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The Infrared Absorption by Hydrogen Sulfide

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Two of the bands in the spectrum of H_2S identified as ν_3 and ν_2 have been remeasured under high dispersion. The center of the band identified as ν_3 is found to be 2685 cm^{-1} and is a type of band showing no single Q branch at the center and is therefore ascribed to an oscillation of the electric movement along the axis of the intermediate moment of inertia. The fundamental ν_2 has been remeasured with two different gratings of different resolving power. It has been found to be of the type displaying a

broad and partially resolved Q branch at the center and is henceforth identified with an oscillation of the electric moment along the axis of smallest moment of inertia. An estimate of the values of the moments of inertia has been made and these are found to agree well with those given by Cross, but the data here presented is interpreted as evidence for a model where the vertex angle is 85° rather than 92° as given by Cross.

I. INTRODUCTION

THE absorption in the infrared by the hydrogen sulfide molecule, presumably a non-linear triatomic molecule similar to water vapor, has been studied by a number of investigators.¹ Absorption bands, enumerated in the order of their intensities, have been located at approximately the following frequency positions: 1260 cm^{-1} , 3795 cm^{-1} , 2685 cm^{-1} , 9911 cm^{-1} , $10,100\text{ cm}^{-1}$, and 2615 cm^{-1} . All of these except the last, which has been found only in the Raman spectrum, have been measured under high dispersion and have been given the following identification, using Dennison's notation:² ν_2 , $\nu_2 + \nu_3$, ν_3 , $3\nu_1 + \nu_3$, $3\nu_3 + \nu_1$ and ν_1 , where the frequency ν_3 is perpendicular to the bisector of the apex angle and where ν_1 and ν_2 are along it. In general the frequencies ν_1 and ν_3 take values relatively high

compared with ν_2 . From an analysis of the rotational structure of the high frequency combination bands at 9911 and $10,100\text{ cm}^{-1}$ Cross has arrived at certain values of the moments of inertia and has inferred that the vertex angle must be slightly in excess of 92° . This would mean that ν_3 would lie along the axis of least moment of inertia while ν_1 and ν_2 would lie along the axis of the intermediate moment of inertia. According to the charts prepared by Dennison on the appearance of infrared bands of asymmetrical type molecules, ν_3 should then present a rotational structure containing a rather broad Q branch while ν_1 and ν_2 should be expected to display an absence of such a Q branch. The band taken to be the fundamental ν_3 is one of the bands measured by Nielsen and Barker and does not appear to give evidence of any Q branch whatever. It has been suggested that this band must have another half which might lie to higher or to lower frequencies. This belief was somewhat further strengthened by the measurements made by Rollefson on the band near 8.0μ interpreted as

¹ A. H. Rollefson, Phys. Rev. **34**, 604 (1929); W. Mischke, Zeits. f. Physik **67**, 106 (1931); H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931); H. H. Nielsen and A. D. Sprague, Phys. Rev. **37**, 1183 (1931); P. C. Cross, Phys. Rev. **47**, 7 (1935).

² D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

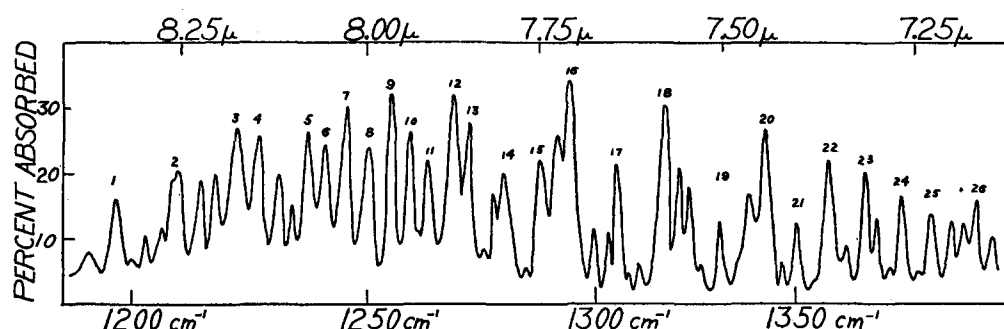


FIG. 1.

ν_2 and which gave evidence of a minimum near the center. It has therefore seemed important to remeasure these two absorption regions and in the 3.7μ region to extend the measurements well beyond the limits at both ends of the region as shown in the work of Nielsen and Barker. This has been the purpose of this investigation.

II. EXPERIMENTAL WORK

The hydrogen sulfide gas used in making these measurements was obtained in tanks from the Ohio Chemical and Manufacturing Company in Cleveland. To insure that the gas was free from water vapor and carbon dioxide the gas was collected in a trap surrounded by liquid air and then fractionally distilled into the evacuated absorption cell. For both regions the same cell was used. It was made from a glass tube five centimeters in diameter and thirty centimeters long closed at the ends by windows of polished rocksalt.

For making the measurements a spectrometer of the usual design was available. Three echellette gratings ruled by R. W. Wood were used, one with 3600 lines per inch for the 3.7μ region and two others with 800 lines per inch and 2000 lines per inch for the region near 8.0μ . It was found feasible in each case to use slit widths equivalent to a spectral breadth of about 0.5 cm^{-1} and deflections were taken along the circle at these intervals.

III. EXPERIMENTAL RESULTS. THE 3.7μ REGION

This is one of the two regions originally mapped by Nielsen and Barker. This region has here been carefully remeasured from 3.57μ to 3.83μ and these measurements extend beyond the

region measured by Nielsen and Barker at each end by about 50 cm^{-1} . In none of the sets of data taken could anything be found in addition to that shown in the original work by these authors. Bailey, Thompson and Hale, in a recent article³ have reported an absorption maximum at a slightly shorter wave-length than this and have suggested that the -7 line reported in Nielsen and Barker's work is to be interpreted to be a weak Q branch. This view we can definitely not ascribe to since then what we have observed must be only one branch. As we have already pointed out we can find no evidence of any other half of this band and what further absorption that may be found on either side of what we have measured is certainly far less intense and can hardly be identified as another branch. Moreover it would seem extremely difficult to account for a Q branch having a relative intensity as small as that of line -7 reported by Nielsen and Barker. Moreover no evidence of the frequency 2615

TABLE I. The 8.0μ region under low dispersion. Wave numbers and wave-lengths.

LINE NO.	FREQUENCIES IN CM^{-1}	LINE NO.	FREQUENCIES IN CM^{-1}
1	1196.8	14	79.6
2	1209.6	15	87.5
3	21.1	16	93.8
4	26.3	17	1304.5
5	35.9	18	16.8
6	40.3	19	30.4
7	44.2	20	41.2
8	48.7	21	48.5
9	54.1	22	56.4
10	58.2	23	66.0
11	62.3	24	74.6
12	67.8	25	82.3
13	71.1	26	94.5

³ C. R. Bailey, J. W. Thompson and J. B. Hale. J. Chem. Phys. 4, 625 (1936).

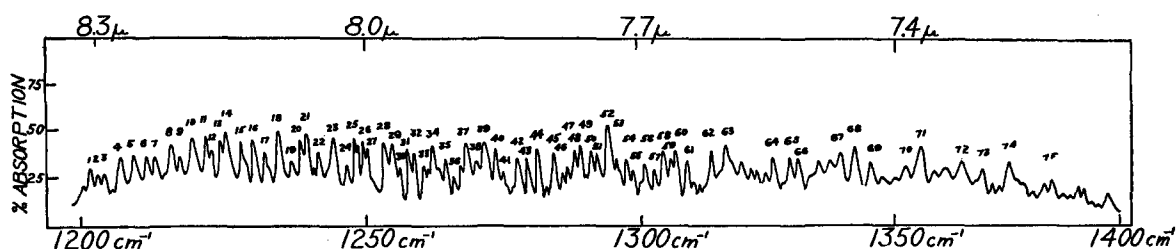


FIG. 2.

cm^{-1} was to be found. The band appears then to have its center at about 2685 cm^{-1} instead of 2630 cm^{-1} and in our opinion very definitely does not show a Q branch. This band must therefore be ascribed to an oscillation of the electric moment along the axis of the intermediate moment of inertia. These measurements are not shown graphically since they repeat almost exactly those given in the work of Nielsen and Barker; neither has any tabulation of frequency and wave-length positions of the lines been included, these also being in excellent agreement with the values given by them.

THE 8.0μ REGION

This band, originally reported by Rollefson, has here been remeasured under two different dispersions, one about equivalent to that available to Rollefson and one approximately three times as large. Under the lower dispersion the lines found in general agree well with the positions of lines reported by Rollefson, although in many cases the intensities of these are quite different. In fact, the appearance of the band is an entirely different one, in the present case there being no evidence of any minimum near the center, but rather the opposite.⁴ At what appears to be the center of the band there occurs a broad line of appreciably greater intensity than any of its neighbors. The average spacing between principal lines seems to be about 10 cm^{-1} , very

nearly that found between lines in the band at 2.7μ by Nielsen and Barker and by Cross at $10,100 \text{ cm}^{-1}$ between lines arising from his $J_J \rightarrow J_J + 1$ transitions. This spacing appears to be about ten percent larger than the spacing between lines at 3.7μ . The absorption pattern delineating those characteristics that repeated in the many runs made are shown in Fig. 1 and the frequencies of the principal lines measured under low dispersion are set down in Table I. It was found necessary to guard against falsification by water vapor in the atmosphere. This was accomplished by taking readings with the cell containing the gas in the beam, then with the evacuated cell in the beam, and comparing. Also as a further check, the deflections obtained with the evacuated cell in the beam were plotted underneath the percentage absorption curve to see that there was no consistent agreement between the absorption peaks apparently due to gas and the absorption peaks due to the atmosphere. The impression which this band leaves with us is that it resembles the band measured by Nielsen and Barker at 2.7μ in its rotational characteristics and also those reported by Cross much more than it resembles the band at 3.7μ . As its center we have chosen 1290 cm^{-1} , the position of the most intense of the lines in the band which we believe to be a Q branch.

When this region is examined using the grating ruled with 2000 lines per inch a great many new details in the absorption pattern become discernible. The absorption pattern, which has consistently repeated itself in the smallest details, is shown in Fig. 2. At a glance the two curves, Fig. 1 and Fig. 2, appear quite dissimilar but upon careful comparison of the one to the other, the general features of the two will be seen to be the same. Some uncertainty concerning the positions of some of the lines on the high fre-

⁴ In the work by Nielsen and Barker mention was made of the fact that in a set of preliminary grating measurements made by Professor Barker on this region an absorption pattern was obtained, but in subsequent trials nothing was to be found. The above measurements have been compared with the aforementioned run and the two have been found to agree almost exactly with each other. The fact that nothing was to be found in the subsequent runs referred to in this earlier work can be interpreted only as meaning that the monochromator preceding the spectrometer was out of proper adjustment while these measurements were made.

quency side must be allowed, due again to falsification by atmospheric water vapor lines. This falsification is much more difficult to compensate for here than when the dispersion is lower. Table II lists the frequency and wave-length positions of the most important peaks in the band.

Also here the most intense part of the band is at 1290 cm^{-1} and more even than before does this line appear to be a broad and partly resolved Q branch. We shall therefore interpret this band as arising from a vibration along the axis of least moment of inertia.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

The evidence obtained by these measurements seems to indicate that some modification of the model suggested by Cross, which has as the axis of least moment of inertia a line normal to the bisector of the apex angle, is necessary. There can be little doubt concerning the identification of the vibration frequency 1290 cm^{-1} as ν_2 since this frequency must be a relatively small one. Since, however, this band shows a Q branch, ν_2 must be a vibration along the axis of least moment of inertia, a condition which can be fulfilled only provided the apex angle be less than $88^\circ 16'$. Moreover for the frequency 2685 cm^{-1} , which in our opinion definitely shows no Q branch, to be ν_3 it must be required to be a vibration along the axis of the intermediate moment of inertia. This again indicates an apex angle of less than $88^\circ 16'$.

It is now necessary to reexamine the identification of the other bands known to exist in the infrared spectrum of hydrogen sulfide. The frequency of any band will in general be given by the relation $\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3$ where, according to Dennison, when n_3 is odd the electric moment will be induced in a direction normal to the bisector of the apex angle, but will be along the bisector when n_3 is even. On the basis of such a model as we propose, namely one for which the vertex angle is less than $88^\circ 16'$, and taking the Raman line 2615 cm^{-1} as ν_1 , 1290 cm^{-1} as ν_2 and 2685 cm^{-1} as ν_3 it is evident that the band centered at 3790 cm^{-1} and showing a Q branch can no longer be $\nu_2 + \nu_3$, as suggested by Mecke,⁵ and Cross, since with $n_3 = 1$, an odd integer, the

vibration would be along the axis of the intermediate moment of inertia. It would then show no Q branch. This band might, however, be set equal to $\nu_1 + \nu_2$. Likewise the frequencies 9911 cm^{-1} and $10,100\text{ cm}^{-1}$ are of the type in which Q branches occur and on the basis of our proposed model they must be redefined. We suggest that they may be set equal to $2\nu_3 + 2\nu_1$, and $2\nu_2 + 3\nu_1$, say, rather than to $\nu_3 + 3\nu_1$, and $3\nu_3 + \nu_1$ as suggested by Cross. In fact these values agree a little better numerically, especially since ν_3 must be taken to be 2685 cm^{-1} rather than 2630 cm^{-1} . In Table III is summarized the manner in which we have identified the observed bands.

It would be of interest if the actual value of the apex angle of the molecule could be computed. This could of course be accomplished if the

TABLE II. The 8.0μ region under high dispersion. Wave numbers and wave-lengths.

LINE NO.	FREQUENCIES IN cm^{-1}	LINE NO.	FREQUENCIES IN cm^{-1}
1	1203.9	39	1270.3
2	04.7	40	71.9
3	05.7	41	73.3
4	08.1	42	76.1
5	10.3	43	78.1
6	12.3	44	79.9
7	13.3	45	81.2
8	16.1	46	84.3
9	17.6	47	85.4
10	19.9	48	86.6
11	21.9	49	87.5
12	23.0	50	90.0
13	24.3	51	91.1
14	25.3	52	93.4
15	27.6	53	94.4
16	29.4	54	96.7
17	32.1	55	97.8
18	34.4	56	99.8
19	36.4	57	1302.1
20	38.2	58	03.6
21	38.9	59	05.0
22	41.0	60	05.9
23	43.2	61	08.2
24	45.9	62	12.6
25	47.1	63	15.5
26	48.4	64	23.8*
27	49.3	65	27.6
28	52.5	66	30.2
29	53.7	67	39.6
30	54.7	68	41.4
31	55.7	69	43.9
32	57.0	70	52.6
33	59.0	71	55.5
34	60.9	72	64.6
35	63.2	73	69.1
36	64.4	74	74.2
37	67.0	75	83.3
38	68.5		

* From this point on, intense atmospheric water vapor absorption peaks occur from time to time and for this reason the positions of the absorption lines due to H_2S as given may indeed be slightly in error.

⁵ R. Mecke, Zeits. f. physik. Chemie **16**, 431 (1932).

TABLE III. Identification of observed bands.

COMBINATION	FREQUENCY IN CM ⁻¹	COMBINATION	FREQUENCY IN CM ⁻¹
ν_1	2615 cm ⁻¹	$\nu_1 + \nu_2$	3970 cm ⁻¹
ν_2	1290	$2\nu_3 + 2\nu_1$	9911
ν_3	2685	$2\nu_2 + 3\nu_1$	10100

correct values of the moments of inertia could be determined. The values I_A , I_B , and I_C as determined by Cross from his analysis of the two high frequency combination bands seem very convincing indeed, also in the light of our data even though no exact rotational analysis has been made. This may be seen in the following manner. Two quite different types of bands have been observed, namely that at 3.7μ and the other to which we believe those at 2.7μ and 8.0μ belong. The separation between the lines is, however, nearly the same in both types, about 9.0 cm^{-1} and 10 cm^{-1} , respectively. If we approximate the hydrogen sulfide molecule by a rotator where the moments of inertia are $A=B=C/2$ we should expect to find all the bands in the spectrum to be of the perpendicular type with the spacings between their lines identical. From Dennison's charts, however, it is seen that for a vibration along A there will develop a crowding together toward the center of the component lines in the band to form a Q branch as A is made less than B . Moreover, for an oscillation along B quite the opposite effect is to be observed as A is decreased with respect to B . Now clearly the value of Dennison's parameter of asymmetry ρ defined as A/B cannot be much less than 0.9 since at least under not too high dispersion some semblance of regularity in the rotational structure is maintained. Approximating the hydrogen sulfide molecule then by a symmetric rotator where $A'=B'=1/[(A+B)/2]$ and $C'=2A'$ and remembering that prominent lines (i.e., the Q branches of the component bands of the perpendicular band) will arise from transitions of the type $\Delta J=0$, $\Delta K=\pm 1$ we obtain as the spacing between any two lines $\Delta\nu = h/[4\pi^2(A+B)]$. Taking as the value for $\Delta\nu$ the average spacing in the two types of observed bands and letting $A=0.9B$ we obtain

$A=2.7\times 10^{-40}\text{ g cm}^2$, $B=3.1\times 10^{-40}\text{ g cm}^2$ and $C=5.8\times 10^{-40}\text{ g cm}^2$, in good agreement with the values $I_A=2.667\times 10^{-40}\text{ g cm}^2$, $I_B=3.076\times 10^{-40}\text{ g cm}^2$, and $I_C=5.845\times 10^{-40}\text{ g cm}^2$ given by Cross. These values for the moments of inertia, when the axis of the smallest moment of inertia is taken along the bisector of the apex angle, lead to a value for the apex angle of about 85° .^{6, 7}

It is interesting to compare the fundamental bands here observed with the fundamentals observed in the spectrum of water vapor. In the water vapor molecule where the vertex angle appears to be about 104° the axis of smallest moment of inertia is normal to the bisector of the apex angle. The low frequency of vibration ν_2 along the bisector of the vertex angle has here been identified as the observed frequency 1595 cm^{-1} and its position in the spectrum as well as its rotational character is consistent with such an identification. The frequency ν_3 , a high frequency vibration normal to the bisector of the apex angle, has been taken as the observed frequency 3756 cm^{-1} , and also its position in the spectrum and its rotational character are in agreement with such an identification. This leaves the Raman frequency 3604 cm^{-1} to be taken as ν_1 . Hence the observed fundamentals found in the spectrum of hydrogen sulfide are entirely analogous to those found in the spectrum of water vapor.

⁶ Further evidence in support of such a model will be produced by A. H. Nielsen and H. H. Nielsen in an article soon to appear dealing with the spectrum of D₂S and HDS.

⁷ The value of the vertex angle of 110° given by Bailey, Thompson and Hale as determined from their work seems to us as hardly compatible with the evidence gained from a study of the rotational structure of these bands. Quite aside from the question of whether the molecule is an obtuse or an acute angle isosceles triangle, the ratio of the moments of inertia assumes an impossible value for such a model. Computing the value of the parameter ρ defined above from Bailey, Thompson and Hale's 110° model one obtains a value $\rho=0.45$ and that this is a value much too small is readily seen by an examination of the diagrams prepared by Dennison. These show that for one of the band types, for a value of $\rho=0.5$ the Q branches are already quite sharp and by far the most intense lines in the bands while in the other type of band a definite absence of lines at the center of the band is to be expected. This can hardly be said to be what is observed experimentally. Moreover, the regularity in the rotational structure observed in the H₂S bands at low dispersion and especially the fact that the spacings between lines is almost the same in both types of bands seems incoherent with a value of ρ much less than 0.9.