

The Analysis of the Hydrogen Sulfide Band at 10,100A

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(Received November 8, 1934)

Details of the measurement and procedure of analysis of the $\nu_\sigma + 3\nu_\pi$ band of H_2S are given. An approximate correction for the rotational distortion of the molecule is included. Assignments are made which satisfactorily account for 84 of the 91 measured lines. The remaining 7 lines are considered spurious. The theory for a rigid rotator plus the distortion correction gives a very good

approximation to the rotational energy levels of the H_2S molecule, but many deviations are observed which are definitely larger than the experimental error. The moments of inertia in the normal vibrational state are 2.667, 3.076, 5.845×10^{-40} g cm², the axis of least inertia being perpendicular to the symmetry axis of the molecule. The bond angle is $92^\circ 20'$ and the H-S distance 1.345A.

I. INTRODUCTION

PREVIOUS work on the infrared absorption of hydrogen sulfide has been confined to the thermocouple region, and has not as yet yielded data capable of complete rotational analysis.¹⁻⁴ A brief summary of the vibrational spectrum is given here which is essentially that suggested by Mecke.⁵

Combina- tion	Fre- quency (cm ⁻¹)	Refer- ence	Combina- tion	Fre- quency (cm ⁻¹)	Refer- ence
ν_δ	1260	1	$\nu_\sigma + \nu_\delta$	3790	2
ν_π	2615	6	$\nu_\sigma + \nu_\pi$	5130	3
ν_σ	2630	2, 3	$\nu_\sigma + 3\nu_\pi$	9911	7, 8, 9
			$3\nu_\sigma + \nu_\pi$	10100	7, 8, 9

It is proposed to describe here the details of the rotational analysis of the band designated above as $\nu_\sigma + 3\nu_\pi$, of which a preliminary report has recently been given.⁷

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¹ A. H. Rollefson, *Phys. Rev.* **34**, 604 (1929).

² H. H. Nielsen and E. F. Barker, *Phys. Rev.* **37**, 727 (1931).

³ A. D. Sprague and H. H. Nielsen, *Phys. Rev.* **43**, 375 (1933).

⁴ W. Mischke, *Zeits. f. Physik* **67**, 106 (1931). These results are falsified by impurities.

⁵ R. Mecke, *Zeits. f. physik. Chemie* **B16**, 431 (1932).

⁶ K. W. F. Kohlrausch, *Phys. Zeits.* **33**, 165 (1932).

⁷ P. C. Cross, *Phys. Rev.* **46**, 536 (1934). Note that $3\nu_\sigma + \nu_\pi = 11,000$ cm⁻¹ is incorrect.

⁸ W. Weizel, *Zeits. f. Physik* **88**, 214 (1934). The intensities of the vibrational combinations of water type molecules are discussed. The results are that the parallel type of bands are very weak in comparison to the perpendicular type. The electric moment changes along the axis perpendicular to the symmetry axis of the molecule only for combinations containing an odd multiple of ν_σ . Combinations with $1\nu_\sigma$ are stronger than those with $3\nu_\sigma$,⁹ hence the identification given here.

⁹ R. Mecke, *et al.*, *Zeits. f. Physik* **81**, 313, 445, 465 (1933). Much of the discussion in connection with this analysis of the water spectrum is equally applicable to the hydrogen sulfide spectrum.

II. EXPERIMENTAL

Photographs of this band were taken in the first order spectrum of a 21-foot grating having 15,000 lines to the inch. The dispersion was approximately 2.5A per mm. Eastman type 1Q infrared plates, supersensitized in 4 percent ammonia were used. The absorption cell consisted of five sections of polished stainless steel one inch in diameter, and a brass section with valves for filling. The total length of the cell was about 71 feet. The source of light was a 32-32 candle power double filament Mazda automobile headlight, burned at 16 volts with the filaments in series. A very short focus lens was mounted on the end of the absorption cell and the source adjusted to give a maximum intensity at the slit as determined by a photronic cell.

Due to the weakness of the absorption it was necessary to take a large number of photographs under various conditions of pressure and exposure. Of these, 14 were selected for detailed measurements. In some instances contact prints were used for measuring. Everything that had any possibility of representing an absorption line was recorded and the results from the 14 plates arranged in series. Real lines were then readily identified by the near coincidence of measurements on several different plates, and the wave numbers were calculated from the mean positions of the groups. The first column of Table III shows the results and includes lines that were observed on at least three plates.

Most of the useful plates were taken with the pressure of hydrogen sulfide at three-quarters of an atmosphere. At pressures of over one and a half atmospheres the lines were so broad that

there was no advantage over the weaker but sharper lines. The well-defined lines appeared to the eye to be about $0.4A$ in breadth on the average plate used for measurement.

III. PREDICTED STRUCTURE FROM OTHER CONSIDERATIONS

The interpretation of a complex spectrum is greatly facilitated by a knowledge of the approximate value of the molecular constants which determine the spectrum. Such a knowledge may now be obtained from certain principles of theoretical and empirical origin. The additivity of atomic radii in covalent bonds gives an estimate of $1.33A$ for the H-S separation in H_2S .¹⁰ The theory of directed valence and qualitative considerations similar to those used by Van Vleck and Cross¹¹ in a treatment of the H_2O molecule lead to an estimate of the bond angle as about 95° . This structure requires that the axis of least inertia be perpendicular to the symmetry axis of the molecule.

A second estimate of the H-S separation may be made by assuming that the Badger relation¹² between force constant and interatomic distance may be extended to polyatomic molecules. The value of ν_e^0 for H_2S may be estimated as about 2700 cm^{-1} , and k_1 obtained from the linear factor, $4\pi^2c^2(\nu_e^0)^2(a_{11}-a_{12})-k_1+k_{12}=0$, of the Eqs. (11) of reference 11, assuming $k_{12}=0$ and by using appropriate approximate values of a_{11} and a_{12} . k_1 is found to be about 4.2×10^5 dynes cm^{-1} , corresponding to an H-S separation of about $1.35A$. Uses of these estimates will be mentioned later.

IV. THE RIGID ROTATOR

The theory of the rigid rotator has been thoroughly discussed in the literature, so reference will be made only to the review article by Dennison¹³ and the treatise by Casimir¹⁴ for the details of the results and further references.

The energies are obtained from the equations

¹⁰ L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

¹¹ J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

¹² R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

¹³ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

¹⁴ H. B. G. Casimir, *Rotation of a Rigid Body in Quantum Mechanics*, J. B. Wolters, The Hague (1931).

$$E(\text{cm}^{-1}) = \frac{1}{2}(A+B)j(j+1) + [C - \frac{1}{2}(A+B)]W_{\epsilon_c}, \quad (1)$$

$$A = h/8\pi^2cI_A, \quad B = h/8\pi^2cI_B, \quad C = h/8\pi^2cI_C, \quad (2)$$

$$\epsilon_c = (B-A)/4[C - \frac{1}{2}(A+B)] = -\frac{1}{2}b, \quad (\text{Wang}^{15}), \quad (3)$$

where I_A , I_B , and I_C are the three principal moments of inertia ($I_A < I_B < I_C$) and the W_{ϵ_c} are the roots of the secular determinant given by Wang.¹⁵ Eqs. (1) and (3) are based on a choice of the C axis as the unique axis of the limiting symmetric rotator $\epsilon_c=0$ ($I_A=I_B$). In some instances it is more convenient to choose the A axis as the unique axis in the limiting case, and the energies are obtained by interchanging A and C throughout Eqs. (1) and (3). The constants of H_2S are such that we shall always employ the former choice, and we shall drop the subscript of ϵ for the remainder of the discussion.

The symmetries of the levels and the selection rules are easily obtained from the simple rules formulated by Dennison.¹³ Levels having the symmetries $+-$ and $-+$ are antisymmetric with respect to a rotation of π about the B axis (i.e., an interchange of the hydrogen atoms) and hence have statistical weights three times those of analogous symmetric levels $++$ and $--$. Transitions originating in antisymmetric levels thus tend to average about three times as intense as those originating in symmetric levels.

For the band in question the electric moment oscillates perpendicular to the symmetry axis of the molecule, along the A axis.⁸ The selection rules are $+- \leftrightarrow --$ and $-+ \leftrightarrow ++$. For practical purposes, one need consider only the transitions which also satisfy the selection rules of the limiting symmetrical rotator.⁹

V. APPROXIMATE VALUES OF C AND C' ¹⁶

An investigation of the intensities for a hypothetical symmetrical H_2S rotator with $r=1.35A$ ($I_A=I_B$; $\theta=88^\circ 16'$) shows the most intense lines in the spectrum to be $j_j \leftrightarrow (j+1)_{j+1}$ in the symmetric rotator notation. For the actual

¹⁵ S. C. Wang, Phys. Rev. **34**, 247 (1929).

¹⁶ The structural constants for the excited vibrational state are designated by the primes.

molecule, provided θ is not too different from $88^\circ 16'$, the degeneracy of these levels will not be effectively removed for moderate j values, and the intensities should approximate closely those for the hypothetical symmetric rotator.¹⁷ The strongest lines will be the unresolved doublets

$$\left\{ \begin{array}{l} j_{-j} \rightleftharpoons (j+1)_{-(j+1)} \\ j_{-(j-1)} \rightleftharpoons (j+1)_{-j} \end{array} \right\}$$

in the asymmetrical rotator notation. In the following paragraph the notation j^* will be used to designate the nearly coincident pair of energy levels j_{-j} and $j_{-(j-1)}$. The energies are given approximately by the equation

$$Ej^* = Cj^2 + \frac{1}{2}(A+B)j + \frac{(B-A)\epsilon}{4} \frac{j(2j-1)}{j-1}. \quad (4)$$

The outstanding feature of the band is the series of strong lines of rapidly converging parabolic spacing which extends throughout the band except for some missing members near the center. These may be identified as specific transitions of the type $j^* \rightleftharpoons (j+1)^*$ after a choice of the position of the center of the band, ν_0 , has been made. The difference between the energies of the lines corresponding to the transitions $j^* - (j-1)^*$ and $j^* - (j+1)^*$ gives directly the energy difference $(j+1)^* - (j-1)^*$ between two pairs of levels of the normal vibrational state. In terms of the structural constants this difference is

$$E(j+1)^* - E(j-1)^* = 4jC + A + B + \frac{(B-A)\epsilon}{4} \left\{ \frac{(j+1)(2j+1)}{j} - \frac{(j-1)(2j-3)}{j-2} \right\}. \quad (5)$$

Subtracting the value of this energy difference for $j=n$ from that for $j=n+1$ gives a value of $4C$. (The contribution of the final term of Eq. (5) is found to be negligible for values of $(B-A)\epsilon$ which seem probable from the considerations of Section III.) The constancy of these values of $4C$ obtained from different values of n upholds the validity of the assumptions that were necessary.

¹⁷ G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934). This article contains a discussion of the relative positions of the energy levels and intensities for nearly symmetrical rotators. The formula $(J-K+1)(J-K)/(J+K)(J+K-1)$ of the Eqs. (7) should read $(J-K+1) \times (J-K)/8J$. (reference 14, p. 53).

The value of r can be obtained from that of C without accurate knowledge of the angle since

$$I_C = 2mr^2(M+2m \sin^2 \phi)/(M+2m) \quad (6)$$

is not strongly dependent upon ϕ ($M/2m=16$). The two choices for the position of the band center which seem most likely from the intensities and distribution of lines in the band lead to the values 1.35A and 1.39A for r . Again, referring to Section III, strong preference is found for the value 1.35A. The corresponding value of C is $4.73 \text{ (cm}^{-1}\text{)}$. By an analogous treatment the value of C' is found to be 4.47. These values were used with but little variation throughout the numerous approximations in the determination of the remaining constants of the band.

VI. APPROXIMATE DETERMINATION OF A, B, A', B' AND ν_0

The energy levels considered in the preceding section are those for which the rotation is chiefly about the C axis and are little dependent upon the angle. To determine the angle and obtain a complete analysis of the band it is necessary to consider weaker lines and, in particular, those near the band center. The strongest lines arising from transitions between levels for which the rotation is chiefly about the A and B axes are, for the hypothetical symmetrical H_2S rotator,

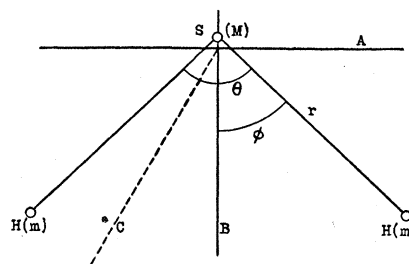


FIG. 1. H_2S rotator.

those between the two upper levels of a given j value. If the molecule were symmetrical with $2C=A=B=2C'=A'=B'$, these transitions would fall into two groups displaced from the band center by C wave numbers on either side. The asymmetry, however, causes the transitions for higher j values to approach the center, as

shown in the charts of Dennison.¹⁸ The difference in the moments of inertia of the normal and excited states causes a shift toward the low frequency side which may be roughly approximated by $2j(j+1)(C-C')$. These simple considerations enabled the recognition of the transitions between the two upper levels of a given j state which originated in antisymmetric levels. From this point the procedure was largely one of trial and error to determine values of the constants which would fit the already identified lines and enable identification of additional ones. Considerable use was made of the differentials derived in the following section.

VII. DEPENDENCE OF ENERGY LEVELS ON THE INDIVIDUAL CONSTANTS

After the identification of the majority of the lines was obtained, and values of the constants determined which gave the positions within a

wave number of two, the rotational energies up to $j=8$ were calculated for both vibrational states. A simple method of solving the factors of the Wang equation by numerical approximation to the desired accuracy greatly reduced the labor involved in these calculations.¹⁹

The problem thus became one of adjusting these levels in accordance with the theory to give the best fit to the observed spectrum. Let

$$\alpha = \partial E / \partial A = \frac{1}{2}j(j+1) - \frac{1}{2}W_\epsilon + \frac{1}{4}(B-C)[C - \frac{1}{2}(A+B)]^{-1}(dW_\epsilon/d\epsilon), \quad (7)$$

$$\beta = \partial E / \partial B = \frac{1}{2}j(j+1) - \frac{1}{2}W_\epsilon + \frac{1}{4}(C-A)[C - \frac{1}{2}(A+B)]^{-1}(dW_\epsilon/d\epsilon); \quad (8)$$

$$\gamma = \partial E / \partial C = W_\epsilon + \frac{1}{4}(A-B) \times [C - \frac{1}{2}(A+B)]^{-1}(dW_\epsilon/d\epsilon). \quad (9)$$

The values of $dW_\epsilon/d\epsilon$ were calculated by the approximate formulas

$$\begin{aligned} dW_\epsilon(j_i)/d\epsilon &= 4\epsilon J_1^2/[W_\epsilon(j_i) - W_\epsilon(j_{i-4})], \\ dW_\epsilon(j_{i-1})/d\epsilon &= -J_0 + 2\epsilon J_2^2/[W_\epsilon(j_{i-1}) - W_\epsilon(j_{i-5})], \\ dW_\epsilon(j_{i-2})/d\epsilon &= J_0 + 2\epsilon J_2^2/[W_\epsilon(j_{i-2}) - W_\epsilon(j_{i-6})], \\ dW_\epsilon(j_{i-3})/d\epsilon &= 2\epsilon J_3^2/[W_\epsilon(j_{i-3}) - W_\epsilon(j_{i-7})], \\ dW_\epsilon(j_{i-4})/d\epsilon &= 4\epsilon J_1^2/[W_\epsilon(j_{i-4}) - W_\epsilon(j_i)] + 2\epsilon J_3^2/[W_\epsilon(j_{i-4}) - W_\epsilon(j_{i-8})], \\ dW_\epsilon(j_{i-\kappa})/d\epsilon &= 2\epsilon J^2_{\frac{3}{2}\kappa-1}/[W_\epsilon(j_{i-\kappa}) - W_\epsilon(j_{i-\kappa+4})] + 2\epsilon J^2_{\frac{3}{2}\kappa+1}/[W_\epsilon(j_{i-\kappa}) - W_\epsilon(j_{i-\kappa-4})]. \end{aligned} \quad (10)$$

$\kappa(\text{even}) > 4$. If κ is odd, substitute $\frac{1}{2}(\kappa+1)$ for $\frac{1}{2}\kappa$ in the subscripts of the J 's.

$$J_x = [(j-x)(j-x+1)(j+x)(j+x+1)]^{\frac{1}{2}}.$$

If we use the small letters a , b and c to denote increments in A , B and C , respectively, the increment in the energies of the various levels for small changes in A , B and C will be

$$\Delta E = \alpha a + \beta b + \gamma c. \quad (11)$$

Further discussion of the use of these formulas will be postponed until after the discussion of the effect of the non-rigidity of the molecule.

VIII. CORRECTION FOR THE ROTATIONAL DISTORTION OF THE MOLECULE

The centrifugal force of rotation will alter both r and θ . To determine the approximate magnitude

¹⁸ Fig. 19 of reference 13.

of the energy change due to these distortions it will be assumed that the molecule is rotating as would a classical rotator having the same values of α , β and γ .²⁰ α , β and γ may be considered as representing the square of the component of the angular momentum along the A , B and C axes, respectively ($\alpha + \beta + \gamma = j(j+1)$ \propto square of the total angular momentum). Thus the energy may be divided into three components representing the energy of rotation about the three principle axes.

$$E = \alpha A + \beta B + \gamma C. \quad (12)$$

Since the center of gravity is so near the S atom,

¹⁹ The author is indebted to Professor Badger for suggesting this procedure.

²⁰ This may be partially justified by considering that the distortion will be important for only large values of the quantum number, where the results of classical theory are more likely to be good approximations.

we may further simplify the treatment by assuming that the rotation takes place about the S atom.

The centrifugal force on each H atom due to rotation about the A , B and C axes, respectively, is

$$f_A = \alpha A/r \cos \phi, f_B = \beta B/r \sin \phi, f_C = \gamma C/r. \quad (13)$$

Resolving these forces into components \parallel and \perp to the direction of the H-S bond gives

$$f_{\parallel} = \alpha A \cos \phi/r \cos \phi + \beta B \sin \phi/r \sin \phi + \gamma C/r = E/r. \quad (14)$$

$$f_{\perp} = -\alpha A \sin \phi/r \cos \phi + \beta B \cos \phi/r \sin \phi = (-\alpha A \tan \phi + \beta B \cot \phi)/r. \quad (15)$$

These forces must be in equilibrium with the restoring forces of the distorted molecule, which may be approximated by the "valence" force system. Thus

$$E/r = k_1(\Delta r) \quad (16)$$

$$(-\alpha A \tan \phi + \beta B \cot \phi)/r = k_3 r(\Delta \theta), \quad (17)$$

$$\text{and } \Delta r = E/k_1 r, \quad (18)$$

$$\Delta \theta = (-\alpha A \tan \phi + \beta B \cot \phi)/k_3 r^2. \quad (19)$$

The change in the kinetic energy due to each of these displacements may be readily obtained.²¹

$$\begin{aligned} \Delta E_{\text{kin.}} &= [\alpha \partial A / \partial r + \beta \partial B / \partial r + \gamma \partial C / \partial r](\Delta r) \\ &\quad + [\alpha \partial A / \partial \theta + \beta \partial B / \partial \theta](\Delta \theta) \quad (20) \\ &= -2E^2/k_1 r^2 - (\alpha A \tan \phi \\ &\quad - \beta B \cot \phi)^2/k_3 r^2. \quad (21) \end{aligned}$$

The change in the potential energy is

$$\begin{aligned} \Delta E_{\text{pot.}} &= 2 \times \frac{1}{2} k_1 (\Delta r)^2 + \frac{1}{2} k_3 r^2 (\Delta \theta)^2 \\ &= E^2/k_1 r^2 + (\alpha A \tan \phi - \beta B \cot \phi)^2/2k_3 r^2. \quad (22) \end{aligned}$$

Hence the total change in energy due to rotational distortion is

$$\Delta E = [-E^2/k_1 r^2 - (\alpha A \tan \phi - \beta B \cot \phi)^2/2k_3 r^2] \times 1.963 \times 10^{-16}. \quad (23)$$

²¹ The derivatives of A, B and C with respect to r and θ are calculated for the assumed rotation about the S atom.

The factor $hc = 1.963 \times 10^{-16}$ is introduced to reduce the dimensions to cm^{-1} .

IX. DETERMINATIONS OF MOLECULAR CONSTANTS BY LEAST SQUARES

In applying the results of the two preceding sections to the $\nu_r + 3\nu_\tau$ band of H_2S the following procedure was used. Since the distortion corrections are small, it was assumed that they could be calculated from the approximate values of the molecular constants which were obtained as described in Section VI. The correction due to the change in r was applied numerically, with the value of k_1 given in Section III. Inasmuch as there has been some controversy² over the existence of the ν_s band measured by Rollefson,¹ the value of k_3 was introduced as a constant to be determined.

The energy of the line $j'_r - j_r$ from our nearly correct values of molecular constants is (corrected for stretching of r by rotation)

$$E_{\text{calc.}} = \nu_0 + E(j'_r) - E(j_r). \quad (24)$$

By knowing the dependence of the energy levels upon the individual molecular constants and the correction for angular distortion in terms of k_3 , it is possible to form an equation which must be satisfied in order to bring $E_{\text{calc.}}$ into coincidence with $E_{\text{obs.}}$

$$\begin{aligned} \Delta \nu_0 + \alpha' a' + \beta' b' + \gamma' c' - \alpha a - \beta b - \gamma c \\ + \{(\alpha A \tan \phi - \beta B \cot \phi)^2/2r^2 \\ - (\alpha' A' \tan \phi' - \beta' B' \cot \phi')^2/2r'^2\} (hc/k_3) \\ = E_{\text{obs.}} - E_{\text{calc.}} \quad (25) \end{aligned}$$

Seventy-eight equations of the type of Eq. (25) were formed involving energy levels up to $j=8$. In some instances two or more transitions were correlated with a single observed line. These equations were then solved by least squares to obtain the best values of the increments in ν_0 , A' , B' , C' , A , B , C and a value of k_3 .

X. RESULTS

The value of k_3 was found to be $(4.7 \pm 1.0) \times 10^4$ dynes cm^{-1} . The corresponding value of ν_s^0 may

be approximated from the equation

$$2\pi^2c^2m(M+m)(\nu_0^0)^2 - (M+2m)k_3 = 0;$$

$$\nu_0^0 = 1280 \pm 140 \text{ cm}^{-1}. \quad (26)$$

This value is in excellent agreement with the value estimated from Rollefson's measurements. It should be pointed out, however, that the agreement is in a certain measure fortuitous, as is seen by the large probable error. This calculation cannot be expected to be very accurate because of the smallness of the distortional effect. That it is even of the proper order of magnitude gives some encouragement.

The value of ν_0 , the position of the center of the band ($\nu_\sigma + 3\nu_\pi$ of H_2S), was found to be $9911.05 \pm 0.03 \text{ cm}^{-1}$.

In Table I there is given for $j=3$ and $j=6$, the energies of a rigid rotator having the molecular constants which were used for the normal vibrational state of H_2S in the final approximation, the corresponding values of α , β , γ and the corrections to the energy due to the distortion in r and θ . Due to the use of approximate formulas, the errors in α , β and γ may be as large as 2 percent. Errors in the correction $E(\Delta\theta)$ are possibly as large as 25 percent. Table II gives the rotational energies as finally determined by the least squares solution for the increments in the molecular constants and corrected for rotational distortion. The symmetries of the levels are also included.

TABLE I. Energy of rigid rotator.

($A=10.38$, $B=8.97$, $C=4.726$.)

Level	E	α	β	γ	$-E(\Delta r)$	$-E(\Delta\theta)$
3 ₃	117.51	7.7	4.0	0.3	0.03	0.03
3 ₂	115.55	8.7	2.3	1.0	0.03	0.07
3 ₁	107.13	2.8	8.2	1.0	0.03	0.02
3 ₀	96.30	4.0	4.0	4.0	0.02	0.00
3- ₁	94.90	2.3	6.0	3.7	0.02	0.01
3- ₂	71.39	1.3	1.8	9.0	0.01	0.00
3- ₃	71.35	1.3	1.8	9.0	0.01	0.00
6 ₆	419.57	33.9	6.9	1.2	0.44	1.09
6 ₅	419.35	34.9	5.5	1.6	0.44	1.27
6 ₄	392.56	16.7	23.5	1.8	0.38	0.00
6 ₃	388.74	21.8	15.8	4.4	0.38	0.12
6 ₂	375.71	9.6	29.0	3.4	0.35	0.24
6 ₁	359.71	13.9	19.5	8.6	0.32	0.00
6 ₀	356.89	11.2	22.4	8.4	0.31	0.06
6- ₁	325.31	10.6	15.7	15.7	0.26	0.01
6- ₂	325.12	10.0	16.5	15.5	0.26	0.01
6- ₃	281.59	7.1	10.1	24.8	0.20	0.00
6- ₄	281.58	7.1	10.1	24.8	0.20	0.00
6- ₅	227.85	2.6	3.5	35.9	0.13	0.00
6- ₆	227.85	2.6	3.5	35.9	0.13	0.00

TABLE II. Rotation energy and symmetry.

Level	Symmetry	Rotational Energy (cm^{-1})		Level	Symmetry	Rotational Energy (cm^{-1})	
		Normal state	Excited state			Normal state	Excited state
0 ₀	++	0.00	0.00	7 ₅	-+	528.26	498.04
1 ₁	+-	19.36	18.22	7 ₄	++	525.55	496.16
1 ₀	--	15.11	14.36	7 ₃	+-	506.59	474.20
1- ₁	-+	13.72	12.81	7 ₂	--	494.40	464.87
2 ₂	++	58.37	55.04	7 ₁	-+	488.29	456.52
2 ₁	+-	55.20	52.33	7 ₀	++	459.42	431.67
2 ₀	--	51.06	47.71	7- ₁	+-	458.71	430.49
2- ₁	+-	38.29	36.12	7- ₂	--	415.98	391.25
2- ₂	++	38.01	35.74	7- ₃	-+	415.96	391.20
3 ₃	+-	117.48	111.04	7- ₄	++	362.52	341.51
3 ₂	--	115.44	109.23	7- ₅	+-	362.52	341.51
3 ₁	-+	107.24	100.32	7- ₆	--	299.06	282.33
3 ₀	++	96.36	90.77	7- ₇	-+	299.06	282.33
3- ₁	+-	95.00	89.00	8 ₈	++	719.67	683.85
3- ₂	--	71.46	67.38	8 ₇	-+	718.92	683.19
3- ₃	-+	71.42	67.32	8 ₆	--	684.77	646.68
4 ₄	++	197.08	186.66	8 ₅	+-	682.59	644.96
4 ₃	+-	195.92	185.84	8 ₄	++	657.10	616.05
4 ₂	--	182.56	171.02	8 ₃	-+	648.35	610.06
4 ₁	-+	173.98	163.91	8 ₂	--	637.49	595.71
4 ₀	++	170.27	159.23	8 ₁	+-	612.33	575.20
4- ₁	+-	148.41	139.63	8 ₀	++	610.42	572.00
4- ₂	--	148.14	139.21	8- ₁	-+	569.11	534.88
4- ₃	+-	114.18	107.70	8- ₂	--	568.95	534.62
4- ₄	++	114.18	107.69	8- ₃	+-	516.03	485.53
5 ₅	+-	297.29	281.96	8- ₄	++	516.03	485.52
5 ₄	--	296.66	281.53	8- ₅	-+	452.77	426.67
5 ₃	-+	277.49	260.46	8- ₆	--	452.77	426.67
5 ₂	++	271.30	255.74	8- ₇	+-	379.53	358.38
5 ₁	+-	263.73	246.50	8- ₈	++	379.53	358.38
5 ₀	--	244.48	229.88	9- ₂	++	688.29	647.11
5- ₁	-+	243.47	228.33	9- ₃	-+	688.29	647.11
5- ₂	+-	210.30	197.93	9- ₄	--	625.36	588.68
5- ₃	+-	210.26	197.85	9- ₅	-+	625.36	588.68
5- ₄	--	166.37	156.99	9- ₆	++	552.38	520.69
5- ₅	-+	166.37	156.99	9- ₇	-+	552.38	520.69
6 ₆	++	417.96	396.78	9- ₈	--	469.39	443.31
6 ₅	+-	417.52	396.47	9- ₉	-+	469.39	443.31
6 ₄	--	392.57	369.33	10- ₅	+-	744.11	700.72
6 ₃	-+	388.46	366.44	10- ₆	++	744.11	700.72
6 ₂	++	375.68	351.26	10- ₇	-+	661.38	623.61
6 ₁	-+	359.65	338.22	10- ₈	--	661.38	623.61
6 ₀	--	356.96	334.17	10- ₉	+-	568.67	537.16
6- ₁	+-	325.39	305.93	10- ₁₀	++	568.67	537.16
6- ₂	+-	325.22	305.59	11- ₈	++	779.70	735.38
6- ₃	-+	281.70	265.25	11- ₉	-+	779.70	735.38
6- ₄	--	281.69	265.25	11- ₁₀	--	677.31	639.83
6- ₅	+-	227.99	215.20	11- ₁₁	-+	677.31	639.83
6- ₆	+-	227.99	215.20	12- ₉	-+	907.46	856.00
7 ₇	++	558.89	530.97	12- ₁₀	--	907.46	856.00
7 ₆	--	558.37	530.47	12- ₁₁	+-	795.33	751.39
				12- ₁₂	++	795.33	751.39

Table III gives the positions of the observed lines in comparison with the spectrum calculated from the rotational term values of Table II and the above value of ν_0 . The calculated positions of a number of unobserved lines which should first be observed on increasing the path of absorbing H_2S are included. In cases where a transition is between unresolved doublets, only the strong component is specifically designated. The strong components are those having odd τ values in the normal state. (Transitions are written in the customary form of excited state—normal state.) The column headed I gives an approximate intensity which is a composite of estimated

TABLE III. Transition values, calculated and observed.

Observed (cm ⁻¹)	I	Calculated (cm ⁻¹)	$\Delta j = \pm 1$ Transitions	$\Delta j = 0$ Transitions	Observed (cm ⁻¹)	I	Calculated (cm ⁻¹)	$\Delta j = \pm 1$ Transitions	$\Delta j = 0$ Transitions
		9987.46	7 ₂ -6 ₃				02.66		6 ₂ -6 ₁
9987.09	2	87.35	12 ₋₁₀ -11 ₋₉		01.77	4	01.79		4 ₄ -4 ₃
85.96	1	86.96	8 ₋₂ -7 ₋₁		9899.89	2	9899.81		4 ₃ -4 ₄
		86.41	10 ₋₆ -9 ₋₅		97.25	3	97.33	0 ₀ -1 ₋₁	
85.01	4	85.13	12 ₋₁₂ -11 ₋₁₁		95.47	4	95.29		5 ₄ -5 ₅
		85.05	11 ₋₈ -10 ₋₇		94.59	1	94.58		3 ₀ -3 ₁
		84.82	0 ₂ -5 ₃		94.01	2			
83.44	4	83.70	9 ₋₄ -8 ₋₃		92.61	2	92.40		4 ₁ -4 ₂
		83.09	0 ₄ -5 ₅				91.92		0 ₄ -0 ₃
		83.07	7 ₀ -6 ₁		91.34	1	91.59		2 ₋₂ -2 ₋₁
82.25	5	82.28	10 ₋₈ -9 ₋₇		90.43	2	90.31		0 ₆ -0 ₅
81.33	2	81.49	11 ₋₁₀ -10 ₋₉		88.78	1	89.30		5 ₂ -5 ₃
80.30	4	80.61	6 ₀ -5 ₁		87.03	1	87.12	1 ₀ -2 ₋₁	
78.86	5	78.97	8 ₋₄ -7 ₋₃		85.88	1	85.85	1 ₋₁ -2 ₋₂	
76.57	1	78.82	9 ₋₈ -8 ₋₅		83.30	1	83.43		3 ₋₂ -3 ₋₁
74.93	5	76.91	10 ₋₁₀ -9 ₋₉		82.22	1	82.63		7 ₆ -7 ₇
73.30	3	75.20	7 ₋₂ -6 ₋₁		80.09	2	82.01		3 ₋₃ -3 ₋₀
71.93	1	74.83	8 ₋₆ -7 ₋₅		78.90	1	80.41		4 ₋₁ -4 ₋₀
70.73	3	73.17	9 ₋₈ -8 ₋₇		76.72	3	78.95		7 ₄ -7 ₅
70.45	5	72.50	6 ₋₂ -5 ₋₁				77.20		5 ₀ -5 ₁
67.42	1	70.87	6 ₋₁ -5 ₋₀				76.28		4 ₋₂ -4 ₋₁
65.94	4	70.86	5 ₋₂ -4 ₋₃		75.47	4	75.71	2 ₋₁ -3 ₋₂	
65.40	5	70.37	7 ₋₄ -6 ₋₃		74.28	1	75.37	2 ₋₂ -3 ₋₃	
62.96	1	66.95	8 ₋₈ -7 ₋₇		73.47	1	74.36		4 ₀ -4 ₃
60.46	4	66.04	5 ₀ -4 ₁		72.22	1			
59.87	5	65.39	4 ₀ -3 ₁		70.37	1	70.33		4 ₋₄ -4 ₋₁
55.54	4	63.04	4 ₂ -3 ₃		69.36	2	69.33		7 ₂ -7 ₃
54.63	1	60.76	5 ₋₃ -4 ₋₂		65.51	1	65.51		5 ₋₂ -5 ₋₁
53.88	5	60.57	5 ₋₂ -4 ₋₁		64.18	4	64.25	3 ₋₂ -4 ₋₃	
52.11	1	59.88	6 ₋₈ -5 ₋₅				64.19	3 ₋₃ -4 ₋₄	
47.30	5	55.26	4 ₋₂ -3 ₋₁		58.63	1	63.76	2 ₀ -3 ₋₁	
42.62	1	54.32	4 ₋₁ -3 ₀		57.78	1	58.85	2 ₂ -3 ₁	
40.07	4	53.86	5 ₋₄ -4 ₋₃				57.78		5 ₋₄ -5 ₋₃
34.89	1	52.37	2 ₂ -1 ₋₁		53.38	3	56.99		6 ₋₂ -6 ₋₁
33.31	2	48.31		6 ₋₄ -6 ₋₅	52.40	4	56.76		6 ₀ -6 ₃
32.01	1	47.32	4 ₋₄ -3 ₋₃		51.57	1	53.41	3 ₀ -4 ₋₁	
30.41	1	47.29	4 ₋₃ -3 ₋₂		46.41	2	52.37	4 ₋₄ -5 ₋₅	
25.24	1	46.62	3 ₀ -2 ₁		44.70	2	51.91	3 ₋₁ -4 ₋₂	
23.14	1	42.61		5 ₋₂ -5 ₋₅	44.70	2	50.91		6 ₋₄ -6 ₋₁
21.84	1	40.36	3 ₋₃ -2 ₋₂		43.80	1	46.30	3 ₂ -4 ₁	
20.48	1	40.14	3 ₋₂ -2 ₋₁		41.19	1	44.79		6 ₂ -6 ₃
14.20	1	39.78	2 ₀ -1 ₁				44.55		6 ₋₆ -6 ₋₃
12.18	1	39.40		7 ₋₂ -7 ₋₅			43.59		7 ₋₂ -7 ₋₁
10.87	4	36.08		4 ₋₂ -4 ₋₃			41.28	2 ₀ -3 ₃	
08.02	2	34.94		6 ₋₂ -6 ₋₃			41.10	3 ₁ -4 ₀	
06.72	1	34.93		7 ₆ -7 ₃			40.38	4 ₋₁ -5 ₋₂	
06.07	1	33.07					40.05	5 ₋₄ -6 ₋₅	
04.44	1	32.06					40.00	4 ₋₂ -5 ₋₃	
02.99	4	30.67					27.28	5 ₋₂ -6 ₋₃	
		30.40					27.19	6 ₋₆ -7 ₋₇	
		28.85					26.81	4 ₀ -5 ₋₁	
		25.37					20.22	4 ₄ -5 ₃	
		25.28					18.19	4 ₂ -5 ₁	
		23.86					15.40	5 ₀ -6 ₋₁	
		23.32					13.85	7 ₋₆ -8 ₋₇	
		21.87					13.78	6 ₋₄ -7 ₋₅	
		20.47					07.14	5 ₂ -6 ₁	
		19.83					04.12	5 ₄ -6 ₃	
		14.16					02.32		
		10.89					01.10	6 ₋₂ -7 ₋₃	
		08.09					9800.00	8 ₋₈ -9 ₋₉	
		06.65					9799.79	7 ₋₄ -8 ₋₅	
		06.05					9791.53		
		05.01					86.45	6 ₀ -7 ₋₁	
							86.27	7 ₋₂ -8 ₋₃	
							85.69	9 ₋₈ -10 ₋₉	
							85.34	8 ₋₆ -9 ₋₇	
							79.04		

intensities and the number of times the lines were observed. Because of the extreme weakness of the absorption the accuracy of these estimates is very low. The probable error in the positions of the lines varies from about 0.03 cm⁻¹ for the best lines to about 0.15 cm⁻¹ for the poorest. Seven lines are reported for which no transitions can be assigned. These need not cause any concern over the validity of the analysis since they are all

weak and the method of measuring would readily admit a few spurious lines.

The mean deviation of the calculated values from the observed is about 0.13 cm⁻¹. That so many of the deviations are of larger magnitude than the probable error of the experimental measurements is probably due to the failure of the theory, and may be anticipated from some of the assumptions which are necessary in order

to set up the theoretical treatment in a form capable of solution. It should be mentioned that there are deviations of the same order of magnitude in Mecke's results for the water spectrum, but they are not so evident because Mecke's term values are experimental, and comparison with theory requires a calculation of the term values from the molecular constants which Mecke obtained from sum rules.

A summary of the results of the determination of the molecular constants will be found in Table IV.

TABLE IV. Constants of H_2S molecule.

	Normal State	Excited State
A	$10.373 \pm 0.005 \text{ cm}^{-1}$	$9.883 \pm 0.005 \text{ cm}^{-1}$
B	8.991 ± 0.004	8.340 ± 0.004
C	4.732 ± 0.003	4.474 ± 0.003
I_A	$2.667 \times 10^{-40} \text{ g cm}^2$	$2.799 \times 10^{-40} \text{ g cm}^2$
I_B	3.076	3.317
I_C	5.845	6.182
Bond angle	$92^\circ 20'$	$93^\circ 10'$
H-S distance	1.345Å	1.383Å
	$\nu_0(\nu_\sigma + 3\nu_\pi) = 9911.05 \pm 0.03 \text{ cm}^{-1}$	

XI. STRUCTURE OF THE H_2S MOLECULE

It will be observed from the "effective" moments of inertia that $I_A + I_B \neq I_C$, which is also true for H_2O . This is not compatible with any planar structure, so Mecke's example will be followed and r and θ calculated from the equations

$$r = [(M + 2m)I_C / 2m(M + 2m \sin^2 \phi)]^{1/2}. \quad (27)$$

$$\theta = 2 \tan^{-1} [MI_B / (M + 2m)I_A]^{1/2}. \quad (28)$$

The results are given in Table IV.

It has been supposed for some time that the angle in the H_2S molecule was about 90° since this angle was given by Kohlrausch⁶ from an

interpretation of the Raman spectrum. It was purely fortuitous that Kohlrausch's result was so nearly correct, as can readily be seen by applying the same reasoning to the water molecule. Cross and Van Vleck²² have discussed reasons why structures cannot be determined from the vibrational frequencies when the central mass is much larger than the attached masses. Furthermore, when the attached masses are very small, the amplitudes will be large and the anharmonic factors so large that the mechanical frequencies (i.e., the frequencies corresponding to infinitesimal amplitude) may be quite different from the observed fundamentals.²³ Calculations of structures using the observed frequencies instead of the mechanical frequencies would in such cases be meaningless.

In using structures given with the precision of those in Table IV, it must be borne in mind that they are only "effective" structures for the particular type of experiment used in their determination. For a molecule such as H_2S the atoms are vibrating over paths which admit displacements of the interatomic distances of as much as a tenth of the equilibrium values. The particular path of vibration depends to a certain extent on the rotational state of the molecule. The instantaneous structure may vary widely from these effective structures, especially in excited vibrational states, where the atoms spend more time near the extremes of their vibration paths.

In conclusion the author wishes to acknowledge the kind cooperation and the helpful suggestions given by Professor R. M. Badger during the progress of this work.

²² P. C. Cross and J. H. Van Vleck, *J. Chem. Phys.* **1**, 350 (1933).

²³ L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).