INFRARED ABSORPTION BANDS IN HYDROGEN SULPHIDE

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Abstract

Absorption spectrum of H_2S in the region from 1.0μ to 10.0μ.—The absorption spectrum of hydrogen sulphide in the infrared has been investigated with a prism spectrometer from 1.0μ to 10.0μ. Two regions of absorption, one at 2.6μ and another 3.7μ were located, both of which revealed fine structure when examined under high dispersion.

Structure of the 2.6μ absorption band of H_2S.—The band at 2.6μ was found to consist of P, Q, and R branches, the P and R branches being made up of somewhat irregularly spaced lines and the Q branch broadened unsymmetrically, sloping off more steeply toward lower frequencies. The separation between the most prominent lines in the P and R branches was found to be about 10 cm^{-1}. A slight convergence was observed toward higher frequencies.

Structure of the 3.7μ absorption band of H_2S.—The 3.7μ band was found to consist of but one branch, made up of several prominent lines with weaker satellites on either side. The average spacing between these is about 9.0 cm^{-1}, and no convergence was discernable.

Qualitative quantum mechanical discussion of structure of absorption bands of H_2S.—Only a qualitative discussion of the structure of the observed bands is given, based on the classical quantum mechanical solution of an asymmetric rotator due to Witmer. The band at 2.6μ is accounted for by a vibration of the electric moment along the least axis of inertia while the band at 3.7μ is shown to arise from a vibration along the intermediate axis. It is pointed out that the rigorous quantum mechanical solutions of asymmetric rotators confirm the conclusions drawn herein and in addition satisfactorily explain the broadening of the Q branch.

R ECENT quantum mechanical studies of asymmetric rotators[1] have emphasized the importance of investigating the vibration rotation spectra of molecules belonging to this class. The water-vapor absorption bands measured by W. W. Sleator[2] and again by Sleator and Phelps[3] are characteristic of this kind, and they have suggested that a study of the infrared spectrum of hydrogen sulphide might prove fruitful.

W. W. Coblentz[4] has mapped the spectrum of hydrogen sulphide in the region from 3μ to 12μ with a prism spectrometer. More recently A. H. Rollefsen[5] has published two bands in hydrogen suphide at 4.2μ and 8.0μ. In the present work an absorption cell forty centimeters long with mica windows was used, and the spectrum carefully remapped from 1.0μ to 10.0μ with a Wadsworth type prism spectrometer. It was, however, impossible to dupli-

[1] Kramers and Ittman, Zeits. f. Physik **53**, 553 (1929); Wang, Phys. Rev. **34**, 243 (1929); Klein, Zeits. f. Physik **58**, 730 (1929).

[2] Sleator, Astrophys. J. **48**, 125 (1918).

[3] Sleator and Phelps, Astrophys. J. **62**, 28 (1926).

[4] Coblentz, Pub. Carnegie Inst. No. 35, pp. 52 and 178.

[5] Rollefsen, Phys. Rev. **34**, 604 (1929).

cate any of the bands previously reported, but two other absorption maxima were located, lying at 2.6μ and 3.7μ. The prism curve of the absorption spectrum of hydrogen sulphide as determined in this investigation is shown in Fig. 1 A. The maximum near 4μ reported by Coblentz and Rollefsen was found in the first trial, but upon careful purification of the gas it disappeared and almost certainly is to be ascribed to carbon dioxide as an impurity. Likewise in another series of observations when a cell with rock salt windows was used, the band reported by Rollefsen at 8.0μ was found. In all other trials, mica windows were used and although this spectral region was carefully searched, the 8μ band could not be found. It appears that this band can not be due to the hydrogen sulphide molecule, for on all occasions before searching for it, the presence of the absorption maxima at 2.6μ and 3.7μ was first confirmed. It is suggested that the 8.0μ band may be characteristic of some substance formed by the interaction of hydrogen sulphide with the rock salt windows.
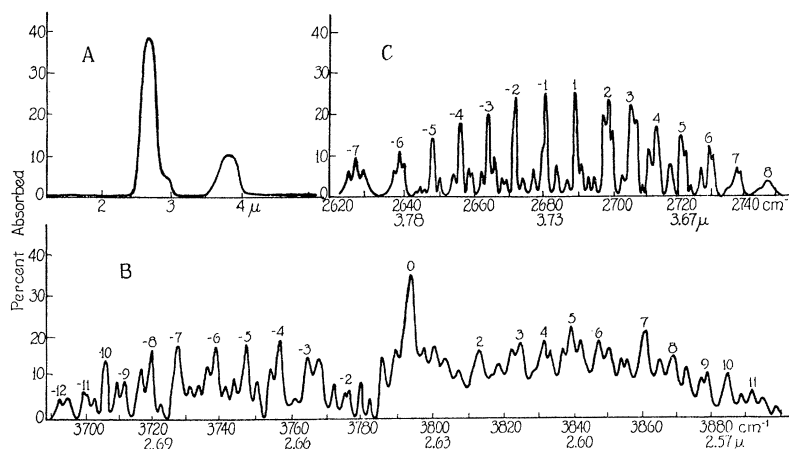

Fig. 1. Absorption bands in hydrogen sulphide. A, Prism curve with low dispersion. B, Fine structure in the band at 2.6μ. C, Fine structure in the band at 3.7μ.

A prism grating spectrometer designed by C. F. Meyer was available for further investigation of the hydrogen sulphide spectrum under high dispersion. The apparatus was equipped with a vacuum thermopile constructed by Meyer and was used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity galvanometer. This gave a sensitivity sufficiently high to make the use of slit widths of 16 angstrom units feasible. The grating used in both regions was one with a spacing of 7200 lines per inch (2834 lines per centimeter) ruled on a copper-nickel surface. The calibration of this grating was obtained from a table prepared by A. A. Levin for this spectrometer, based upon the positions of the -3 and -4 lines of hydrogen chloride determined by Colby, Meyer and Bronk.[6]

Two lengths of absorption cell were used, the H_2S being at atmospheric

[6] Colby, Meyer and Bronk, Astrophys. J. 57, 7 (1923).

pressure in each. For the band at 2.6μ, a length of ten centimeters was found most advantageous. This cell was double, one side being filled with dried air to compensate for the water-vapor absorption in the atmosphere. At 3.7μ a cell twenty five centimeters long was used. Compensating windows were not necessary here since the diminution of the energy due to the mica could satisfactorily be taken into account by making a preliminary run with the cell empty, and no atmospheric absorption occurs in this region.

The hydrogen sulphide gas was obtained in ordinary lecture bottles from the Matheson Company, their analysis showing a purity of 99.7 percent. In order to remove any carbon dioxide, carbon disulphide and hydrogen chloride,

TABLE I. *Wave numbers and intensities of lines in the band at 2.7 μ.*

Intensity	Wave No. (cm⁻¹)	Line No.	Intensity	Wave No. (cm⁻¹)	Line No.
2.0	3692.5	−12	6.5	3786.0	
2.0	3694.7		7.0	3789.5	
2.5	3700.0	−11	15.0	3793.9	0
2.0	3701.3		6.5	3797.7	
6.0	3706.5	−10	6.5	3800.5	
3.5	3709.6	− 9	6.0	3804.1	
3.5	3712.0		5.0	3808.2	
5.0	3716.6		7.0	3813.7	2
7.0	3720.1	− 8	5.0	3819.9	
1.0	3722.5		6.5	3822.9	
7.0	3728.0	− 7	7.5	3825.0	3
2.5	3731.8		7.5	3831.8	4
2.5	3733.4		6.5	3834.0	
5.0	3736.0		6.5	3837.7	
7.0	3737.6	− 6	8.0	3840.3	
3.0	3740.3		6.5	3843.6	
3.0	3743.1		6.5	3848.5	6
7.0	3746.6	− 5	6.4	3851.5	
3.0	3750.7		5.0	3855.6	
5.0	3754.0		5.0	3757.1	
8.0	3756.2	− 4	7.5	3861.2	7
1.0	3760.8		5.5	3866.1	
6.0	3764.5	− 3	6.0	3870.5	8
6.0	3768.0		5.0	3873.3	
3.0	3772.6		4.0	3878.5	
2.5	3775.1		4.5	3879.7	9
2.5	3776.9	− 2	4.5	3886.0	10
3.0	3780.1		2.0	3889.9	
2.0	3782.5		2.5	3892.5	11
			2.0	3895.8	

the gas was passed through three successive wash bottles each of which contained a solution of potassium hydrosulphide (KHS). After drying over phosphorus pentoxide, the gas was gathered by freezing with liquid air and finally purified by partial distillation. This was done immediately before each run.

The two absorption maxima which had been located prismatically, reveal fine structure when examined under high dispersion. They are distinctly different in type, but are both characterized by an irregularity of structure suggestive of water vapor bands. When only the most intense lines are considered however, the patterns resemble the bands due to certain symmetrical molecules.

The 2.6μ region. The 2.6μ band shows distinct *P*, *Q* and *R* branches, the *P* and *R* branches being made up of irregularly spaced lines. The average spacing for those of greatest intensity is about 10 cm^{-1}. Moreover, proceeding from the center outward it seems possible to identify the various lines in the *P* branch with corresponding lines in the *R* branch. A slight convergence is noticeable toward higher frequencies, and the *Q* branch is broadened unsymmetrically, sloping off more steeply toward lower frequencies. Curve B shows those details of this band which repeated themselves in the many sets of data taken. Original circle settings have been replaced for convenience by a scale of frequencies, and in Table I the frequencies and approximate relative intensities of the lines are given.

TABLE II. *Wave numbers and intensities of lines in the band at 3.7μ.*

Intensity	Wave No. (cm^{-1})	Line No.	Intensity	Wave No. (cm^{-1})	Line No.
2.5	2624.3		10.0	2690.1	1
3.5	2626.9	−7	2.0	2692.2	
2.5	2629.7		1.0	2693.3	
3.0	2636.5		1.0	2694.6	
5.0	2637.8	−6	8.8	2697.8	
3.5	2638.9		9.5	2698.7	2
.3	2642.6		8.0	2701.2	
.4	2643.7		1.5	2704.1	
.3	2645.2		9.0	2706.6	3
6.2	2647.8	−5	8.5	2707.0	
2.2	2650.2		.5	2709.8	
2.2	2654.4		5.0	2712.7	
7.5	2656.6	−4	7.5	2714.4	4
2.2	2658.6		3.5	2719.1	
2.1	2660.6		6.0	2721.9	5
2.1	2663.2		4.0	2722.8	
8.7	2665.1	−3	.5	2724.5	
2.5	2666.6		2.5	2727.0	
1.0	2669.5		5.0	2729.5	6
1.0	2670.9		3.0	2730.5	
10.0	2673.8	−2	.8	2737.7	
1.0	2675.6		3.0	2738.4	7
2.0	2679.4		2.0	2739.4	
10.0	2682.5	−1	.8	2743.3	
2.0	2684.9		2.0	2745.3	8
1.0	2687.8		.8	2746.7	

The 3.7μ region. The 3.7μ band is of the type which shows an envelope with but one maximum. It also has been resolved, at least partially, revealing a number of prominent lines, characterized in general by accompanying satellites of lesser intensity on either side. No apparent convergence is discernible and the most prominent lines are separated by an average spacing of about 9.0 cm^{-1}. Details repeating themselves in all sets of data are shown in curve C where as before a frequency scale replaces the original circle settings. Table II gives the frequencies and relative intensities of the lines measured in this region.

INTERPRETATION OF THE OBSERVED BANDS

It is hoped in a later communication to give a complete description of this spectrum in terms of the rigorous quantum mechanics of an asymmetrical

rotator model. At present, it seems better, however, to consider qualitatively only the general characteristics of the two observed bands.

A solution for the asymmetrical rotator by a perturbation method is given by E. E. Witmer[7] in the classical quantum mechanics where the perturbation function involves the third moment of inertia. Taking A, B, and C as the three principal moments of inertia where $A < B < C$, the energy levels are shown to be of two kinds, A-levels arising when the molecule rotates principally about the least axis of inertia, and C-levels, arising when the molecule rotates principally about the largest axis of inertia; their combined number being $J+1$. The energy values of A-levels are those of a symmetric rotator rotating about the A-axis plus a certain perturbation component to the energy involving C. The C-levels are similarly determined by the energy expression of a symmetric top rotating about the C-axis plus another perturbation component involving A.

Hund[8] and Dennison[9] have shown that isosceles triatomic molecules have three fundamental modes of vibration, two of which are along the bisector of the apex angle, and a third perpendicular to this. If the three absorption bands corresponding to these three vibrations can be observed, the dimensions of the triangle (i.e., the apex angle and the lengths of the sides) may be calculated, from which the three moments of inertia may in turn be determined. In hydrogen sulphide only two bands have been observed, however; hence this means of determining the shape and moments of inertia is not available. The indeterminacy of the shape of the molecule introduces the further limitation that one can not know whether the bisector of the apex angle will be the least or the intermediate axis of inertia, since this depends upon the magnitude of the angle. Consequently the appearance of the third fundamental, were it observable, cannot be predicted, for if the bisector of the apex angle were the least axis of inertia, there would be two identical bands of one kind, while if it is the intermediate axis of inertia there would be two identical bands of the other type.

In hydrogen sulphide the electric moment vibrates in the plane of the three atoms, i.e., along either the A-axis or the B-axis. When the electric moment changes along A, and the rotation is principally about the same axis, quantum transitions occur among the A-levels governed by the rules (retaining the nomenclature of the symmetric rotator) $\Delta J = \pm 1, 0; \Delta K = 0$. When, however, the rotation is principally about C, quantum transitions occur among the C-levels and are determined by the rules, $\Delta J = \pm 1, 0; \Delta K = \pm 1$. This gives rise to a band having P, Q and R branches, the P and R branches originating from the transitions $\Delta J = \pm 1, 0; \Delta K = \pm 1$; and $\Delta J = \pm 1, \Delta K = 0$; and the Q branches from $\Delta J = 0, \Delta K = 0$. The band observed at 2.6μ having distinct, P, Q and R branches, is consequently due to a vibration of the electric moment along the least axis of inertia; i.e., the A-axis.

Vibrations of the electric moment along the B axis are perpendicular to

[7] Witmer, Proc. Nat. Acad. **12**, 602 (1926).

[8] Hund, Zeits. f. Physik **31**, 81 (1925).

[9] Dennison, Phil. Mag. **1**, 195 (1926).

rotations about both the A and C-axis, hence quantum transitions among both A and C-levels must be governed by the selection rules $\Delta J = \pm 1$, 0; $\Delta K = \pm 1$ alone. It may easily be seen that the resulting band is of the type observed at 3.7μ with no Q-branch. The regularity in spacing and intensity of the lines of bands of symmetric rotators is due to the fact that many transitions are over the same frequency range giving rise to lines which are precisely superposed. In the case of asymmetric rotators the positions of successive energy levels are altered by the asymmetry, but with no definite order; hence no regularity of line structure is here to be expected since only rarely do two or more lines fall at the same place.

The general characteristics are borne out also in the rigorous quantum mechanical solutions of the asymmetric rotator given by Kramers and Ittman and by Wang. One of the main differences is the splitting up of the $J+1$ levels of the old theory into $2J+1$ levels on the basis of the new. The magnitude of this doubling as given by Wang is:

$$\Delta \nu = \left\{ \frac{1}{2}\ \frac{\left(\dfrac{1}{C}-\dfrac{1}{B}\right)}{\dfrac{1}{A}-\dfrac{1}{2}\left(\dfrac{1}{C}+\dfrac{1}{B}\right)} \right\}^{K} \left\{ \frac{h\left[\dfrac{1}{A}-\dfrac{1}{2}\left(\dfrac{1}{C}+\dfrac{1}{B}\right)\left((J+K)!\right)\right]}{2^{3K}\pi^{2}(J-K)!(K-1)!^{2}} \right\}$$

This is seen to be small when K is small and the rotation is almost entirely about either A or C, but becomes large for those levels which mark the transition from rotation principally about one axis to rotation principally about the other. It is this doubling of the levels that accounts for the broadening of the Q branch. In the symmetric rotator, the Q branch arises from transitions from a rotational level in one vibrational state to the corresponding rotational level in another vibrational state. In the asymmetric case each rotational level save one is a doublet, and transitions now occur from the one doublet component of such rotational levels in one vibrational state to the other doublet component of the corresponding rotational level in another vibrational state. The Q branch thus arising is not a sharp maximum, but consists of many lines near the center of the band.