences $\Delta_2 F_{1c}'', \Delta_2 F_{1d}'', \Delta_2 F_{2c}'', \Delta_2 F_{2d}''$. Since it was not possible in general to derive all these quantities for a given value of J from the usual combination relations¹⁴ without using blended lines, it was decided to calculate the term values of the ²II state from those of the ²Σ state and the wave numbers of the unblended lines. When more than one value for a given term value was obtained, the mean was taken. The rotational constants B_{v}'' and D_{v}'' were determined by plotting $[\Delta_2 F_1''(J) + \Delta_2 F_2''(J)]/[4J+2]$ against $(J+\frac{1}{2})^2$ and determining the best straight line by the method of least squares, each point being given a weight of $(J+\frac{1}{2})^2$. The values obtained are given in Table V.

The formulas of Almy and Horsfall²² give a similar expression to Eq. (11) except that the intercept is $(2B_v"-2D_v")$. The slopes are identical. There is thus a discrepancy of $2\frac{1}{2} D_v"$ between the $B_v"$ values calculated by the two methods although the $D_v"$ values are identical. It should be remembered that the $B_v"$ and $D_v"$ values obtained by these methods are effective rotational constants and to obtain true $B_v"$ values a small correction term must be applied.²²

(b) Determination of the Λ -Doubling.—The doublet separations $\Delta \nu_{dc}$ for the Λ -doubling in a ² Π state are given by^{16,21}

$$\Delta \nu_{dc}(J) = \left[(\frac{1}{2}p+q)(\pm 1+2X^{-1}-YX^{-1}) + 2qX^{-1}(J-\frac{1}{2})(J+\frac{3}{2}) \right] (J+\frac{1}{2}), \quad (12)$$

²² G. M. Almy and R. B. Horsfall, Phys. Rev. 51, 491 (1937).

where the + sign in ± 1 refers to F_2 levels and the sign to F_1 levels and $X = + [Y(Y-4) + (J+\frac{1}{2})^2]^{\frac{1}{2}}, Y = A/B_v,$

$$p = p_0 / \left[1 + \frac{D_v}{B_v} J(J+1) \right], \quad q = q_0 / \left[1 + \frac{D_v}{B_v} J(J+1) \right]^2.$$

For the case of "pure precession"

$$p_{0} = \frac{2AB_{\nu}l(l+1)}{\nu(\Pi, \Sigma)}, \quad q_{0} = \frac{2B_{\nu}^{2}l(l+1)}{\nu(\Pi, \Sigma)}.$$
 (13)

The doublet separations were calculated directly from the energy levels of the ²II state and were checked by means of combination relations.^{14, 21} The doublet separations are shown in Fig. 5. The Λ -doubling curves for SH are remarkably similar to those for the isoelectronic molecule HCl⁺ both in form and magnitude.²¹ The values of p_0 and q_0 in Eq. (12) required to give the best fit with the experimental data were found by trial and error and were compared with the theoretical values calculated from Eq. (13) assuming pure precession. The values obtained were found to be in reasonable agreement, *viz.*,

	Expe	rimental	Theoretical		
	Þo	q_0	po	q_0	
SH	0.304	-0.012	0.465	-0.012	
SD	0.160	-0.0031	0.238	-0.0031	

TABLE IV. Vacuum wave numbers for the (1, 0) SD band.

 J	P1	Q1	Rı	Q _{P21}	RQ21
1.5	32,267.67	32,275.79 ^в	32,292.49*	32,275.79ª	32,291.99*
2.5	32,251.73	32,268.28	32,292.49	32,267.97*	32,292.49*
3.5	32,234.48	32,259.19	32,291.99*	32,258.62	32,291.57*
4.5	32,215.76	32,248.68	32,289.95	32,248.00	32,289.09
5.5	21,195.61	32,236.84	32,286.25	32,235.89	32,285.18
6.5	32,174.06ª	32,223.43	32,280.89	32,222.39	32,279.74
7.5	32,151.13	32,208.54	32,274.26	32,207.26	32,272.95
8.5	32,126,70	32,192.32	32,266.08	32,190.88	32,264.56
9.5	32,100.98	32,174.46	32,256.49	32,172.97	32,254.67
10.5	32,073.64	32,155.29		32,153.61	32,243.27
11.5	32.044.85	32.134.26		32,132.52	
12.5	,	32,112.09		· .	

* Denotes blended line.



FIG. 4. Spin doubling in the (0, 0) SH band as a function of J.

(c) Determination of the spin-coupling constant A.— It is readily seen from (10) that

$$\left\{\frac{F_{1}^{\prime\prime}(J) - F_{2}^{\prime\prime}(J) - D_{v}^{\prime\prime}[(J+1)^{4} - J^{4}]}{B_{v}^{\prime\prime}}\right\}^{2} - 4(J+\frac{1}{2})^{2} = Y(Y-4). \quad (14)$$

Values of Y and A were calculated for different J using the $F_1''(J)$, $F_2''(J)$, $B_{v'}''$ and $D_{v''}'$ values obtained above. The values of A obtained were not constant but depended slightly on J. By plotting A against $(J-\frac{1}{2})^2$ a linear relationship was obtained (see Fig. 6). The values of A given in Table V were obtained by extrapolating to $(J-\frac{1}{2})^2=0$.

Further values of A were calculated using the Almy and Horsfall formulas and were found to be linearly dependent on $(J-\frac{1}{2})^2$ (see Fig. 6). The slope of the graph using the Almy and Horsfall values was somewhat less than with the Hill and Van Vleck values, though the intercepts in the two cases were the same to within 0.10 cm⁻¹.

(d) Determination of ν_{00} .—The quantity ν_{00} was ob-

TABLE V. Molecular constants of SH and SD.





FIG. 5. A-doubling in the ${}^{2}\Pi_{\frac{3}{2}}$ and ${}^{2}\Pi_{\frac{1}{2}}$ states of SH.

tained from the wavenumbers of the Q_1 and Q_2 lines by means of the equation

$$Q_{1}(J) + Q_{2}(J) + D_{v}' [(J - \frac{1}{2})^{2}(J + \frac{1}{2})^{2} + (J + \frac{1}{2})^{2}(J + \frac{3}{2})^{2}] - D_{v}'' [J^{4} + (J + 1)^{4}] \cdot + \varphi_{1}(J) - \varphi_{2}(J) = 2\nu_{00} + 2(B_{v}' - B_{v}'')J(J + 1) + \frac{1}{2}B_{v}' + \frac{3}{2}B_{v}'' - \gamma.$$
(15)

The LHS was plotted against J(J+1) and the best straight line determined by the method of least squares. The values obtained for ν_{00} for SH and SD are given in Table V. Identical values of ν_{00} were obtained using the formulas of Almy and Horsfall.

(e) Comparison of the HVV and AH formulas.—Term values for the ²II state were calculated using the formulas of Hill and Van Vleck and Almy and Horsfall using the molecular constants determined above. The values obtained by the AH formulas were found to be in better agreement with the experimental term values than those calculated by the HVV formulas, the discrepancies for term values of 1000 cm⁻¹ being ~0.3 cm⁻¹ for the AH formulas and ~0.8 cm⁻¹ for the HVV formulas (see Fig. 7).



FIG. 6. The spin-coupling constant A as a function of $(J-\frac{1}{2})^2$.



FIG. 7. The differences between the observed rotational term values for the 2II state and those calculated using the energy formulas of Hill and Van Vleck and Almy and Horsfall, plotted as a function of the rotational term value.

2. Molecular Constants Derived from **Isotopic Relations**

The molecular constants above have been determined with a high degree of precision. Further molecular constants may be calculated with a moderate degree of accuracy using certain isotopic relations.

A. The $^{2}\Sigma$ State

(a) Estimation of ω_e' and $\omega_e' x_e'$.—The quantities ω_e' and $\omega_e' x_e'$ were determined by means of the isotopic relations.23

$$\Delta G_{\frac{1}{2}} = \omega_e' - 2\omega_e' x_e', \qquad (16)$$

$$\Delta G_{\frac{1}{2}}i' = \rho \omega' - \rho^2 \omega_e' x_e', \qquad (17)$$

where $\rho = (\mu/\mu^i)^{\frac{1}{2}}$. The values obtained are given in Table VI.

B. The $^{2}\Pi$ State

(a) Estimation of $B_{e}^{\prime\prime}$, $I_{e}^{\prime\prime}$, and $r_{e}^{\prime\prime}$.—Although only B_0'' values have been determined accurately for SH and SD, fairly reliable estimates for the B_e'' values (see Table VI) may be obtained using the conditions²⁴

$$\begin{aligned} r_e{}^i = r_e, \\ \alpha_e{}^i = \rho^3 \alpha_e. \end{aligned}$$
 (18)

Values of I_e'' and r_e'' are then easily deduced.

(b) Estimation of ω_e'' , $\omega_e''x_e''$, and ν_e .—The quantities ω_e'' , $\omega_e'' x_e''$, and ν_e were estimated from the relations25

$$\nu_{00} = \nu_e + \frac{1}{2}\omega_e' - \frac{1}{4}\omega_e' x_e' - \frac{1}{2}\omega_e'' + \frac{1}{4}\omega_e'' x_e'', \qquad (20)$$

$$\nu_{00}{}^{i} = \nu_{e} + \frac{1}{2}\rho\omega_{e}{}' - \frac{1}{4}\rho^{2}\omega_{e}{}'x_{e}{}' - \frac{1}{2}\rho\omega_{e}{}'' + \frac{1}{4}\rho^{2}\omega_{e}{}''x_{e}{}'', \quad (21)$$

$$\alpha_{e} = \frac{6(\omega_{e}x_{e}B_{e}^{3})^{\frac{1}{2}}}{\omega_{e}} - \frac{6B_{e}^{2}}{\omega_{e}}.$$
 (22)

- ²³ G. Herzberg, reference 13, p. 142.
 ²⁴ G. Herzberg, reference 13, p. 144.
 ²⁵ Reference 13, pp. 162. 108.

Equation (22) is based on a Morse potential function and is accurate to 2 percent for the ${}^{2}\Sigma$ states of SH and SD. By using the values of α estimated above and the accurate values determined for ν_{00} and ν_{00} ^{*i*}, values for $\omega_e'', \omega_e'' x_e''$, and ν_e were calculated with the accuracies indicated in Table VI.

NATURE OF THE PREDISSOCIATION AND DISCUSSION OF DISSOCIATION ENERGIES

The possible electronic states of SH formed from the low lying electronic states of sulfur and hydrogen may be determined by means of the Wigner-Witmer correlation rules²⁶ as follows:

$$H({}^{2}S_{g}) + S({}^{3}P_{g}) \rightarrow {}^{2}\Sigma^{-}, {}^{2}\Pi, {}^{4}\Sigma^{-}, {}^{4}\Pi, \\ H({}^{2}S_{g}) + S({}^{1}D_{g}) \rightarrow {}^{2}\Sigma^{+}, {}^{2}\Pi, {}^{2}\Delta, \\ H({}^{2}S_{g}) + S({}^{1}S_{g}) \rightarrow {}^{2}\Sigma^{+}.$$

The only low-lying electronic state of the united atom Cl is the ${}^{2}P_{u}$ ground state which splits²⁷ into the observed ${}^{2}\Sigma^{+}$ and ${}^{2}\Pi$ states for SH. All the other possible electronic states of SH given above have to be correlated with excited states²⁸ of the united Cl atom at \sim 70,000-80,000 cm⁻¹ above the ground state. It seems probable, therefore, that these other states are either repulsive or have shallow potential minima.

The existence of only two low lying electronic states for SH is consistent with predictions based on electron configuration,29 viz.,

$$\begin{array}{l} (3s\sigma)^2(3p\sigma)^2(3p\pi)^3 \longrightarrow ^2 \Pi_i \\ (2s\sigma^2)(3p\sigma)(3p\pi)^4 \longrightarrow ^2 \Sigma^+. \end{array}$$

For all these reasons it seems highly probable that the ${}^{2}\Pi_{i}$ ground state of SH dissociates into normal atoms while the ${}^{2}\Sigma^{+}$ state dissociates into $S({}^{1}D_{g}) + H({}^{2}S_{g})$ (see Fig. 8).

The diffuseness of the rotational lines of the (1, 0)band of SH indicates a predissociation into normal atoms and immediately establishes both an upper and a

TABLE VI. Molecular constants of SH and SD derived from isotope relationships.

	SH	SD	Units
A. The $^{2}\Sigma$ state			
ωe	1971	1415	cm ⁻¹
we'xe'	93	48	cm ⁻¹
Ve	31,036	31,036	cm ⁻¹
B. The III state			
B,''	9.611	4.95 ₆	cm ⁻¹
α,"	0.30	0.11	cm ⁻¹
I.''	2.91_{2}	5.646	×10 ⁻⁴⁰ g cm ²
T."	1.34_{0}	1.34_{0}	AŬ
ω,"	2702	1940	cm ⁻¹
$\omega_e^{\prime\prime} x_e^{\prime\prime}$	60	31	cm ⁻¹

²⁶ Reference 13, p. 318.

²⁷ Reference 13, p. 322. ²⁸ Charlotte E. Moore, *Atomic Energy Levels*, Vol. 1, National Bureau of Standards, Circular No. 467, (1949).

²⁹ Reference 13, p. 336.

lower limit for the dissociation energy of SH in the ground state. Since for the SH (1, 0) band, $\nu_{10} = 32,477 \cdot 05$ cm⁻¹, the upper limit is given by $D_0'' < 32,477$ cm⁻¹ (=92.7 kcal=4.02 ev), while the lower limit is obtained by subtracting the energy of excitation of a sulfur atom from the ³P to the ¹D state, viz., $D_0'' > 23,208$ cm^{-1} (= 66.3 kcal = 2.88 ev).

A further rough estimate of the dissociation energy of SH may be obtained using the Birge-Sponer relation³⁰

$$D_0 = (\omega_e^2 / 4\omega_e x_e) - G(0).$$
 (23)

For the ${}^{2}\Sigma^{+}$ state this gives a value of $D_{0}' = 9450 \text{ cm}^{-1}$. It should be remembered however that the values of ω_e and $\omega_e x_e$ were obtained using isotope relationships. If it is assumed that a linear Birge-Sponer extrapolation gives a value which is about 20 percent too high³¹ as has been found for many molecules with non-ionic binding, then $D_0' = 7560 \text{ cm}^{-1}$. The dissociation energy of the ground state of SH may now be obtained by adding ν_{00} and subtracting the energy of excitation of a sulfur atom from a ³P to a ¹D state, giving $D_0^{\prime\prime} = 28,980$ cm⁻¹ (=82.8 kcal=3.59 ev). Fortunately, the ${}^{2}\Sigma^{+}$ state is a shallow state, so that even if the dissociation energy for this state is in error by as much as 50 percent, the ground state dissociation energy will still be accurate to $\sim 4000 \text{ cm}^{-1}$ ($\sim 11 \text{ kcal} \sim 0.5 \text{ ev}$). These figures are in good agreement with the results of Porter³² and Darwent and Sehon,³³ but are at variance with the dissociation energy quoted by Franklin and Lumpkin.34

Since the widths of the rotational lines of the (1, 0)SH band are ~ 0.1 cm⁻¹, the lifetime of the SH radical in this state is $\sim 10^{-10}$ sec compared with the normal radiation lifetime $\sim 10^{-8}$ sec. This indicates a fairly strong predissociation which is somewhat surprising



FIG. 8. Approximate potential curves for SH.

since the only states which could produce the predissociation are the $^{2}\Sigma^{-}$, $^{4}\Sigma^{-}$, and $^{4}\Pi$ states, and predissociation by these states is forbidden by the selection rules³⁵ $\Delta S = 0$ and $\Sigma^+ \leftrightarrow \Sigma^-$. It is well known, however, that these selection rules hold less rigorously for molecules containing heavy atoms. A similar predissociation in the ${}^{2}\Sigma^{+}$ state of OH has been found by Gavdon and Wolfhard³⁶ and attributed by them to predissociation by the $^{2}\Sigma^{-}$ state.

The author is indebted to Dr. G. Herzberg for his continued interest in this work and for many helpful discussions. The author wishes to express his thanks to Dr. A. E. Douglas for many helpful experimental suggestions. The author is indebted to Mr. G. Ensell for his skill and patience in the construction and repair of the flash tubes. Finally, the author wishes to express his thanks to Mr. F. Doren for valuable assistance in the construction of the apparatus and to Miss R. H. Craig for much help with the numerical computations.

³⁶ A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London), A208, 63 (1951).

 ³⁰ G. Herzberg, reference 13, p. 100.
 ³¹ A. G. Gaydon, Proc. Phys. Soc. (London), 58, 525 (1946).

³² G. Porter, Disc. Faraday Soc. No. 9, p. 60 (1950)

³³ A. H. Sehon and B. deB. Darwent, J. Chem. Phys. (to be published); see also A. H. Sehon, J. Chem. Phys. (to be published).

³⁴ J. L. Franklin and H. E. Lumpkin, J. Am. Chem. Soc. 74, 1023 (1952).

³⁵ G. Herzberg, reference 13, p. 416.