The Infrared Absorption Spectrum of the Deuterium Sulfides

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The spectra of HDS and D_2S have been investigated under high dispersion using a grating spectrometer. An absorption band at 9.0μ in HDS has been identified as ν_2 and has an average spacing of the rotation lines of about 6.85 cm^{-1}. In D_2S bands were located at 3.75μ, 5.0μ and 10.7μ which have line spacings of 4.8 cm^{-1}, 5.0 cm^{-1}, 5.0 cm^{-1} and may be identified as $\nu_1+\nu_2$, ν_3 corresponding to a similar identification in H_2S. As in H_2S, ν_2 appears to have a Q branch while ν_3 does not. If this is actually so, ν_2 must arise from a vibration of the electric moment parallel with the axis of least moment of inertia and ν_3 from a vibration along the middle axis. Since ν_2 is a vibration parallel with the symmetry axis of the triangle then this axis must be identified with the axis of least moment of inertia. This argument supports the acute angled model suggested by Sprague and Nielsen, and the evidence is interpreted to favor a vertex angle of 85° instead of the 110° angle of Bailey, Thompson and Hale.

I. INTRODUCTION

THE spectrum of the water molecule has perhaps been more completely studied in the infrared than any other triatomic molecule. Due to its intense absorption of radiation a host[1] of bands have been accurately located throughout the spectrum from the photographic region to beyond 6.5μ, all of which have been investigated under high dispersion. This wealth of data supplemented by similar, though less extensive measurements on the HDO and D_2O[2] molecules has made it possible to adopt a quite convincing model for the water vapor molecule.

It would be desirable to pursue a similar course with the hydrogen sulfide molecule, but unfortunately this gas absorbs very unwillingly and its spectrum is only imperfectly known. Two bands at 2.7μ and 3.8μ have been mapped by Nielsen and Barker[3] and a third near 8.0μ was located by Rollefson.[4] Recently the 3.8μ region and the 8.0μ region have been carefully remeasured by Sprague and Nielsen[5] and while nothing new was found at 3.8μ the band of 8.0μ presented an entirely different appearance, although in general verifying the line positions given by Rollefson. Two other bands have been observed by Cross[6] in the photographic infrared at 9911 cm^{-1} and 10,100 cm^{-1}. These he has subjected to a rotational analysis, thereby determining values for the moments of inertia.

[1] W. W. Sleator, Astrophys J. **48**, 125 (1918); Sleator and Phelps, Astrophys J. **62**, 28 (1926); E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931); R. Mecke, Zeits. f. physik. Chemie, Abt. **B16**, 6, 409 and 17.1, 1 (1932); R. Mecke and W. Baumann, Physik. Zeits. **33**, 833 (1932).

[2] E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).

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

[4] A. H. Rollefson, Phys. Rev. **34**, 604 (1929).

[5] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937).

[6] P. C. Cross, Phys. Rev. **47**, 7 (1935).

Very recently one of these regions has been rephotographed by Carvin[7] who finds several of Cross' strong lines to be missing from the spectrum. This, of course, casts some doubt upon the validity of Cross' work and his values for the moments of inertia. In addition to this data a Raman line has been reported by Bhagavantam[8] at 2615 cm^{-1}.

These bands do not, without further assumptions, suffice to fix the shape of the molecule. Neither does a knowledge of the actual values of the moments of inertia alone serve uniquely to determine the shape of the molecule since there will always be two isoceles triangular models, an acute and an obtuse, which will satisfy any set of moments of inertia. If, however, the values of these are known and in addition the rotational character of at least one fundamental band, correctly identified, can be decided upon (i.e., whether, for example, it contains P, Q and R branches or not) then the shape may be uniquely fixed. This may be seen in the following manner. In the XY_2 type molecule three modes of oscillation are possible, two of which ν_1 and ν_2 are parallel to the axis of symmetry of the molecule and the third ν_3, which is normal to it. Since in general ν_1 and ν_3 take values relatively high to ν_2, the latter fundamental may usually be identified without difficulty. If now its rotational characteristics can be decided upon then it is at once determined how the axes of inertia of the molecule will lie. For example, if ν_2 has P, Q and R branches, it must be an oscillation along the axis of the smallest moment of inertia. Since it is also an oscillation along the axis of symmetry, the axis of smallest moment of inertia and the axis of symmetry must be the same. If on the other hand the band does not contain P, Q and R branches it must be an oscillation along the axis of the intermediate moment of inertia and consequently the axis of symmetry must in this case be the axis of the intermediate moment of inertia. It is with the object in view of obtaining further information regarding the shape of the hydrogen sulfide molecule from the rotational character of the absorption bands that we have undertaken this study of the HDS and D$_2$S spectrum.

II. APPARATUS

A prism grating spectrometer having a collimating mirror of two-meter focal length was available for the investigation. The recording apparatus of the spectrometer consisted of a highly sensitive vacuum thermocouple, constructed by Mr. Paul Weyrich of the University of Michigan technical staff, used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity galvanometer. Two echelette gratings ruled by Professor R. W. Wood at Johns Hopkins University were used in analyzing the spectra. The bands at 3.75μ were measured in first order of a 3600-lines-per-inch grating while the bands at 9.0μ and 10.7μ were measured in first order of a grating having 800 lines per inch. The latter grating was used in second order for the 5.0μ region.

The D$_2$S was made in a vacuum system by dropping 99.2 percent heavy water on the purest obtainable aluminum sulfide and trapping out any heavy water vapor by means of a liquid-air bath. The HDS was made in the same way but 55 percent heavy water was substituted for the 99.2 percent variety. The ensuing gas was therefore a mixture composed of about 25 percent H$_2$S, 25 percent D$_2$S and 50 percent HDS. It is believed that some aluminum carbide occurred in the aluminum sulfide as an impurity because of two peaks found in the spectrum of D$_2$S which correspond to the Q branches of CD$_4$.[9]

The absorption cells were of glass tubing 30 cm long and 5 cm in diameter and have a stopcock sealed in for evacuating and admitting the gas. The ends were closed with windows of polished rocksalt coated thinly with gum damar to protect them against clouding in the humid weather prevailing while most of these measurements were made.

III. EXPERIMENTAL RESULTS

HDS

In our preliminary paper[10] we reported bands in the spectrum of HDS at 2.1μ, 3.1μ, 4.1μ and 9.0μ. The band at 2.1μ is quite weak and has not been investigated under high dispersion.

[7] F. D. Carvin, J. Chem. Phys. 5, 159 (1937).
[8] Bhagavantam, Nature 126, 502 (1930).

[9] H. H. Nielsen and A. H. Nielsen, Abstract No. 29, Chicago meeting of the Am. Phys. Soc. Nov. 27, 1936.
[10] A. H. Nielsen and H. H. Nielsen, J. Chem. Phys. 4, 229 (1936).
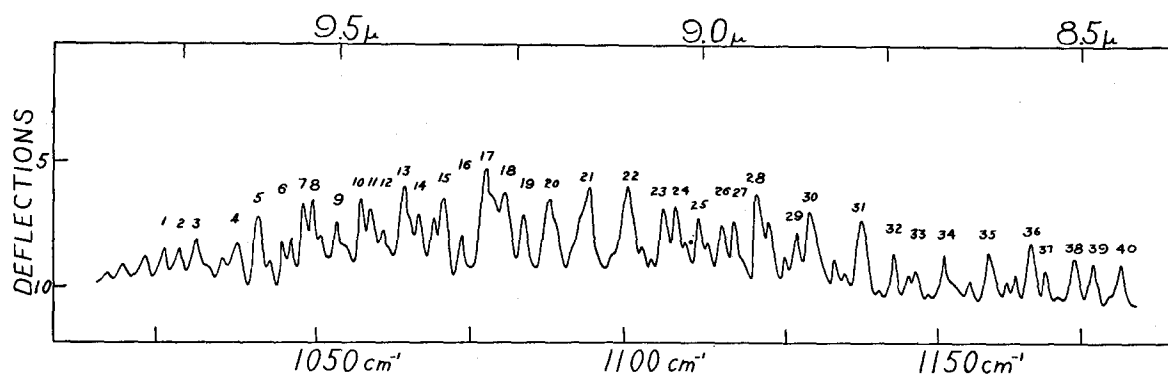
FIG. 1. The absorption in HDS at 9.0μ.

That at 3.1μ is undoubtedly the same observed by Bailey, Thompson and Hale[11] at 2.8μ. Our prism curve shows absorption from about 2.6μ to beyond 3.1μ, probably due to overlapping of the 2.7μ H$_2$S band with the region reported by Bailey, Thompson and Hale. Our prism instrument was, however, unable to resolve the two bands and we estimated that the part due to HDS was situated near 3.1μ. The value given by them is probably a more accurate one than ours. Due to the weakness of absorption, and the overlapping with the atmospheric water vapor fundamental it has not proved feasible to map this region under high dispersion. The region we reported at 4.1μ was due to an impurity in our gas. We have been able to demonstrate that the peak at 4.55μ reported in the spectrum of D$_2$S is actually due to the presence of a little CD$_4$[9] in our cell. This CD$_4$ was undoubtedly due to traces of Al$_4$C$_3$ occurring as an impurity in the Al$_2$S$_3$ which we used in preparing the D$_2$S. This 4.55μ region overlapping with the 3.8μ H$_2$S region gave the impression in our prism curve that there was a band at 4.1μ. Upon examination of this region with our grating instrument it became evident that there actually was no HDS band there. The 9.0μ band has been carefully measured, and the 3.8μ–3.9μ band reported by Bailey, Thompson and Hale investigated.

The 9.0μ region

The band reported by us at 9.0μ has been observed under high dispersion and is reproduced in Fig. 1. The curve is plotted in deflections of
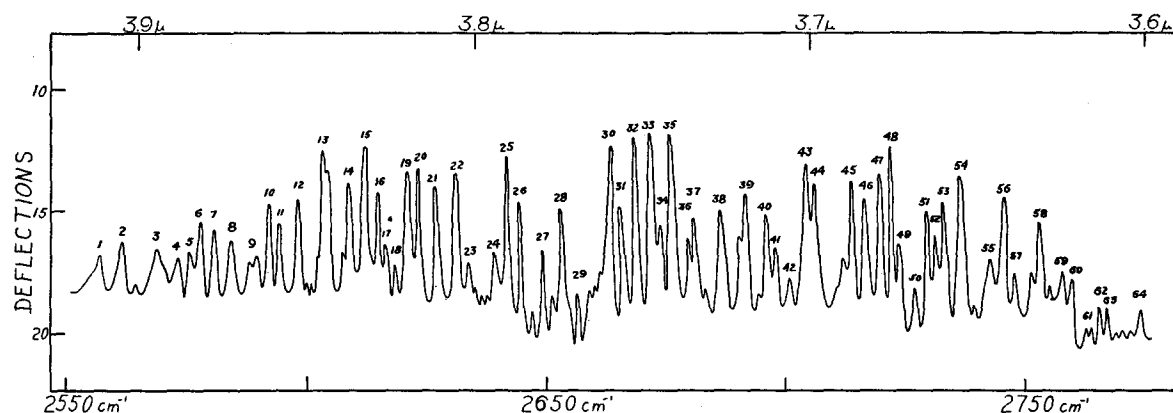
[11] Bailey, Thompson and Hale, J. Chem. Phys. 4, 625 (1936).

the galvanometer against a scale of frequencies in cm^{-1} and wave-lengths in μ. The deflections were read at intervals of 0.70 cm^{-1} with the spectrometer slits set to include a spectral interval of 0.8 cm^{-1}.

As may be seen from Fig. 1, the band is quite well resolved and shows a series of evenly spaced groups of lines, the average spacing of which is 6.85 cm^{-1}. This band contains no line or group of lines that can definitely be pointed to as a probable Q branch. Table I gives the frequency positions of the principal lines to which perfectly arbitrary numbers have been assigned. The center of this band we estimate to be at about 1090 cm^{-1}. A careful search was made to verify the strong line reported by Bailey, Thompson and Hale at 988 cm^{-1}, but it was not found. A fairly intense line was, however, located at 995 cm^{-1} which we have almost certainly identified as the Q branch of the low frequency fundamental of the CD$_4$ spectrum which occurs at exactly this point. We suggest that the line reported by the above authors at 988 cm^{-1} is probably the same one that we have found.

TABLE I. *Frequency positions of the lines in the HDS band at 9.0μ.*

Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}	Line No.	Frequency in cm^{-1}
1	1030.8	11	1068.0	21	1102.6	31	1147.1
2	1034.8	12	1071.7	22	1108.4	32	1152.0
3	1042.2	13	1074.3	23	1113.7	33	1156.2
4	1048.2	14	1076.6	24	1115.5	34	1160.9
5	1051.6	15	1080.4	25	1122.3	35	1169.4
6	1055.5	16	1084.0	26	1124.2	36	1174.9
7	1058.3	17	1087.0	27	1125.6	37	1178.1
8	1059.9	18	1090.4	28	1130.0	38	1182.9
9	1063.7	19	1093.7	29	1135.5	39	1186.2
10	1066.4	20	1096.6	30	1138.8	40	1191.8

FIG. 2. The absorption band at 3.75μ in D_2S.

The 3.8μ region

This region, reported by Bailey, Thompson and Hale, we have carefully explored but we are unable to detect any absorption here by HDS although the lines of H_2S were observed. This would seem to indicate that this band is very faint since the gas we used was, as related above, a mixture of about 25 percent H_2S, 25 percent D_2S and 50 percent HDS.

D_2S

In our preliminary report we gave positions of bands in D_2S at 3.75μ, 4.55μ and 10.7μ. The 4.55μ band which we originally thought must correspond to the 3.8μ band in H_2S is, as we

TABLE II. *Frequency positions of the lines in the 3.75μ band of D_2S.*

Line No.	ν cm⁻¹	Line No.	ν cm⁻¹	Line No.	ν cm⁻¹
1	2559.3	22	2631.4	43	2704.4
2	2561.9	23	2634.1	44	2705.8
3	2568.8	24	2639.1	45	2713.6
4	2573.1	25	2641.9	46	2716.5
5	2575.3	26	2644.2	47	2719.9
6	2577.9	27	2649.2	48	2721.8
7	2581.0	28	2652.9	49	2723.8
8	2584.5	29	2656.6	50	2727.2
9	2589.8	30	· 2663.1	51	2729.4
10	2592.4	31	2665.5	52	2731.1
11	2594.2	32	2668.3	53	2732.6
12	2698.1	33	2671.6	54	2736.6
13	2603.0	34	2673.9	55	2743.0
14	2608.8	35	2675.8	56	2745.5
15	2612.4	36	2679.6	57	2748.0
16	2615.1	37	2681.0	58	2752.9
17	2616.4	38	2686.7	59	2756.9
18	2618.7	39	2691.4	· 60	2760.0
19	2621.4	40	2696.0	61	2763.0
20	2623.2	41	2697.2	62	2765.5
21	2626.8	42	2701.0	63	2767.0
				64	2774.6

have already indicated, not due to D_2S but to the presence of a small quantity of CD_4 in our cell. Instead, Bailey, Thompson and Hale report a band at 1940 cm⁻¹. This band and the two others reported by us have been studied using a grating spectrometer.
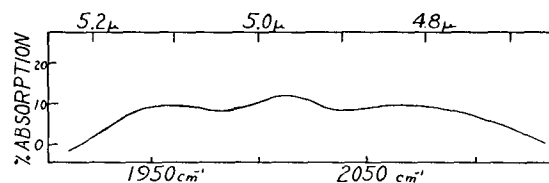
The 3.75μ region

The shortest wave-length band observed in D_2S lies at 3.75μ and is shown in Fig. 2. The spectral region in which this band lies is quite free from atmospheric bands and galvanometer deflections were therefore plotted against a scale of frequencies in cm⁻¹, and wave-lengths in μ. The deflections were read at intervals of 0.90 cm⁻¹ and the slit width included 0.70 cm⁻¹.

This band, the center of which appears to be about 2685 cm⁻¹, undoubtedly corresponds to the 2.6μ band in H_2S which, it will be recalled, has a somewhat broadened but unresolved Q branch. The band in D_2S also clearly shows a Q branch, but it is much broader than the one in the H_2S band and is seen to be partially resolved into a number of closely spaced components. The lines in the P and R branches are, of course, complex but a fairly uniform spacing taken between the centers of these groups is discernible and averaged over the band takes the value of 5.0 cm⁻¹.
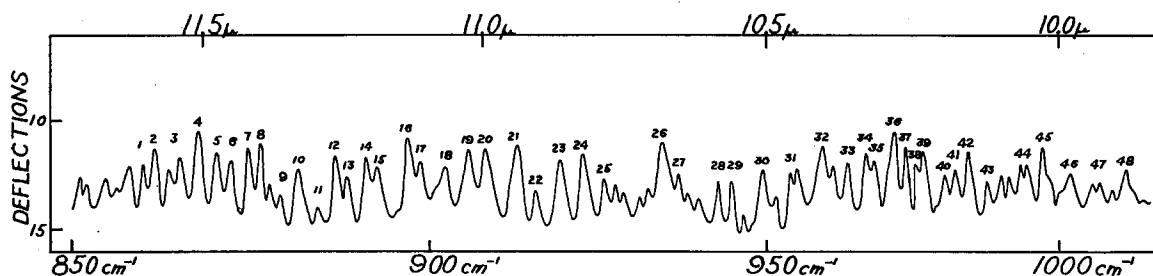

FIG. 3. Envelope of 5.0μ absorption band in D_2S.

FIG. 4. The 10.7μ vibration-rotation band of D$_2$S in absorption.

Table II gives the frequency positions of 64 of the principal lines.

The 5.0μ region

This band, the center of which is given by Bailey, Thompson and Hale as 1940 cm^{-1} has been measured by us and an envelope of the band is shown in Fig. 3. The band, as suggested by these authors, undoubtedly corresponds to the 3.8μ band in H$_2$S. It occurs with fairly low intensity and already in this region there occur lines belonging to the 6.2μ water vapor band which are more intense than any lines in the D$_2$S band. These intense lines, we feel, are apt to have injected serious falsifications into the fine structure pattern and rendered it somewhat questionable in several places. For this reason we have not reproduced this fine structure but give only the envelope of the absorption region as is obtained when the spectrometer slits are widened. As may be seen, this envelope in general takes the shape predicted by Gerhard and Dennison for a perpendicular band of a molecule where $\beta = -\frac{1}{2}$.[12] As far as we have been able to discern there occurs no Q branch whatever in this region. The center of the band appears, from our measurements, to lie near 2000 cm^{-1} and in our fine structure pattern we were able to pick out many quite regular spacings of the order of 5.0 cm^{-1}.

The 10.7μ region

Fig. 4 shows the curve obtained for the D$_2$S band at 10.7μ. This band corresponds to the 8.0μ band of H$_2$S which was recently remeasured by Sprague and Nielsen and interpreted by them as one having a Q branch. The appearance of this band is quite similar to that of the corresponding H$_2$S band, in that it also contains a rather in-

[12] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

tense group of lines near the center which we are inclined to interpret as a diffuse and ill-defined Q branch. The rest of the band contains partially resolved multiplets which are fairly uniformly spaced with a $\Delta\nu$ of about 4.8 cm^{-1}.

Deflections were read at intervals of 0.50 cm^{-1} and the spectrometer slits were set to include a spectral region of 0.60 cm^{-1}. Since there was no atmospheric absorption in this region the curve was plotted in galvanometer deflections against a frequency scale in cm^{-1} and a wave-length scale in μ. Table III gives the frequency positions of 48 of the most intense lines in the band. As we have already pointed out, line 45 somewhat more intense than others nearby is almost certainly due to the Q branch of the long wave CD$_4$ band. The relative intensities of the other lines in the CD$_4$ band are much too small when compared with the Q branch, however, to contribute anything to the absorption pattern given in Fig. 4.

Interpretation of the observed data

The rotational analysis carried out by Cross on the band measured by him in the photographic infrared has enabled him to assign to the moments of inertia these values $I = 2.667 \times 10^{-40}$ gcm^2, $I = 3.076 \times 10^{-40}$ gcm^2 and $I = 5.845 \times 10^{-40}$

TABLE III. *Frequencies of the lines in the 10.8μ band in D$_2$S.*

Line No.	ν cm^{-1}	Line No.	ν cm^{-1}	Line No.	ν cm^{-1}	Line No.	ν cm^{-1}
1	860.4	13	888.5	25	925.8	37	973.7
2	862.3	14	890.7	26	934.7	38	975.5
3	866.0	15	893.3	27	937.7	39	977.0
4	868.1	16	896.7	28	942.6	40	980.2
5	870.7	17	898.8	29	944.9	41	981.9
6	872.7	18	902.5	30	950.2	42	984.7
7	875.0	19	905.7	31	954.6	43	988.0
8	876.5	20	908.1	32	959.8	44	991.9
9	879.4	21	912.6	33	964.0	45	997.0
10	881.4	22	915.7	34	967.2	46	1000.4
11	884.6	23	919.3	35	968.8	47	1006.2
12	886.9	24	922.9	36	972.1		

gcm^2. Assuming these values to be correct the H_2S molecule may be approximated by a symmetric model where two of the moments of inertia, say A and B, are alike and set equal to $\frac{1}{2}(I_A + I_B)$ and where the third moment of inertia $C = A + B$. In such an idealized model all three vibration frequencies ν_1, ν_2 and ν_3 would be perpendicular bands of identical appearance. They would consist of lines separated from each other by an interval $\Delta\nu = (h/8\pi^2 A)$. In the actual case where I_A is only approximately equal to I_B this must also be essentially true except that the lines will split up into components certain of which will crowd toward the center of the band when the oscillation is along I_A giving the effect of a diffuse and a partly resolved Q branch; but these components will spread away from the center, leaving it bare, when the oscillation is along I_B. The spacings between what are now groups of closely spaced line components must, however, be very nearly the same in both types of vibration band. In fact, making use of the above values of I_A, I_B and I_C as computed by Cross to calculate what might be expected as the spacings between such line groups one finds a value in good agreement with those observed in the bolometric infrared bands. This has been interpreted by Sprague and Nielsen as confirmatory evidence that the values for I_A, I_B and I_C by Cross are at least of the right order of magnitude.

As indicated in the introduction two models of the H_2S molecule are possible, an obtuse model of vertex angle 92° 20' and an acute model of vertex angle 85° which will satisfy the above values of the moments of inertia. Between these Cross was unable definitely to decide, but influenced by calculations made by himself and Van Vleck and by chemical evidence which definitely favors the obtuse model, he suggested the 92° 20' vertex angle. The frequency 3970 cm^{-1} according to Nielsen and Barker and the frequencies 9911 cm^{-1} and 10,100 cm^{-1} according to Cross are all bands having Q branches and in conformity with his model are identified by Cross, respectively, as $\nu_2 + \nu_3$, $3\nu_1 + \nu_3$ and $3\nu_3 + \nu_1$. This identification, it should be pointed out, gives no real verification for the obtuse model since on the basis of an acute model they might equally well be given the identification $\nu_1 + \nu_2$,

$2\nu_1 + 2\nu_3$ and $2\nu_2 + 3\nu_1$ as suggested by Sprague and Nielsen.

From a vibrational analysis of the bands reported in the spectra of H_2S, HDS and D_2S, Bailey, Thompson and Hale have arrived at a model for this molecule when the vertex angle is 110° a model in sympathy with evidence to be had from chemical sources. As we anticipated in the introduction, these bands alone do not suffice without further assumption to fix the shape of the molecule. This is especially true since from this work no knowledge is to be had concerning the rotational structure of the bands and hence in many cases their identification must have been made arbitrarily. Such a model would, moreover, be inconsistent with the rotational structure of the H_2S bands. For such a model as this nearly all semblance of regularity in rotational structure would have disappeared, certainly the spacings between line groups for the two types of bands could no longer be expected to be of the same magnitude. We are therefore inclined to feel that their value can hardly be regarded as numerically correct, but must be considered as giving only the order of magnitude of the angle.

As we have seen, however, by correctly identifying one of the fundamental bands and deciding upon the character of its rotational structure, we have a means of differentiating between the two models. Now the frequency at 1290 cm^{-1} in H_2S which must almost certainly be identified as ν_2 contains near the center a group of lines suggestive of the diffuse and ill-defined Q branch one might expect in a vibration along the axis of smallest moment of inertia. This fact has led Sprague and Nielsen to suggest that the correct model of the H_2S molecule is probably that where the vertex angle is 85°. Their view in this is supported by the fact that the region near 3.8μ does not resemble that at 8.0μ except insofar that the spacings between lines or line groups are the same. There is no evidence whatever of any piling together at the center of lines tending to form a Q branch; in fact this region resembles a perpendicular band in the spectrum of a symmetric molecule very much. They have, therefore, taken it to be ν_3, a vibration on the basis of their model along the intermediate moment of inertia. These same arguments are

valid in the case of D_2S. By analogy we should identify the frequency 934 cm^{-1} as ν_2 and the frequency 2000 cm^{-1} as ν_3. All the vibrations are in the plane of the molecule and if ν_2, as appears to be the case, has a Q branch it must be due to an oscillation of the electric moment along the axis of the smallest moment of inertia. Since, however, ν_2 is also an oscillation parallel to the symmetry axis of the molecule this must then be identified as the axis of the smallest moment of inertia. This condition would require the adoption of the acute model. In addition ν_3 does not appear to have a Q branch and it would therefore have to arise from an oscillation parallel to the axis of the intermediate moment of inertia. Since ν_3 is a vibration normal to the symmetry axis, the intermediate axis of inertia becomes identified with the normal to the bisector of the vertex angle.

The vibration ν_2 of the hybrid molecule HDS, which undoubtedly is the band lying near 9.0μ and the only one for which the rotational structure has been determined will have components of the electric moment lying along the axes of the smallest and the intermediate moment of inertia. Its appearance might therefore be expected to resemble a superposition of two bands, although not necessarily of the same intensity, one of ν_3 and another of the type ν_2 in the molecules H_2S and D_2S. The spacing between lines in these two types of superimposed bands should, on the assumption that H_2S, D_2S and HDS molecules are all nearly symmetric tops, however, still be nearly the same and one might well expect some regularity of spacing of the rotational lines as is here also apparent. It does not seem unreasonable, moreover, that any Q branch which one might anticipate finding here might very well be obscured because the band effectively may be resolved into two superimposed oscillations, respectively along two axes normal to each other.

Another kind of evidence favoring the acute H_2S molecule is obtained by noting that the Q branch in the band observed in the spectrum of D_2S at 3.8μ is much broader and more resolved than the Q branch in the corresponding band in the H_2S spectrum found at 2.7μ, a fact which one would interpret to mean that the parameter ρ defined by Dennison as the ratio of the smallest to the intermediate moment of inertia, is more nearly unity for D_2S than for H_2S. It is now a simple calculation to show that in order for this ratio to increase when the hydrogen atoms in the hydrogen sulfide molecule are replaced by deuterium atoms, the vertex angle must be less than $88° 16'$. This argument is cited because it is entirely independent of any identification of the observed bands in terms of the normal vibrations of the molecule.

If for the moment of inertia of the H_2S molecule we take the values suggested by Sprague and Nielsen (which are virtually the same as those given by Cross) it is possible to compute the values of these also for HDS and D_2S. This we have done on the basis of a model with vertex angle $92° 20'$ and one with vertex angle $85° 20'$. For the two cases, the values obtained are the following: for HDS $I_A = 3.9 \times 10^{-40}$ gcm$^2 \cdot I_B = 4.6 \times 10^{-40}$ gcm^2 and $I_C = 8.5 \times 10^{-40}$ gcm and $I_A = 4.0 \times 10^{-40}$ gcm^2, 4.4×10^{-40} gcm^2 and 8.4×10^{-40} gcm^2; for D_2S: $I_A = 5.18 \times 10^{-40}$ gcm^2; 6.2×10^{-40} gcm and 11.4×10^{-40} gcm^2 and $I_A = 5.4 \times 10^{-40}$ gcm^2; 5.7×10^{-40} gcm^2 and 11.1×10^{-40} gcm^2. Assuming that the values I_A and I_B are nearly enough alike so that we may approximate the rotational motion of the H_2S molecule by that of a symmetric rotator, we may calculate what the spacing between lines might be expected to be. The predicted values are compared with the actual experimental values in Table IV when also our identifications of the observed bands are given:

The conclusions to be derived from these data may briefly be summarized by stating that the rotational structure of the bands seems to indicate moments of inertia satisfied by one of the two models for the H_2S molecule when the vertex angles are $92° 20'$ and $85° 20'$. We are inclined to feel that the evidence is in favor of the latter model but the ultimate decision between the two can only be made after a complete rotational analysis of the bands has been carried out.

TABLE IV.

	H_2S	HDS	D_2S
ν_1	2615 cm^{-1}	---	---
ν_2	1250 cm^{-1}	1090 cm^{-1}	934 cm^{-1}
ν_3	2685 cm^{-1}	---	2000 cm^{-1}
$\nu_1 + \nu_2$ (85° model)	3790 cm^{-1}	---	2685 cm^{-1}
$\nu_3 + \nu_2$ (92° model)			
Calculated spacings	9.5 cm^{-1}	6.7 cm^{-1}	4.9 cm^{-1}
Experimental "	9.0 cm^{-1}; 10 cm^{-1}	6.9 cm^{-1}	4.8 cm^{-1}; 5.0 cm^{-1}