

One-to-Two Millimeter Wave Spectroscopy. II. $\text{H}_2\text{S}^\dagger$ CHARLES A. BURRUS, JR.,* AND WALTER GORDY
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Pure rotational transitions of H_2S^{32} , H_2S^{33} , and H_2S^{34} have been measured with high precision in the region of one to two millimeters. From these measurements the SH bond length is found to be 1.3226 Å and the bond angle to be $92^\circ 6'$. The S^{33} nuclear quadrupole coupling observed along the principal inertial axes are $eQq_{aa} = -32$ Mc/sec, $eQq_{bb} = -8$ Mc/sec, and $eQq_{cc} = +40$ Mc/sec. Approximate analysis of the quadrupole coupling constants shows that the bonding orbitals of S are sp^d hybrids and yields a value of -0.06×10^{-24} cm² for the quadrupole moment of the S^{33} nucleus. From the known ratio Q^{33}/Q^{35} this gives $Q^{35} = 0.04 \times 10^{-24}$ cm². Zeeman studies show that the molecular g_J factor is approximately, but not exactly, equal for different rotational states. A mean value of 0.24 nuclear magneton is found for g_J .

INTRODUCTION

HARMONIC generators and detectors recently developed in this laboratory¹ extend the bounds of microwave spectroscopy down to one millimeter wavelength. A rotational line of OCS has been measured at 1.03 mm wavelength with a precision of three parts in 10^6 . The line strength at this point was several times the noise level. One of the advantages of this new development is the wider frequency coverage afforded for the investigation of asymmetric-top molecules. The easily analyzed, low J transitions of asymmetric rotors very frequently fall only in the short millimeter-wave region. This is true for H_2S , the molecule which is the subject of the present investigation. It has three low J transitions between 1 mm and 1.8 mm but none at lower frequencies. Internal (Q -branch) transitions in HSD have been measured in the lower frequency microwave region by Hillger and Strandberg.² Because of the large difference between the zero-point vibrational energies of SH and SD they could not improve upon the accuracy of the structure as determined with infrared spectra.

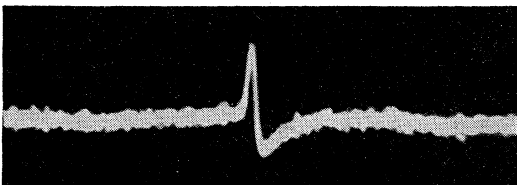


FIG. 1. Cathode-ray display of the $1_{0,1} \rightarrow 1_{1,0}$ line of H_2S^{34} with the natural concentration of S^{34} of 4.2 percent.

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* Texas Company Fellow. The information contained in this paper will be the basis for part of a thesis to be submitted by the author in partial fulfillment of the requirements for the Ph.D. degree at Duke University.

¹ W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953).

² R. E. Hillger and M. W. P. Strandberg, Phys. Rev. **83**, 575 (1951).

The hydrogen sulfide molecule has been the subject of numerous studies in optical spectroscopy.³ The transitions $1_{1,0} \rightarrow 1_{2,0}$ and $2_{1,1} \rightarrow 2_{2,0}$ predicted by King, Hainer, and Cross⁴ to fall at 5.67 cm⁻¹ and 7.28 cm⁻¹ respectively, are the ones observed here. They were found to fall near the predicted frequencies.

EXPERIMENTAL METHOD

The millimeter-wave generator and detector are those described briefly in Part I of this series by King and Gordy.¹ It will be described in more detail by these authors in a paper to follow. An improvement in sensitivity by a factor of 10 or more over the performance described in Part I has been made by the use of a phase-lock-in amplifier with frequency modulation of the klystron and an automatic recording of the lines.⁵ The lock-in amplifier was tuned to 4000 kc/sec, which was twice the frequency of the klystron modulation. This tuning of the amplifier to the harmonic of the modulation discriminates against reflections and hence tends to make the base line flat.

Figure 1 is a cathode-ray display of the $1_{0,1} \rightarrow 1_{1,0}$ line of H_2S^{34} taken with S^{34} in its natural concentration of 4.2 percent with a 60-cps video sweep spectrometer. For this presentation an ordinary P amplifier with a bandwidth of about 6000 kc/sec was employed. Figure 2 shows similar video presentations of the $1_{0,1} \rightarrow 1_{1,0}$ and $2_{1,1} \rightarrow 2_{2,0}$ lines of H_2S^{32} . Figure 3 represents an automatic recording of the $1_{0,1} \rightarrow 1_{1,0}$ transition of H_2S^{33} with S^{33} in its natural concentration of 0.7 percent.

SPECTRAL CONSTANTS AND MOLECULAR STRUCTURE

Table I gives the observed frequencies. The notation used, $J_{K-1, K+1}$, is that of King, Hainer, and Cross.⁴ Explicit expressions can be obtained for these low J transitions. They are, for the rigid asymmetric rotor:

$$\nu(1_{0,1} \rightarrow 1_{1,0}) = C - B, \quad (1)$$

³ For reference see G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945), p. 489.

⁴ King, Hainer, and Cross, Phys. Rev. **71**, 433 (1947).

⁵ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 11.

and

$$\nu(2_{1,1} \rightarrow 2_{2,0}) = A - 2B + C + 2[(B-C)^2 + (A-C)(A-B)]^{1/2}, \quad (2)$$

where $A = h/(8\pi^2 I_a)$, $B = h/(8\pi^2 I_b)$, and $C = h/(8\pi^2 I_c)$, in which I_a , I_b , and I_c are the moments of inertia about the principal axes a , b , and c with $I_a < I_b < I_c$. For a rigid planar molecule there are only two independent inertial moments to be evaluated in the approximation of the rigid rotor. Sufficient data are available for evaluation of these constants for H₂S³². The number of

TABLE I. Observed transitions of H₂S.

	Transition	Observed frequency in Mc/sec
H ₂ S ³²	1 _{0,1} → 1 _{1,0}	168 762.51 ± 0.35
H ₂ S ³²	2 _{1,1} → 2 _{2,0}	216 710.42 ± 0.45
H ₂ S ³³	1 _{0,1} → 1 _{1,0}	168 322.63 ± 0.35*
H ₂ S ³⁴	1 _{0,1} → 1 _{1,0}	167 910.57 ± 0.35

* Corrected for nuclear quadrupole effects.

frequencies measured is insufficient, however, for evaluation of the centrifugal distortion constants. Fortunately, the rotational states involved in the observed transitions are so low that the effects of centrifugal distortion can be safely neglected in the evaluation of the molecular structure. Even for the low J states involved here centrifugal distortions may shift the observed frequency by an amount of the order of megacycles per second. Nevertheless, the error in the structural determination caused by neglect of zero point vibrational effects is likely to be greater than that caused by the neglect of centrifugal distortion. The internal consistency of the structural parameters which were evaluated in three different ways indicate that neither of these effects caused large errors.

TABLE II. H₂S structure.^a

∠HSH	SH distance, A	Transitions employed
92° 6'	1.32261	H ₂ S ³² , 1 _{0,1} → 1 _{1,0} and 2 _{1,1} → 2 _{2,0}
92° 6'	1.32259	H ₂ S ³² and H ₂ S ³³ , 1 _{0,1} → 1 _{1,0}
92° 6'	1.32257	H ₂ S ³² and H ₂ S ³³ , 1 _{0,1} → 1 _{1,0}
92° 6'	1.32259 ± 0.00002	Averaged value

^a Masses and other constants used are those listed in reference 5, Table A1.

For H₂S the axis of intermediate moment of inertia, b , lies along the symmetry axis; a lies in the plane of the molecule perpendicular to b ; and c , the axis of greatest moment of inertia is perpendicular to the plane of the molecule. The principal moments of inertia are readily found to be

$$I_a = [(2M_H M_S)/(M_S + 2M_H)] d_{SH}^2 \cos^2(\theta/2); \quad (3)$$

$$I_b = 2M_H d^2 \sin^2(\theta/2); \quad (4)$$

$$I_c = I_a + I_b, \quad (5)$$

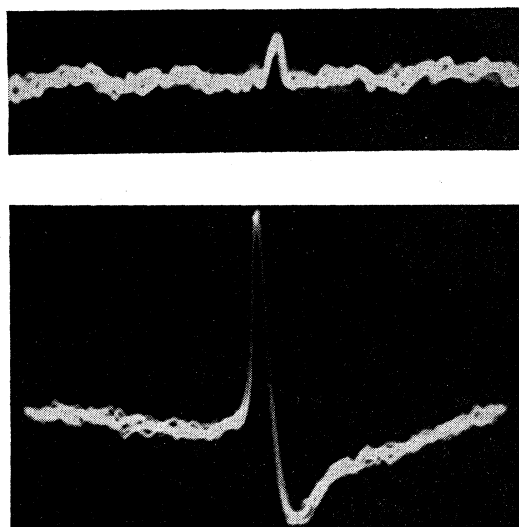


FIG. 2. Cathode-ray display of the 1_{0,1} → 1_{1,0} (lower) and the 2_{1,1} → 2_{2,0} (upper) lines of H₂S³² at 168.7 kMc and 216.7 kMc, respectively.

where d_{SH} is the bond length and θ is the bond angle HSH.

With the above equations and the observed frequencies, the structure of the molecule can be obtained. Since there are only two structural parameters and four observed frequencies (including those for different isotopic combinations), the parameters can be evaluated in more than one way. Table II gives the results. It is seen that the internal consistency is remarkably good. Certainly for the 1_{0,1} → 1_{1,0} transition, where the centrifugal stretching is small, the differences in the stretching effects for the different S isotopes are negli-

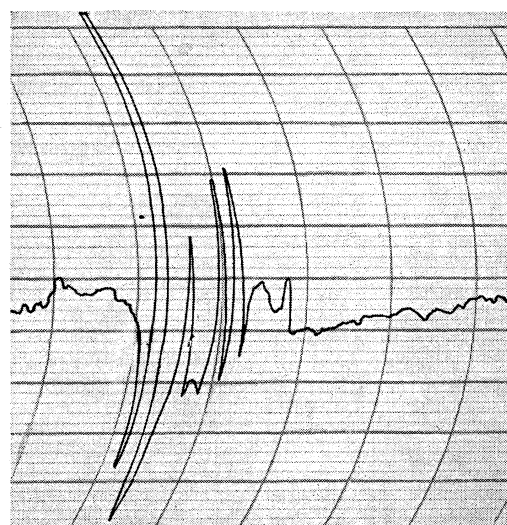


FIG. 3. Recorder trace of the 1_{0,1} → 1_{1,0} transitions of H₂S³³ at 168.3 kMc showing S³³ nuclear quadrupole splitting. Concentration of S³³ is 0.7 percent.

TABLE III. Spectral constants from averaged dimensions^a of Table II.

	Moments of inertia in 10 ⁻⁴⁰ g cm ²		
	<i>I_a</i>	<i>I_b</i>	<i>I_c</i>
H ₂ S ³²	2.6522	3.0339	5.6861
H ₂ S ³³	2.6570	3.0339	5.6909
H ₂ S ³⁴	2.6615	3.0339	5.6954

	Spectral constants in Mc/sec		
	<i>A</i>	<i>B</i>	<i>C</i>
H ₂ S ³²	316 304	276 512	147 536
H ₂ S ³³	315 735	276 512	147 412
H ₂ S ³⁴	315 201	276 512	147 296

^a Masses and other constants employed are those listed in reference 5, Table A1.

gible. Also, as the change in the reduced mass of the molecule for the S substitution is slight, the difference in zero-point vibrational energy is small. It seems, therefore, that isotopic substitution may yield the most accurate structural determination. Nevertheless, it is seen that the values obtained from the two rotational lines of H₂S³² are in excellent agreement with those obtained by isotopic substitution. One should mention that both determinations include errors from zero point vibrational energy. Relation (5) does not hold exactly for the actual non rigid molecule but involves the so called quantum defect, $\Delta = I_c - (I_a + I_b)$. The error limits may be somewhat larger than the mean deviation indicated in Table II. Nevertheless, this small deviation is indicative of small error limits, and it seems likely that the structural parameters are determined to at least four significant figures. Without attempting to estimate the error limits we give the most probable values, $d_{SH} = 1.3226\text{A}$ and $\angle HSH = 92^\circ 6'$.

The presumably more accurate values of the bond distances and bond angles here obtained are slightly lower than the previously accepted values. The best previous values are probably those given by Herzberg,³ $d_{SH} = 1.334\text{A}$ and $\angle HSH = 92^\circ 16'$, as obtained from the infrared work of Crawford and Cross.⁶ It should be mentioned that our values, as well as those quoted from infrared data, are the effective values for the ground vibrational state. The hypothetical equilibrium values have not been obtained.

The moments of inertia and the constants *A*, *B*, and *C* are sometimes needed. They are given to five figures in Table III.

S³³ NUCLEAR QUADRUPOLE COUPLING AND THE NATURE OF CHEMICAL BONDING IN H₂S

The rotational lines of H₂S³³ are split into a multiplet structure by the interaction of the S³³ nuclear quadrupole moment with the molecular field gradient.[†] This

⁶ B. L. Crawford, Jr., and P. C. Cross, J. Chem. Phys. **5**, 621 (1937).

[†] Partial resolution of the S³³ quadrupole hyperfine structure of the 2_{2,1}→2_{2,0} transition in HDS³³ has been accomplished by Hillger and Strandberg (reference 2). This transition has been

structure has been resolved and measured in the 1_{0,1}→1_{1,0} line, with S³³ in its natural concentration of 0.7 percent. A recorder tracing of the transition is shown in Fig. 3. The spin of S³³ is $\frac{3}{2}$. There are, in all, seven components for the 1_{0,1}→1_{1,0} transition. The weakest of these does not show on the tracing, and two of the stronger components fall at essentially the same frequency (see Table V) and hence are not resolved.

The quadrupole splitting is readily analyzed with the formula:⁷

$$E_Q = eQ \left\{ \left(\frac{\partial^2 V}{\partial a^2} \right) \left[J(J+1) + E(\kappa) - (\kappa+1) \left(\frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right. \\ \left. + 2 \left(\frac{\partial^2 V}{\partial b^2} \right) \left(\frac{\partial E(\kappa)}{\partial \kappa} \right) + \left(\frac{\partial^2 V}{\partial c^2} \right) \left[J(J+1) - E(\kappa) \right. \right. \\ \left. \left. + (\kappa-1) \left(\frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right\} \left(\frac{1}{J(J+1)} \right) Y(F),$$

where

$$Y(F) = \frac{\frac{3}{4}C(C+1) - J(J+1)I(I+1)}{2(2J-1)(2J+3)I(2I-1)},$$

TABLE IV. S³³ nuclear quadrupole coupling constants in H₂S³³.

Coupling in Mc	
$eQq_{aa} = -32$	Spin = 3/2
$eQq_{bb} = -8$	$Q^{33} = -0.06 \times 10^{-24} \text{ cm}^2$
$eQq_{cc} = +40$	

values of which are tabulated by Gordy, Smith, and Trambarulo⁵ for *J* up to 20. The quantities $eQ(\partial^2 V/\partial a^2) = \chi_{aa}$, $eQ(\partial^2 V/\partial b^2) = \chi_{bb}$, and $eQ(\partial^2 V/\partial c^2) = \chi_{cc}$ are the quadrupole coupling constants measured along the principal inertial axes. $E(\kappa)$ is the reduced energy of the asymmetric rotor, and $\kappa = (2B - A - C)/(A - C)$ is the asymmetry parameter. For the 1_{0,1} level, $E(\kappa) = \kappa - 1$ and $\partial E(\kappa)/\partial \kappa = 1$; for the 1_{1,0} level, $E(\kappa) = \kappa + 1$ and $\partial E(\kappa)/\partial \kappa = 1$. With these values and the additional simplification $\chi_{bb} = -(\chi_{aa} + \chi_{cc})$ provided by Laplace's equation, the level energies can be written

$$(E_Q)_{1,0} = -\chi_{cc} Y(F), \quad (E_Q)_{1,1} = -\chi_{aa} Y(F).$$

These relations, with the selection rules $\Delta F = 0, \pm 1$ and the Bohr relation with the observed frequencies, yield the coupling constants listed in Table IV. Table V shows the calculated and observed spectrum for this transition.

The most surprising feature of the quadrupole splitting is the large difference in the coupling constants χ_{aa} and χ_{bb} . The asymmetry in the coupling measured

further investigated by G. R. Bird and C. H. Townes, who have obtained preliminary values for the coupling constants in HDS³³ (Quarterly Progress Report, Columbia Radiation Laboratory, March 31, 1953).

⁷ J. K. Bragg and S. Golden, Phys. Rev. **75**, 735 (1949).

by the parameter

$$\epsilon = (\chi_{aa} - \chi_{bb}) / \chi_{cc} = -0.60$$

is remarkably large. From the fact that the bond angle is so nearly a right angle, one would expect the bonds to be formed with nearly *p* orbitals of the S. In fact, from the deviation of only 2 degrees from 90 one would expect no more than 3 percent of *s* contribution to the bonding orbitals, yet it is not possible to account even approximately for the large difference in χ_{aa} and χ_{bb} with nearly pure *p* bonding orbitals of the S, as is indicated by the angles.

It is possible to account for the bond angle as well as the nuclear couplings by postulating roughly equal *s* and *d* contributions to the bonding orbitals. The amount of energy required to promote a 3*s* electron of S to a 3*p* orbital is roughly equal that required to promote a 3*p* electron to a 3*d* orbital. Hence, *s*, *p*, *d* hybridization, a possibility called to our attention by Dehmelt, is a promising solution to the problem. If equal *s* and *d* contributions to the bonding orbitals are assumed with one non-bonding pair in a pure *p* orbital (normal to the molecular plane) and the other in an *sp* hybrid directed along the symmetry axis, then 15 percent *s* and 15 percent *d* character of each bonding orbital is indicated by the coupling with 30 percent *p* character for the *sp* hybrid containing the non-bonding pair. Qualitative estimates indicate that this type of hybridization is also in harmony with the observed bond angles. More quantitative calculations of the *s*, *p*, and *d* admixture are being attempted.

NUCLEAR QUADRUPOLE MOMENTS OF S³³ AND S³⁵

With the hybridized orbitals as postulated above and 20 percent ionic character of the bonds estimated from the difference in electronegativity of S and H the number of unbalanced *p* electrons along *c* is -0.81. This leads to

$$\chi_{cc} = -0.81 Q q_{3,1,0},$$

if we neglect the small contributions of *d* electrons. The $q_{3,1,0}$ here represents the electronic field gradient at the nucleus for one unbalanced *p* electron and can be estimated from the doublet splitting $\Delta\nu = 574 \text{ cm}^{-1}$ in the atomic spectrum of S as 13.8×10^{15} esu. With this value one obtains for S³³:

$$Q^{33} = -0.06 \times 10^{-24} \text{ cm}^2;$$

and for S³⁵, from the ratio⁸

$$Q^{33}/Q^{35} = -0.695,$$

$$Q^{35} = +0.04 \times 10^{-24} \text{ cm}^2.$$

⁸ Cohn, Koski, and Wentink, Phys. Rev. **81**, 948 (1951).

TABLE V. Calculated and observed structure of the $1_{0,1} \rightarrow 1_{1,0}$ transition of H₂S³³.

$F \rightarrow F'$	Frequency Mc/sec		Relative intensity	
	calculated	observed	calculated	observed
1/2 → 1/2	168 304.58	...	7.9	...
5/2 → 5/2	168 318.98	168 318.93	100	} 140
3/2 → 1/2	168 318.98	168 318.93	39.7	
1/2 → 3/2	168 322.58	168 322.63	39.7	40
3/2 → 5/2	168 326.98	168 326.90	42.9	40
5/2 → 3/2	168 328.98	168 329.03	42.5	45
3/2 → 3/2	168 337.18	...	12.7	...

These values include a factor 1.05 to correct for polarization of the inner electron shells⁹ by *Q*. From OCS, Townes and Geschwind¹⁰ estimates $Q^{33} = -0.055$ to -0.103 . From the pure quadrupole coupling in rhombic sulfur Dehmelt¹¹ estimates $Q^{33} = -0.050$.

MOLECULAR *g* FACTOR

The Zeeman effect of the $1_{0,1} \rightarrow 1_{1,0}$ line of H₂S³² was observed with a field of 2.93 kilogauss. The field was found to split the line into a doublet with separation $2\Delta\nu = 1.08 \text{ Mc/sec}$ when imposed at right angles to the *E* vector of the microwaves. This arrangement gives the σ or $\Delta M = \pm 1$ Zeeman components. When the magnet was placed so that *H* was parallel to the *E* vector, no splitting was observed although the line was noticeably broadened by the field of 2.93 kilogauss. If the *g* factor of the upper and lower states were equal, there would be no splitting for the latter arrangement ($\Delta M = 0$). Since broadening was observed it is apparent that *g* for the upper state is nearly but not exactly equal to *g* for the lower state. From the $\Delta M = \pm 1$ component we obtain

$$\bar{g}_J \approx \Delta\nu / 762H = 0.24 \text{ nuclear magnetons.}$$

This factor is approximately 40 percent of that¹² for H₂O, 0.586 nuclear magnetons.

More extensive Zeeman studies on H₂S are planned. Also, a millimeter wave Stark cell is being designed with which it is hoped that the electric dipole moment of H₂S can be obtained.

We wish to thank Dr. H. G. Dehmelt for his helpful discussion of the quadrupole coupling and Dr. W. C. King and Mr. H. G. Robinson for their suggestions about experimental details.

⁹ R. Sternheimer, Phys. Rev. **86**, 316 (1952).

¹⁰ C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).

¹¹ H. G. Dehmelt, Phys. Rev. **91**, 314 (1953).

¹² C. K. Jen, Physica **17**, 379 (1951).

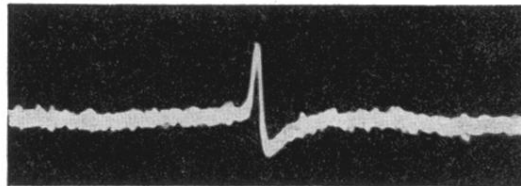


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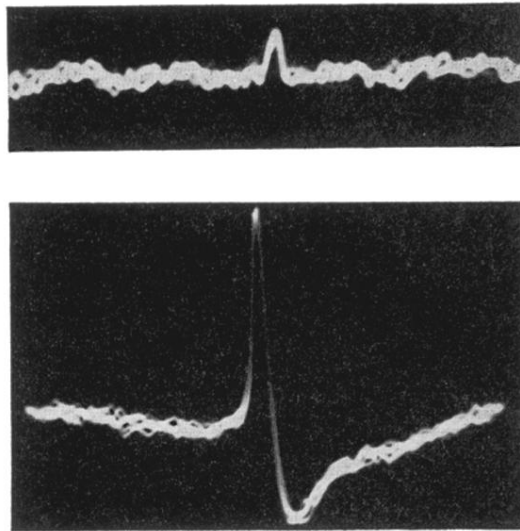


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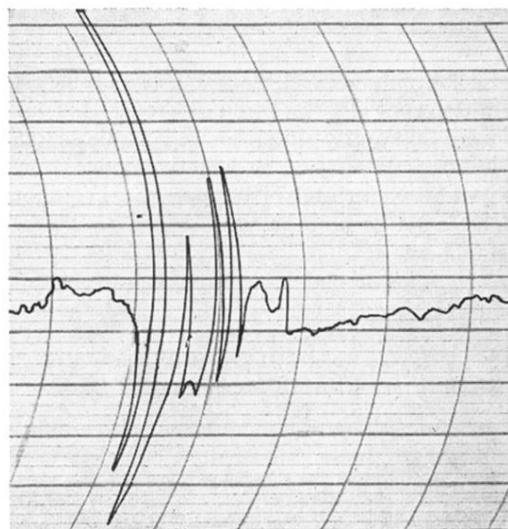


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