AUGUST 15, 1929 *PHYSICAL REVIEW* VOLUME 34

THE INFRA-RED ABSORPTION SPECTRUM OF HYDROGEN SULPHIDE

By A. H. Rollefson
University of Wisconsin

(Received June 27, 1929)

Abstract

The infra-red absorption bands of hydrogen sulphide in the regions of 4.2, 5.6, and 8.0μ were investigated by means of a prism-grating spectrometer. A narrow, intense absorption band was observed at 4.2μ, but could not be resolved. The 5.6μ band observed by Coblentz was not found. Evidence is presented to show that the band observed by Coblentz might have been due to an impurity. Thirty-four lines of the band in the region of 8.0μ were observed.

THE analysis of the fine structure of the infra-red absorption bands of gases in connection with its bearing on molecular structure has been very satisfactory in the case of the diatomic gases. For triatomic molecules, however, the spectra observed have usually been too complex to permit analysis of the fine structure. Water vapor has been extensively studied but without yielding very satisfactory results. With the resolving power of the present instruments, good resolution can be obtained only for those molecules which have small moments of inertia, i.e., those molecules which contain only one atom heavier than hydrogen.

The purpose of the present investigation was to study the fine structure of the infra-red spectrum of hydrogen sulphide in the hope that it might yield a fine structure more readily analyzed than that of water vapor or, in any case, that it would furnish additional data for the study of triatomic molecules.

Coblentz,[1] using a low dispersion prism spectrometer, found weak absorption bands for hydrogen sulphide at 4.24, 5.60, 7.12, 7.78, 8.46, 9.65, 10.08, 10.7, and 11.0 microns. The author has investigated a considerable portion of this region with a high dispersion grating spectrometer. No fine structure was obtained in the case of the 4.2 micron band, but 34 lines were observed in the region of 8 microns.

Apparatus

The apparatus was an auto-collimating, prism-grating spectrometer very similar in design to that used by Sleator and others at the University of Michigan.[2] Radiation from the source was focused on the slit of the double spectrometer by a mirror of 20 cm focal length. The absorption cell was placed immediately ahead of this slit. The prism spectrometer produced a spectrum which was brought to a focus on the slit of the grating spectrometer.

---

[1] Coblentz, "Infra-Red Spectra." (Washington, 1905).

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

After dispersion by the grating, the radiation was focused on an adjustable slit behind which was placed the receiving thermopile. The focal length of the mirrors of the spectrometer was 40 cm.

The double spectrometer was inclosed in a wood case which was sealed to the table top with paraffin. The top portion of the case could be swung out of the way when adjustments were being made. The edges of the top and base which came in contact were lined with felt weather-strips to make a fairly tight joint. The source *S* was mounted in a separate case together with the first mirror and the absorption cell. The joints of this case were also sealed with paraffin and the case was sealed directly to the spectrometer case, the only opening between the two being the first slit. The top was removable.

The apparatus was thus protected from air currents and rapid fluctuations of temperature. The air in the case was partially dried by means of calcium chloride and sulphuric acid to protect the rock-salt prism and the rock-salt windows of the absorption cell. A quantity of potassium hydroxide was placed in the case to absorb any hydrogen sulphide which might escape from the absorption cell.

The source of radiation was a d.c. Nernst glower. The glowers used were rated at 0.8 and 1.2 amperes but were operated on a considerably lower current as it was found that this increased the life of the glower without materially decreasing the energy available in the regions under investigation. The glower was surrounded by a water jacket which absorbed most of the heat liberated by the glower.

The prism was a thirty degree rock-salt prism mounted on a table especially constructed for this purpose in these laboratories. A plane mirror was mounted directly behind the prism so as to reflect the light back through the prism at an angle not far from minimum deviation.[2]

The gratings. The gratings were ruled at the University of Michigan by Dr. Barker and were made available through the kindness of Professor H. M. Randall. They were of the echelette type ruled with 2880 lines to the inch. Two gratings were used, one of which concentrated energy in the region from 3.5 to 6.0 microns; the other from 5.0 to 9.0. These are later referred to as gratings *A*10 and *A*6 respectively.

The gratings were mounted on a spectrometer table the scale of which could be read to one minute intervals by means of a vernier. A slow motion screw on the grating circle was calibrated so that settings could be made by measuring the angle through which the screw had been turned, the circle being used only for reference. This method gave consistent results and permitted setting at smaller intervals. The circle was read by means of a telescope mounted outside the case.

The thermopile and galvanometer. The thermopile was a Coblentz 14-junction, Bi-Ag linear thermopile, of 9.6 ohms resistance, mounted directly behind an adjustable slit which was calibrated so that the slit width could be read from a micrometer screw. The surface of the receivers was 13 mm by 1 mm which was sufficient to collect all the energy falling on the slit for a slit width of 0.5 mm or less but did not utilize the full amount of energy for a 1 mm slit. The thermopile was enclosed in a brass case with limiting diaphragms in front and mounted on a heavy tripod. The case was surrounded by a wood box filled with cotton for better thermal insulation.

The current from the thermopile was measured by means of an iron-clad, astatic galvanometer with a resistance of 4.5 ohms. While the galvanometer usually had to be adjusted at the beginning of each run, no difficulty was found in securing a sensitivity of 1×10^{-10} amperes per millimeter deflection with a lamp and scale at a distance of two meters. Occasional difficulty was experienced with a pronounced shift of the zero position of the galvanometer upon closing the circuit through the thermopile. As this shift varied considerably in magnitude, it was attributed to a thermal e.m.f. some place in the circuit. This e.m.f. was compensated for by impressing an opposing e.m.f. on the circuit so as to bring the galvanometer back approximately to its position on open circuit.

The absorption cells. Two absorption cells were used, one with mica windows and the other with rock-salt windows. The mica cell was a brass tube 5″ by 2.5″ with the ends cut at an angle of sixty degrees with the axis of the tube to eliminate interference effects due to the thin mica windows.[3] The mica windows were mounted with a wax made of beeswax and resin and the inside of the cell was coated with paraffin to prevent the action of the hydrogen sulphide on the brass walls. The cell was provided with a side tube at either end for introducing the gas to be investigated. Compensating windows of mica were mounted on a support attached to the cell and the cell was mounted so that either the cell or the compensating windows could be swung into the path of the light. Each window and its corresponding compensating window were cut from the same piece of mica which had been tested between crossed nicols to insure uniformity of thickness.[3]

The rock-salt cell was constructed in a similar manner except that the ends were normal to the axis of the cell. This cell was 6″ long and 2″ in diameter. The rock-salt windows were plates about 3/16″ thick split from a crystal of rock salt, ground flat on sandpaper and emery cloth, and polished with rouge and water on a block of pitch made of turpentine and resin.

The hydrogen sulphide was generated in a Kipp generator using calcium sulphide and dilute hydrochloric acid. The gas was washed by bubbling it through water and dried by passing it over calcium chloride and phosphorus pentoxide. The cell was filled by flushing it for a short time with the gas, the effluent being absorbed by a solution of sodium hydroxide.

ADJUSTMENTS AND METHOD OF TAKING DATA

All adjustments were made by means of visible light. The zero position of the grating was determined by taking an energy curve with the grating turning through the zero position and finding the position of maximum energy. Grating *A*10 was calibrated by measuring five absorption lines of

---

[3] Meyer and Bronk, Astrophys. J. **59**, 252 (1924).

HCl and using the wave-lengths given by Colby and Meyer.[4] A check was made by taking an energy curve to show the absorption of the atmospheric CO_2 in the path of the light and comparing the results with those obtained by Barker.[5] Grating *A*6 was calibrated by measuring the absorption of atmospheric CO_2 and comparing the curve with that obtained with grating *A*10. The grating constant was found to be the same for both gratings, $K=17.612$ microns.

The wave-length of the radiation falling on the thermopile is given by[6]

$$\lambda = K \sin\theta \qquad (1)$$

where θ is the angle through which the grating has been turned from its zero position, and K is the grating constant. We may calculate the range of wave-lengths included in the slit by means of the formulae:[7]

$$d\lambda = K\cos\theta d\theta,\quad d\theta = d/2f \qquad (2)$$

where θ is the grating angle as above, $d\theta$ is the change in the grating angle to move the center of the image of the slit across the thermopile slit, f is the focal length of the mirror, d is the slit width, and K is the spectrometer constant.

Observations were taken by setting the prism and grating at known positions and observing the deflections of the galvanometer with the absorption cell alternately in and out. Several readings were taken at each point. The absorption was taken as the ratio of the difference between the readings of the galvanometer with the cell in and the cell out to the deflection with the cell out. In measuring the absorption in a particular region, the grating was set at a definite angle which was read on the grating circle by means of the short focus telescope mounted outside the case. The grating angle was then changed by means of the micrometer screw previously mentioned.

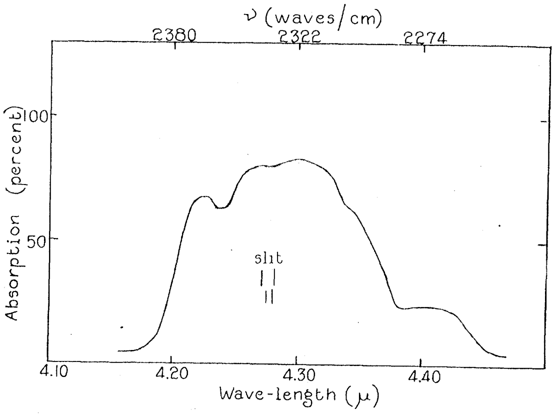

Fig. 1. 4.2μ band.

The correction for slit width is small and does not need to be considered in this type of work. The readings were reduced to the same temperature, 20°C. No correction was made for the difference in absorption between the cell windows and the compensating windows because this difference was small and would not affect the frequencies of the absorp-

---

[4] Colby and Meyer, Astrophys. J. **53**, 302 (1921).

[5] Barker, Astrophys. J. **55**, 391 (1922).

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

[7] Imes, Astrophys. J. **50**, 251 (1919).

tion lines. We are interested in the frequencies rather than in the absolute absorption.

Results

4.2 micron band. The absorption in this region is shown in Fig. 1. The entire curve was gone over at least twice with $\frac{1}{2}$ mm slits. Portions of the curve were investigated with $\frac{1}{4}$ mm slits but no indication of fine structure was obtained. For this region, the mica cell was used. A few check points were taken later with the rock-salt cell and were found to agree very well.

5.6 micron region. The region from 4.83 to 6.48 microns was investigated for absorption with 0.5 mm slits but no indication of absorption was found.

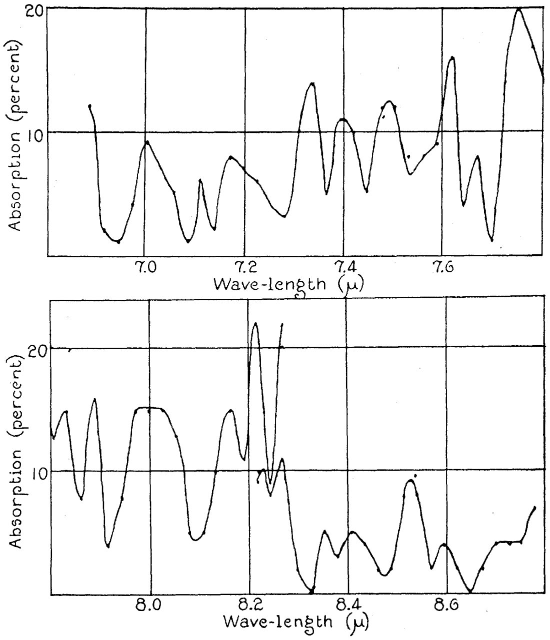

Fig. 2. Preliminary run.

In order to facilitate rapid exploration, observations were taken by watching the galvanometer reading as the cell was moved alternately in and out. If no change was observed, this was taken as an indication that there was no absorption. At the end of one of the runs, the absorption in the 4.2 micron region was checked in the same manner and a maximum absorption of about 90 percent was found, indicating that the cell was well filled with hydrogen sulphide.

Coblentz[1] gives an absorption band at 5.6 microns with a maximum absorption of 17 percent as compared with 21 percent in the case of the 4.2 micron band. With our narrower slit, we should have expected to find a region of very strong absorption, at least 50 percent, if this band is a real hydrogen sulphide band. Coblentz shows an absorption band for SO$_2$ in this region which is almost identical with that which he gives for H_2S,—and it is the only band which shows any similarity. In the case of SO_2, he gives two curves, one for ordinary SO_2 and the other for the same gas when purified by fractional liquefaction and distillation. The two curves practically coincide except for a marked change in the intensity of the 5.6 micron band. It is quite possible, therefore, that the 5.6 micron band which he observed may have been due to an impurity which was present in both cases.

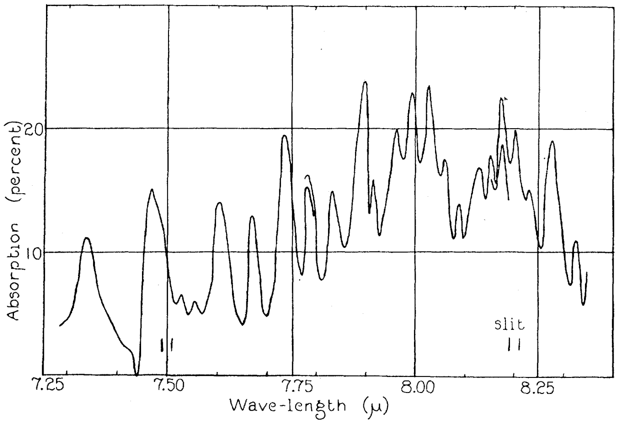

Fig. 3. Final run.

8.0 micron region. The results for this region are shown in Fig. 2, Fig. 3 and Table I. The entire region from 6.89 to 8.78 microns was covered in a preliminary survey taking readings at intervals of 0.027 microns. The portion from 7.3 to 8.35 microns was covered by a more careful survey with readings taken at intervals of 0.009 microns, a small portion (from 8.35 to 8.15 microns) being taken at intervals of 0.0045 microns.

TABLE I. *Observed lines. 8.0 micron region.*

Line No.	L (μ)	Wave-No. (waves/cm)	Line No.	L(μ)	Wave-No. (waves/cm)
1	6.885	1453.4	15	7.994	1250.9
2a	7.000	1428.6	16	8.026	1245.9
2b	7.040	1420.5	16b	8.058	1241.0
3	7.115	1405.5	17	8.088	1236.4
4a	7.180	1392.8	18	8.126	1230.6
4b	7.235	1382.2	19	8.150	1227.0
5	7.335	1363.3	20	8.175	1223.2
6	7.402	1351.0	21	8.208	1218.3
7	7.480	1336.9	21b	8.232	1214.7
8	7.607	1314.6	22	8.276	1208.3
9	7.671	1303.6	23	8.325	1201.2
10	7.739	1292.2	24a	8.360	1196.2
11	7.785	1284.5	24b	8.410	1189.1
12	7.835	1276.3	25	8.527	1172.7
13	7.893	1266.9	26	8.594	1163.6
13b	7.916	1263.3	27a	8.71	1148.1
14	7.963	1255.8	27b	8.78	1139.0

As the available energy in this region was small, it was necessary to work with 1 mm slits, but in spite of this handicap a considerable amount of fine structure was obtained. Unfavorable weather conditions combined with lack of time prevented the duplication of the entire curve. It was possible, however, to duplicate portions of the curve and the results were of such a nature that the author feels confident that the remainder of the curve cannot be in error to any great extent. The energy available on the long wave-length side of the curve was small and this difficulty, combined with those mentioned above, precluded the extension of the curve to longer wave-lengths. On the short wave-length side, the absorption of the water vapor in the air became troublesome and it was not considered feasible to carry the observations further into this region under existing conditions.

The wave-lengths and wave-numbers of 34 lines observed in this region are given in Table I. Good agreement is found between the preliminary and final curves in every case except for the two lines designated as 6 and 18 respectively. It is hoped that these data may aid in the development of the theoretical interpretation of the band structure for triatomic molecules.

In conclusion, the author wishes to express his appreciation to Dr. C. E. Mendenhall for his advice and encouragement throughout the investigation and to Dr. L. R. Ingersoll for his assistance in the last part of the experimental work.