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INFRARED SPECTRUM OF HYDROGEN
SULFIDE IN THE 3795 CM^{-1} REGION

THESIS FOR THE DEGREE OF M. S.
MICHIGAN STATE COLLEGE

CARLETON McNEAL SAVAGE
1955



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IN THE 3795 cm^{-1} REGION

by
Carleton McNeal Savage

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Physics and Astronomy

1955

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Carleton M. Savage

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AN ABSTRACT

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Approved E. O. Hume

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ABSTRACT

The absorption of hydrogen sulfide in the region from 3730 to 4030 cm^{-1} has been measured under high resolution. The absorption has been assigned partly to an A-type band $(n_1, n_2, n_3) = (0,1,1)$ and partly to a B-type band $(1,1,0)$.

The absorption was measured at pressures between 8 and 14 cm of Hg with a path length of 285 cm using a multiple traverse cell. The spectral slit width was between .15 and .20 cm^{-1} . The spectrograph was a self-recording, vacuum, grating instrument built by R. H. Noble and recently improved by the installation of a new Bausch and Lomb 15,000 line per inch grating and a Baird Associates 450 cycle amplifier and phase-sensitive detector. The source was an argon filled zirconium concentrated arc lamp. The detector was an Eastman Kodak lead sulfide photconducting detector.

Calibration was made using Fabry-Perot interference fringes to give divisions of equal wave number spacing between two argon lines used as standards.

The analysis was made through the use of published energy tables for the rigid rotor. A classical centrifugal distortion correction was applied to the rigid rotor energy levels. A least squares fit of observed lines to assigned transitions, assuming known ground state energy levels, gives for the excited state inertial parameters (0,1,1) band, $A = 10.517 \text{ cm}^{-1}$, $B = 9.124 \text{ cm}^{-1}$, $C = 4.619 \text{ cm}^{-1}$, $\nu_0 = 3789.07 \text{ cm}^{-1}$; (1,1,0) band, $A = 10.595 \text{ cm}^{-1}$, $B = 8.985 \text{ cm}^{-1}$, $C = 4.603 \text{ cm}^{-1}$, $\nu_0 = 3779.23 \text{ cm}^{-1}$.

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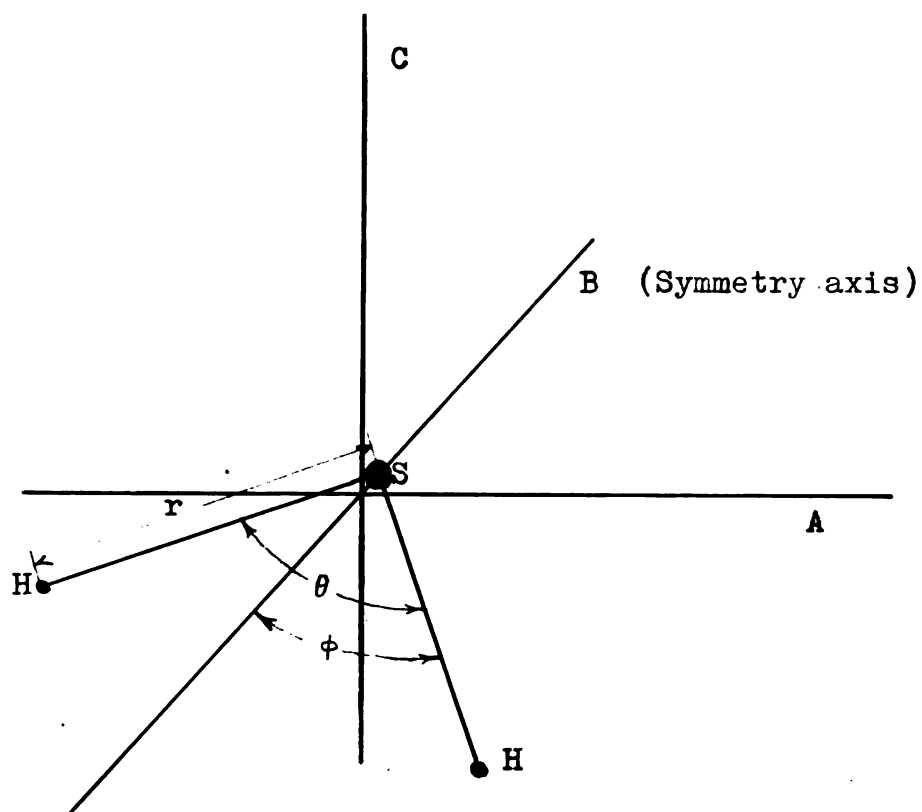
INTRODUCTION

Hydrogen sulfide (H_2S) is an asymmetric top rotator similar to the H_2O molecule. Much work has been done with both low and high resolution in the photographic infrared and the nearinfrared region¹ to 7.

The absorption near 2.5 microns was observed and reported in 1931 by H. H. Nielsen.¹ Since no analysis has been reported in the literature, the purpose of this paper is to present an analysis of the rotational fine structure in this region.

The absorption has been assigned to the combination bands (011) and (110). This notation represents the vibrational quantum numbers of the upper state involved in the transitions. The lower state would be designated (000). Thus the (011) band consists of transitions from the ground vibrational state to a vibration of the ν_2 and ν_3 modes. An alternate method of labeling found in some papers gives the vibrations in the order (ν_3, ν_1, ν_2) and the vibrational quantum numbers are designated by ($n_\sigma, n_\pi, n_\delta$) following the early notation used in the studies of H_2O .

The accepted molecular model for H_2S is shown in Figure 1. The three fundamental modes of vibration are shown in Figure 2. The modes ν_1 and ν_2 are symmetric and ν_3 is antisymmetric with respect to rotation about the symmetry axis (B axis).



Constants for ground state².

$$\theta = 92^{\circ} 20'$$

$$r = 1.345 \text{ \AA}$$

$$I_A = 2.667 \times 10^{-40} \text{ g cm}^2$$

$$I_B = 3.076 \times 10^{-40} \text{ g cm}^2$$

$$I_C = 5.845 \times 10^{-40} \text{ g cm}^2$$

Figure 1. H₂S Molecule.

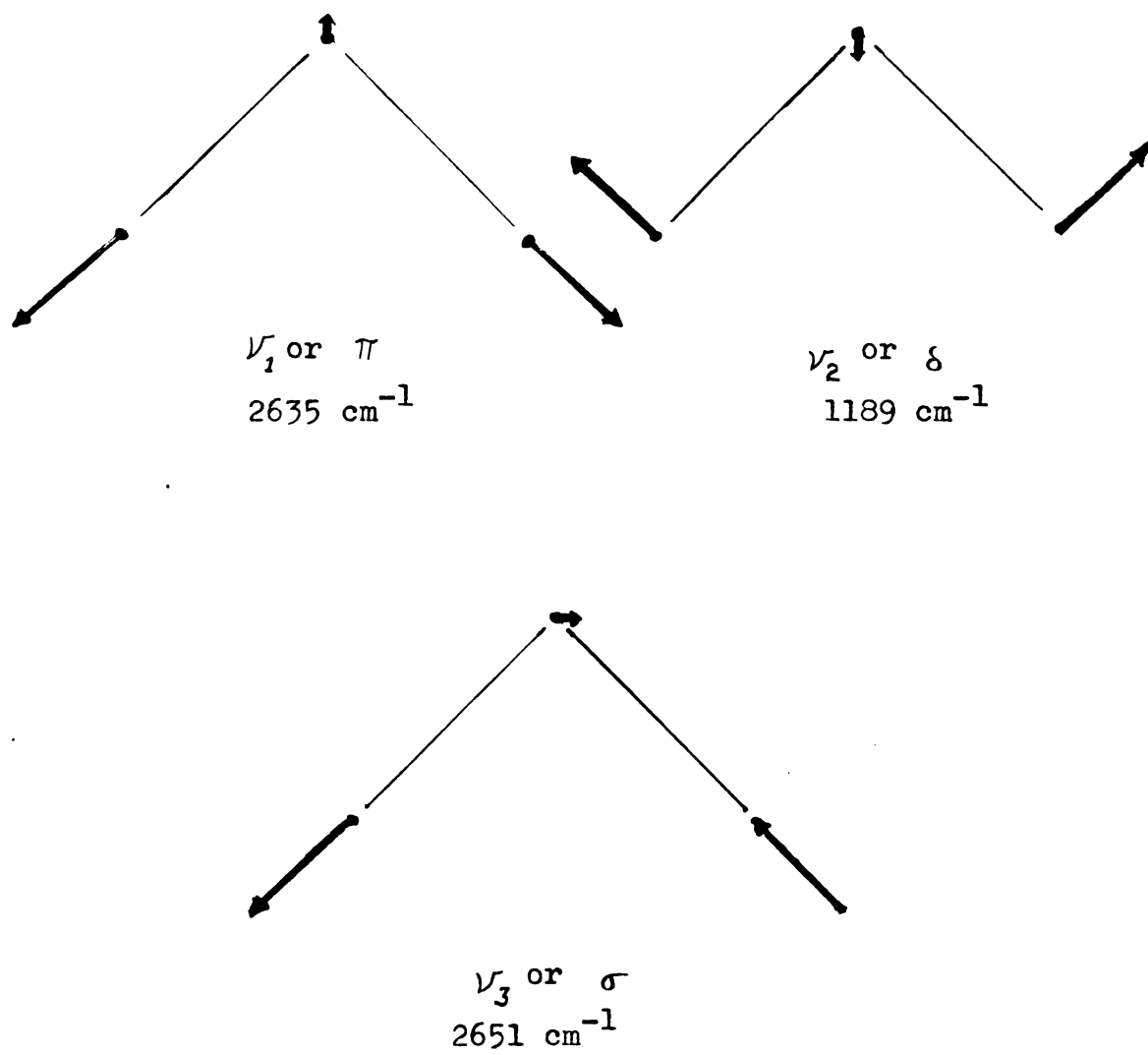


Figure 2. Normal vibrations of the H_2S molecule (not to scale)

APPARATUS

A self-recording, vacuum, prism-grating spectrometer constructed by R. H. Noble⁸ and described in a thesis by N. L. Nichols⁹ was used for this work. The portion of the optical system enclosed in the principal vacuum tank is shown in Figure 3. It includes a foreoptic section, monochromator and detector. The foreprism was not used, being replaced by a plane, front surfaced mirror. Under these circumstances, the second order argon emission lines used in calibration appeared directly on all the records.

The new Bausch and Lomb 15,000 line per inch grating, purchased by the Research Corporation, was used for this work. The grating has a ruled area of about 6" x 8" and is blazed at about 27° . The first order wave length at the blaze is 1.5 microns. At first it was not expected that this grating could be used in the region of 2.5 microns (an angle of 49° to 55°); however, it was found to give better results than the 7,200 line per inch grating originally tried. (The 7,200 line grating is blazed at 15° and has a useable ruled area of 4" x 5".)

Although the vacuum feature of the spectrograph greatly reduced the atmospheric water vapor absorption inside the tank, much absorption was found to take place in the optical path before entering the spectrograph proper. A cardboard box was constructed around the external optical section, and

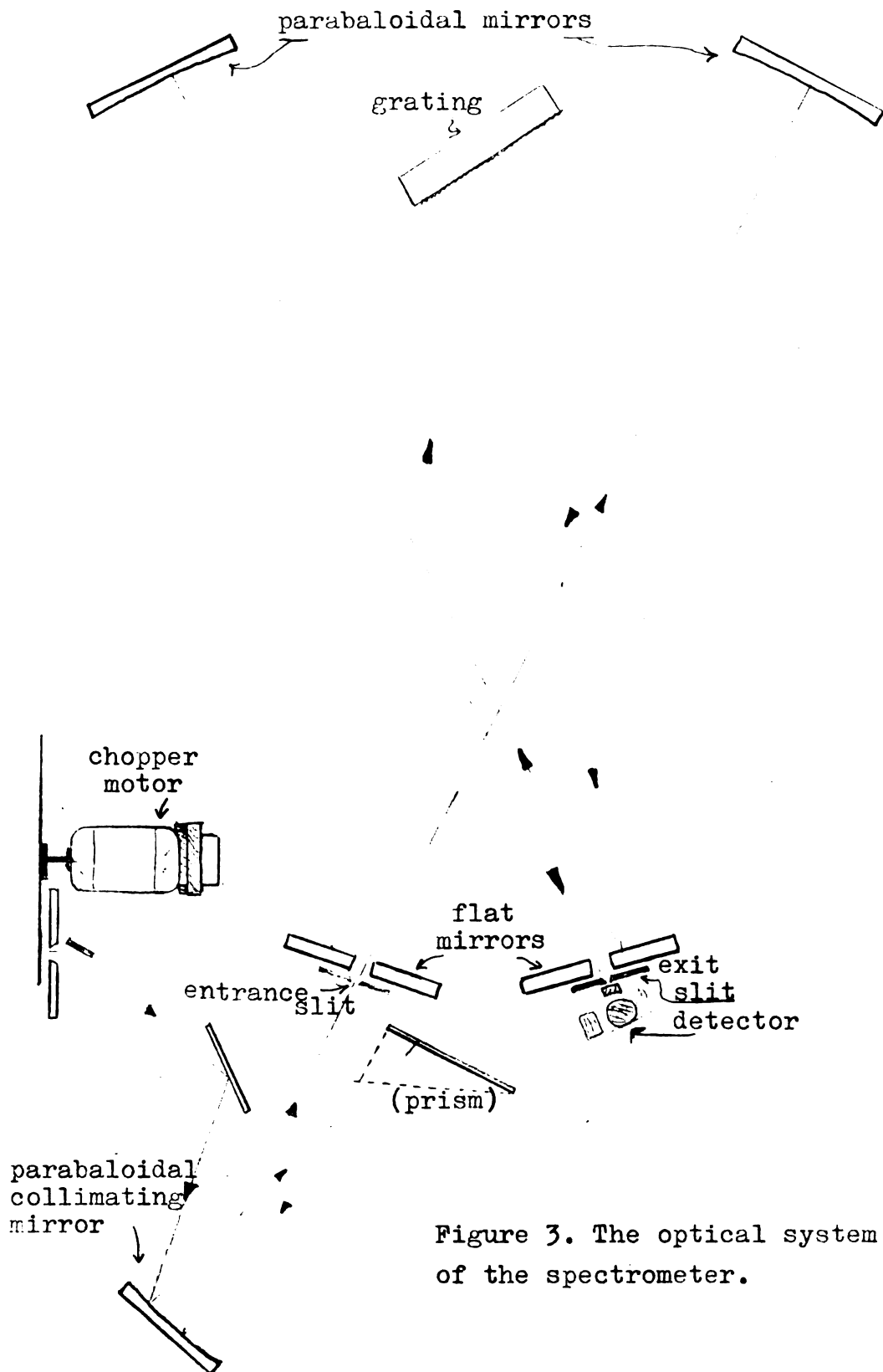


Figure 3. The optical system of the spectrometer.

a solution of CO_2 dissolved in acetone was put into a copper vessel designed to freeze out the H_2O in this part of the apparatus. This was found to reduce the water absorption greatly and showed that most of the absorption took place in the optical path outside the tank. An auxiliary steel tank was constructed to house the absorption cell and its necessary lenses. Two quartz windows were placed in the tank and were so designed that the concentrated zirconium arc lamp used as a source could be placed in contact with the window. This allowed the lamp to be operated outside the vacuum system where it might be cooled easily and moved for slight optical adjustments without introducing additional atmospheric absorption.

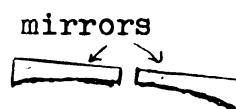
Provision was made so that the absorption cell might be filled without removing it from the spectrograph, thus making it unnecessary to let air into the tank whenever the pressure or material in the cell was to be changed.

The auxiliary tank was connected to the main spectrograph at the light entrance port of the spectrograph. The quartz window was removed, thus making it possible to evacuate the auxiliary tank with the same pump as that used to evacuate the spectrograph. A pressure of about .2 mm of Hg could be maintained throughout the system when pumping steadily.

A zirconium concentrated arc lamp was used to obtain the spectrum. This lamp is argon filled, and the argon emission lines were used for calibration. An attempt was made to use a carbon arc as a source but it was found to be too unsteady for this type of instrument.

The absorption cell, a multiple reflection system, is also described by Nichols⁹. The absorption cell is made of brass and the inside is readily attacked by the H_2S . To minimize this, the inside was painted with clear glyptal and baked to give a hard surface. Several coats of glyptal were applied and baked. The absorption cell had been previously used with DCl and the mirrors were badly corroded. It was therefore necessary to re-aluminize the mirrors before this work could be carried out. Figure 4 shows the absorption cell as used in the work. The source is shown at the side window of the auxiliary tank.

For calibration of the spectrograph, interference fringes produced by a Fabry-Perot interferometer were used. The optical setup of the interferometer is shown in Figure 5. The source is shown at the end window of the auxiliary tank. Typical fringes are shown in Photograph 1. The plates of the interferometer were adjusted for parallelism by use of Haidinger fringes. That is, the interferometer is placed in front of an extended monochromatic source, and by looking toward the source through the interferometer a ring pattern of fringes is observed. If the plates of the interferometer are parallel, this pattern will not change as the eye is moved vertically or horizontally across the field of view. If the plates are not parallel, the fringes seem to "expand out of" or "collapse into" the center of the pattern as the eye is moved across the field.



(8 traversals)

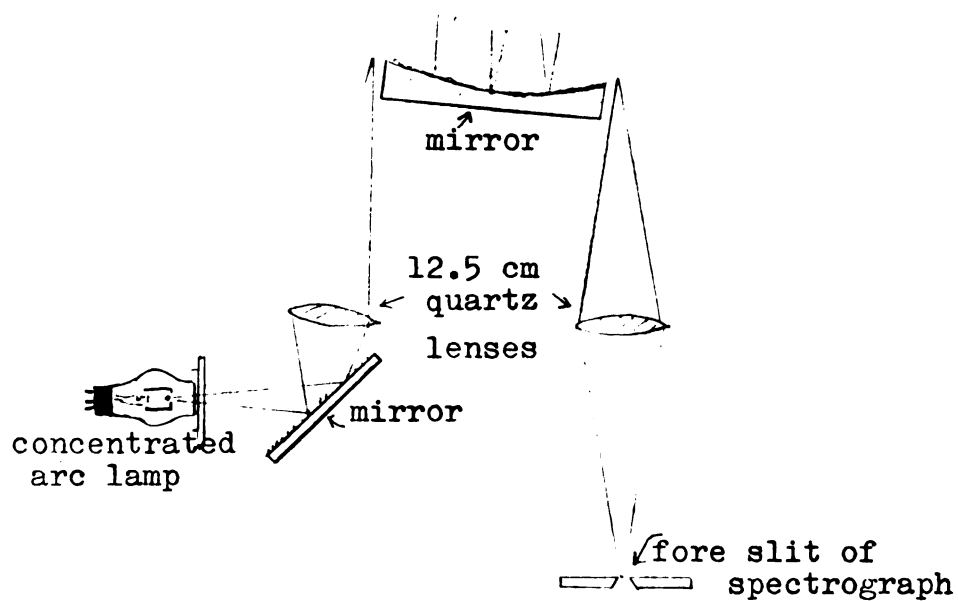


Figure 4. The optical system of the absorption cell in use.

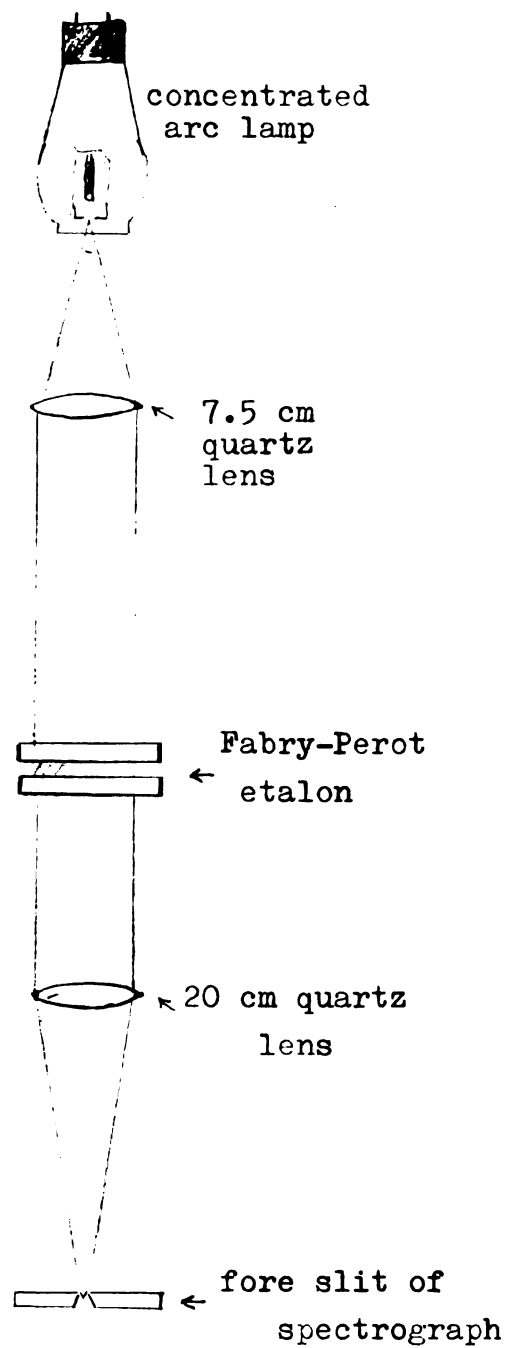
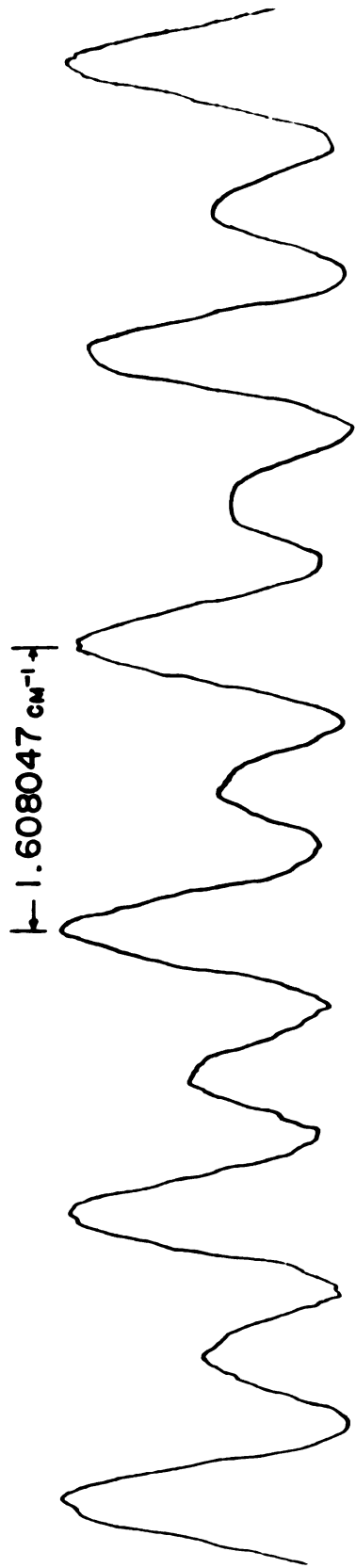


Figure 5. The optical system of the Fabry-Perot interferometer in position.



TYPICAL CALIBRATION FRINGES

For proper alignment in the tank, the interferometer is placed in position without the lenses. By looking at the source through a circular hole at the spectrograph slit, multiple images of the source can be seen if the interferometer is at an angle with the line of light (five images could be seen with this setup). The interferometer is rotated about a vertical axis until the multiple images are in a vertical line. Then by rotating about a horizontal axis, the images may be made to overlap. The lenses are then put into place. The light is collimated for visible light. This does not collimate it for the infrared however. Therefore, the lenses are moved by amounts calculated from the indices of refraction of quartz for visible and infrared.

Although the chopper motor was not designed to operate in a vacuum, it was decided to install it inside the evacuated spectrograph. The grease was removed from the bearings and replaced with Dow Corning high vacuum grease (a silicone lubricant).

At one stage of the work considerable trouble was experienced with the fuses blowing for the circuits connected to the apparatus in the evacuated tank. Photographic film was placed at various places in the tank near motors, terminals, etc. where arc discharges might occur. A number of the film strips were blackened when the spectrograph was evacuated and the fuses purposely blown. A complete rewiring job was done on the spectrograph. The electrical equipment inside

the tank consists of a selsyn to adjust the slit widths, a selsyn to rotate the prism table, a selsyn to rotate the grating, the chopper motor and the cathode follower circuit. Although it helped, the rewiring did not completely eliminate the fuse blowing. The chopper motor was suspected and removed, and the area near the starter coil switch was cleaned and painted with clear glyptal. The apparatus has worked satisfactorily thereafter.

From previous work on the instrument, it was found to have a nonlinearity of about .4 percent between the marker signals placed every $.1^{\circ}$ on the record. The transmission on the grating drive was dismantled and a badly worn fiber gear was replaced. The cone bearing on which the grating rotates was also removed and relapped. This gave an improvement by a factor of four.

The detector, amplifier and recorder now in use consists of an Eastman Kodak lead sulfide cell with a cross-sectional area of $1/2$ by 10 mm, together with a new 450 cycle amplifier which replaced the original 10 cycle equipment⁹ and a Speedomax recorder.

The detector has two matched sections of about 5 megohms impedance each, one to be used as a photoconductive detector and the other section as a load resistor. This has the advantage that when the cell is cooled the two sections remain matched. The impedance of the PbS cell did not match the impedance of the amplifier and it was therefore necessary

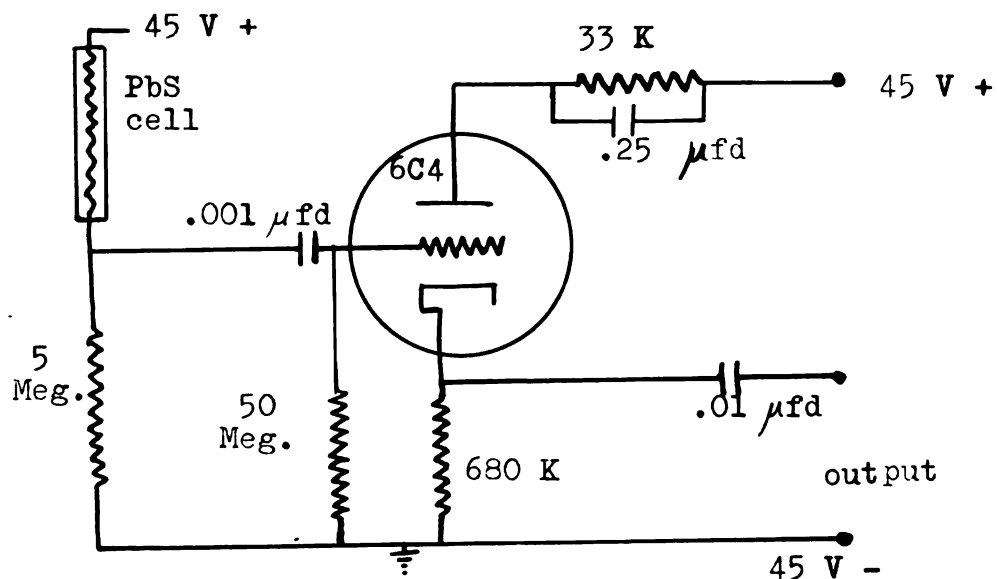


Figure 6. Cathode follower circuit.

to construct a cathode follower circuit as shown in Figure 6. This was constructed to be operated inside the vacuum tank as near as possible to the PbS cell. Tests were run on the effects of cooling the lead sulfide cell, and it was found that cooling did not help in this particular installation. The signal was increased by about 50 percent during the initial stages of cooling, but when equilibrium was reached the energy was actually less than at room temperature. It was therefore decided when the cathode follower was constructed not to cool the cell and to use only half of the PbS cell as a detector and to use a White resistor as a load resistor. This was done in an attempt to minimize inherent noise from the PbS cell.

The cathode follower feeds into a 450 cycle amplifier and phase-sensitive detector, Model CM 2-3, made by Baird Associates, Inc. A block diagram of this instrument is shown in Figure 7.

Its input impedance is on the order of 0.68 megohms. Included but not shown in the diagram of the amplifier is a voltage regulated power supply and a high voltage power supply for a photomultiplier tube. The reference input signal is generated by a small synchronous generator mounted on the shaft of the light chopper motor such that by rotating the generator with respect to the chopper the phase between the signal and reference voltages can be adjusted for best rectification of the signal. The output of the amplifier is fed into the Speedomax recorder.

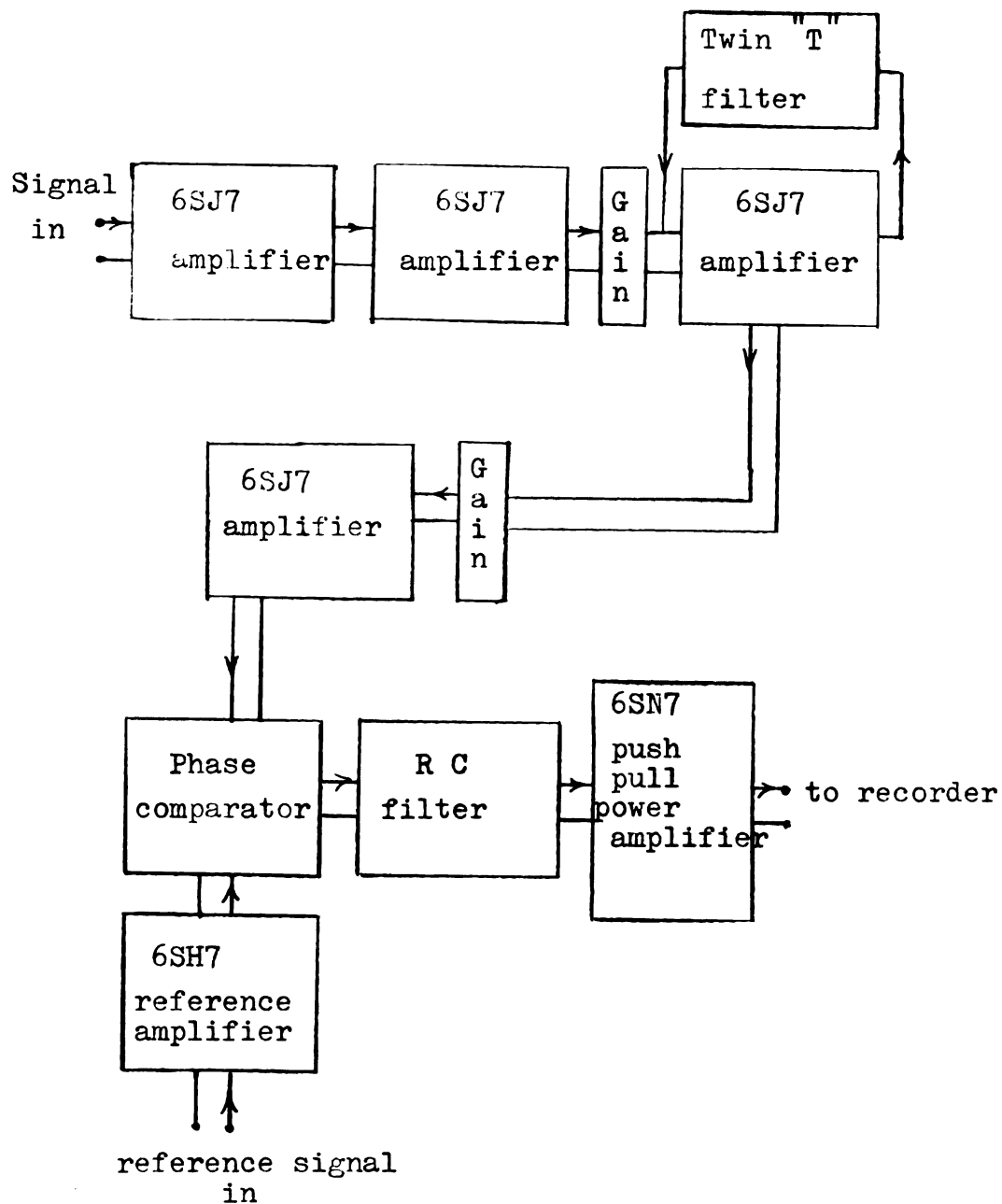


Figure 7. Block diagram of 450 cycle amplifier.



Spectrometer



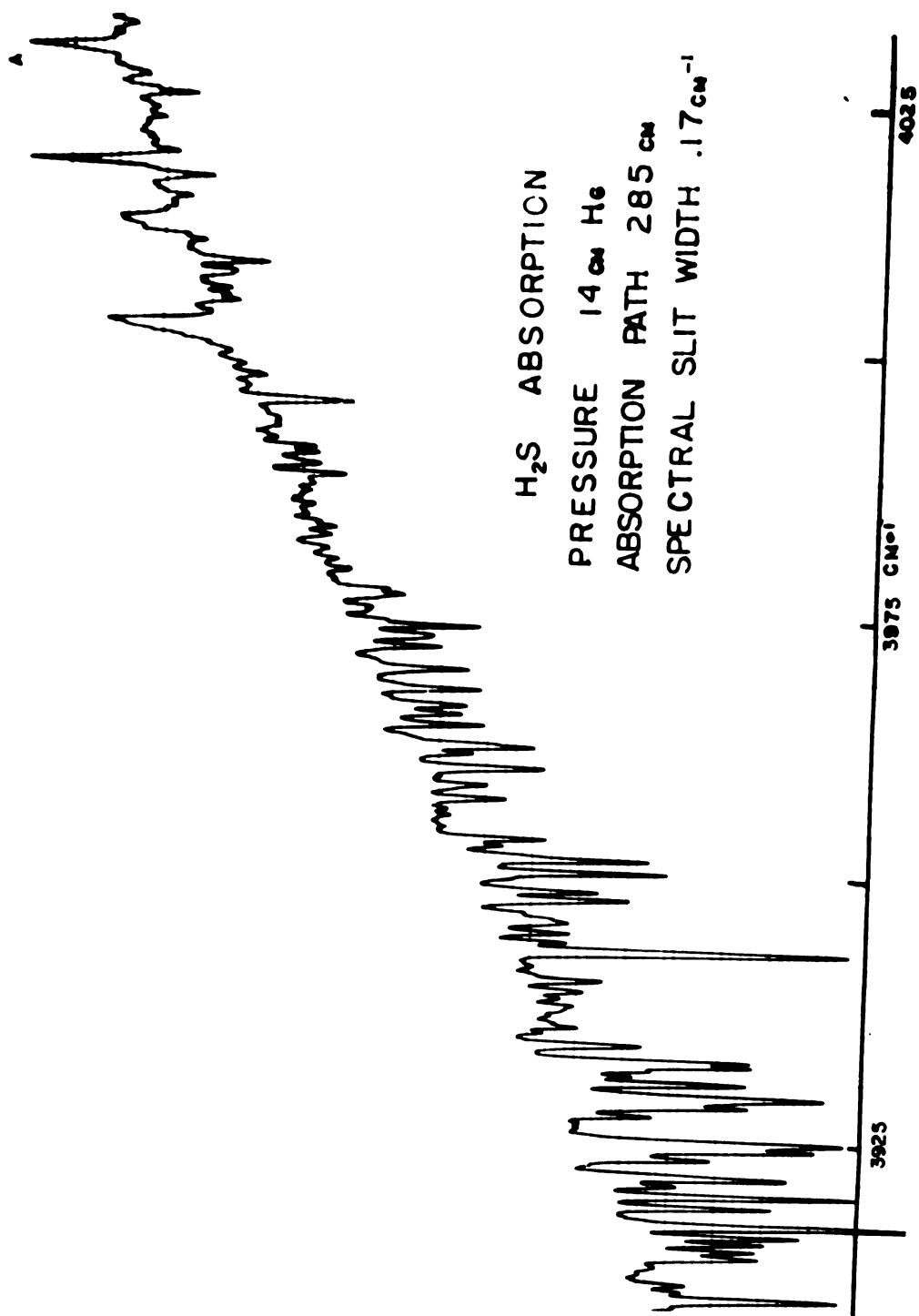
Auxiliary tank and Absorption cell

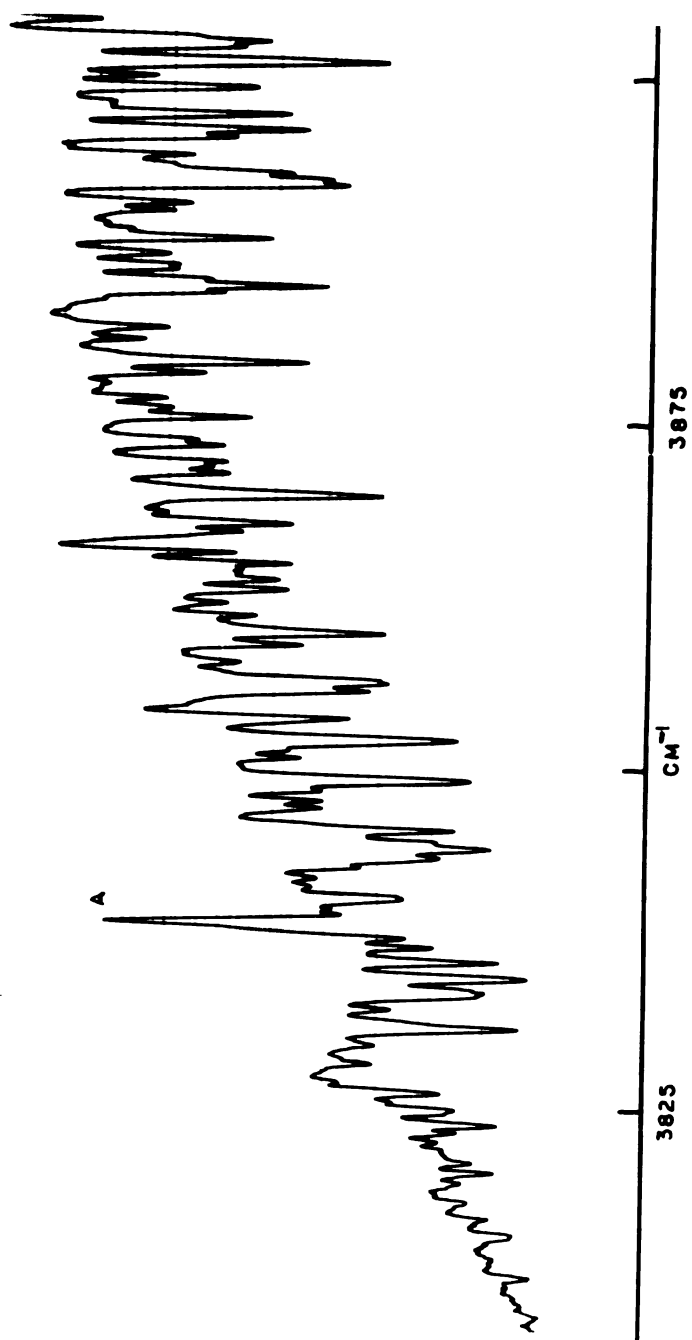
EXPERIMENTAL

The hydrogen sulfide was obtained from the Matheson Company. As the cylinder was nearly empty, we were limited in the amount of H_2S that could be put into the absorption cell. The maximum pressure that could be obtained was 14 cm of Hg. As the H_2S contained a considerable amount of water vapor, the shipping container was cooled in an acetone and dry ice bath; and the H_2S was passed through a similarly cooled U-shaped trap filled with glass beads. Even with these precautions an appreciable amount of water absorption was recorded.

For the absorption expected in the region of 2.5 microns, little energy was available with this apparatus. There are several reasons for this. First, the black body radiation of the arc is rapidly falling off. Second, the glass envelope of the arc lamp, although thin, transmits less in this region. Third, the angle of the grating used (49° to 55°) results in less energy. Fourth, the sensitivity of the PbS cell is decreasing. As mentioned before, cooling did not result in the expected increase in signal.

The total effect of the aforementioned resulted in a spectrum of the "downhill" type as shown in Photographs 4, 5 and 6. For the narrow slit widths necessary to resolve these lines, the energy was so low below 3730 cm^{-1} that a suitable spectrum could not be recorded. In addition, water absorption

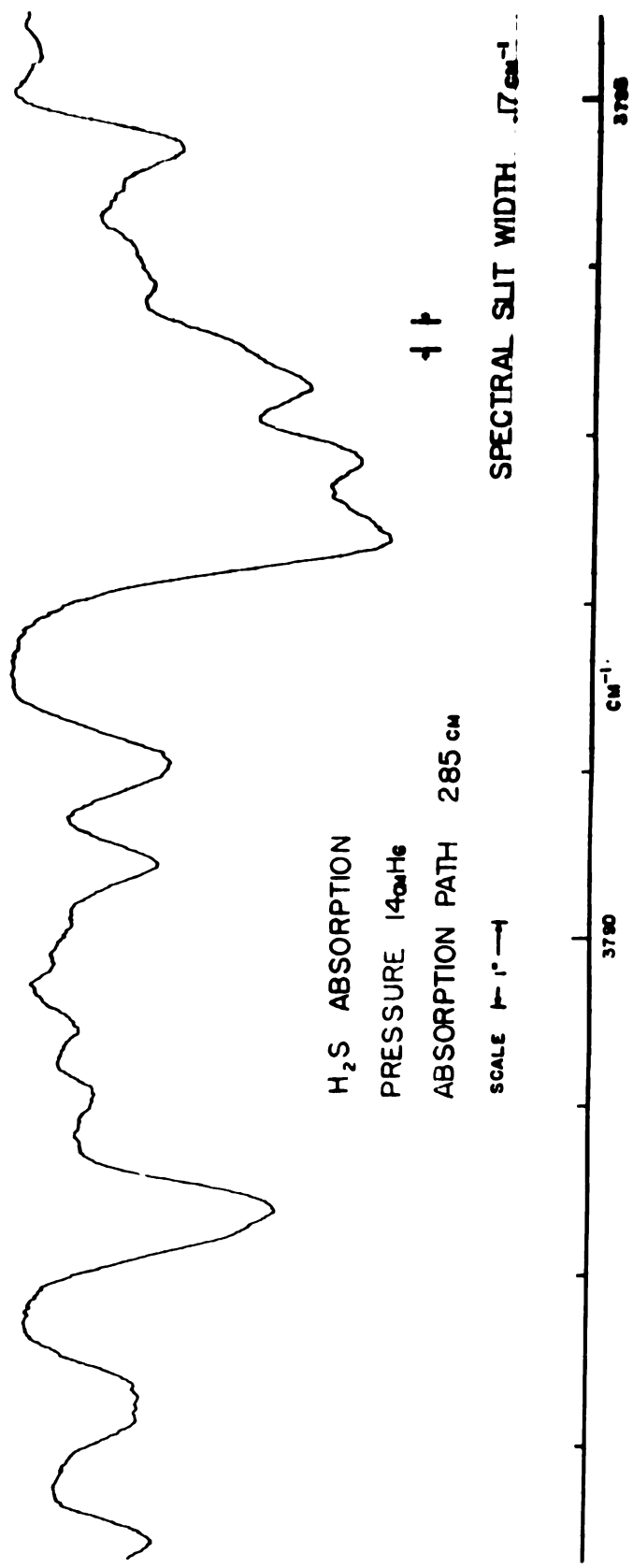


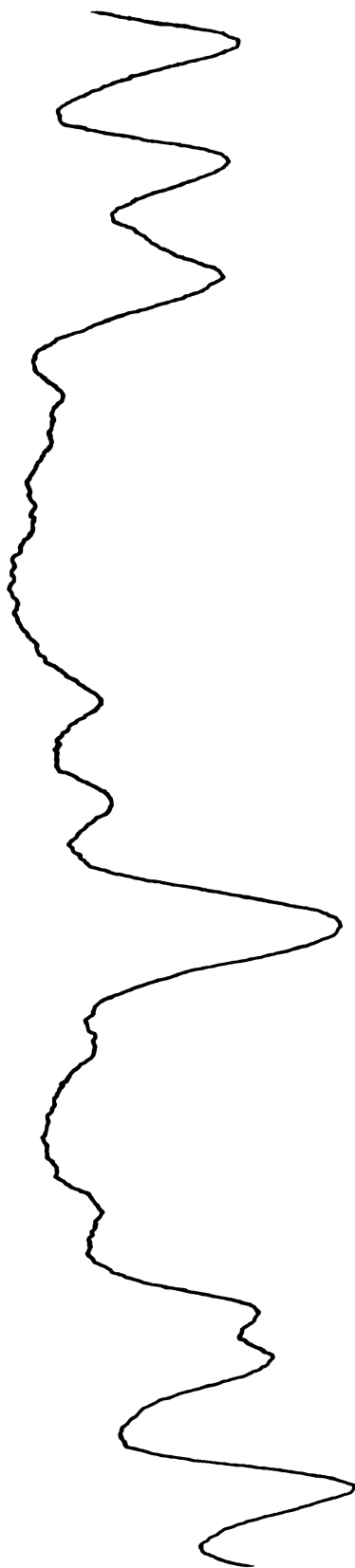


in this region is especially intense. For these reasons, much of the low frequency side of the bands could not be observed.

The spectrum was obtained under the following conditions. Eight traversals in the absorption cell gave a path length of 285 cm. Five runs were made with pressures from 8 to 14 cm of Hg (14 was the total pressure obtainable). The slit widths were from 95 to 135 microns. The grating was turned at a speed of about 1.25 degrees of arc per hour. The chart paper was fed at 120 inches per hour. A run from 3750 to 4030 cm^{-1} took about five hours and resulted in a record fifty feet long.

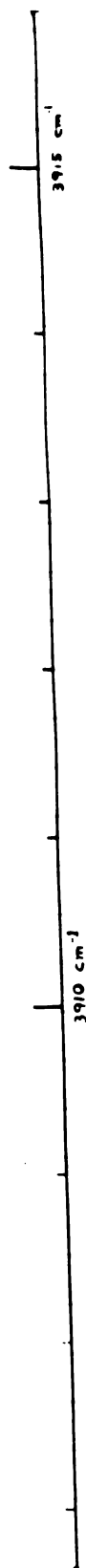
Sections of a typical run as they were used for measurements are shown in Photographs 7 and 8.





H_2S
 Pressure 19 cm Hg
 Absorption path 285 cm
 Scale $\frac{1}{2}$

Spectral Slit Width
 $.17 \text{ cm}^{-1}$
 (Slit Width 95μ)



CALIBRATION

Previous work with the instrument shows a cyclic variation of one degree length. No constant "grating constant" could therefore be calculated. Because of this, other means had to be used to obtain the frequencies of the lines.

Two prominent second order argon lines appeared on either end of the spectrum in all records. These lines were used as standards. The wave numbers used for these lines are those measured and reported by Humphreys and Kostkowski.¹⁰ The values are 7478.84 cm^{-1} and 8060.43 cm^{-1} . Their second order positions appear at 3739.42 cm^{-1} and 4030.215 cm^{-1} respectively. The region between these two lines was divided into divisions of equal wave number spacing with the use of a Fabry-Perot interferometer. The interferometer was placed in the spectrograph as shown in Figure 5, and was allowed to reach equilibrium with its surroundings. Records made on successive days reproduced within limits of linearity of the recorder. The spacing of the etalon was therefore considered constant throughout these runs.

The fringe run was compared with the runs containing the argon emission lines. The frequency difference between the argon lines divided by the number of fringes between them gives an approximate wave number separation of the fringes. The fractional part of a fringe between one of the argon lines and the nearest fringe was measured and an approximate frequency of the fringe was computed using the relationship

$$\nu = M \Delta \nu \quad (\Delta \nu = 1/2t) \quad (1)$$

where ν is the frequency of the fringe, M is the order of the fringe and $\Delta \nu$ the separation of the fringes, M was determined for the fringe. As this should be an integral number, the nearest integer was assumed to be the correct one. From this selection the order of the two argon lines were calculated. From equation (1) $\Delta \nu$ is calculated from the order and frequency of the two argon lines.

The two values of $\Delta \nu$ thus obtained were averaged giving

$$\Delta \nu = 1.608047 \pm .000007 \text{ cm}^{-1}$$

This uncertainty would result in a difference of about $.01 \text{ cm}^{-1}$ in the computed values of the two argon lines.

The order of the argon line at 4030.22 cm^{-1} was measured to be 2506.28. The order of the argon line at 3739.42 cm^{-1} was measured to be 2325.44.

The fringe pattern as shown in Figure 1 contains both first and second order fringes. This accounts for the alternate intensity of the fringes. The large peaks contain both first and second order, while the small peaks contain only the second order. The large peaks were used in calibration. As the etalon was used in a vacuum, no displacement of the first and second order fringes would be expected.

Measurement of Lines

The wave number of the absorption lines were found by the following method. Using the two argon lines as reference points, an absorption run was compared with the fringe runs. Assuming a constant separation of the fringes and linear interpolation between them, the fringe run was used as a ruler to assign an order number to the absorption lines. The wave number was then found by direct multiplication using relation (1). (Using $\Delta \nu = 1.608047$)

Five runs were measured and averaged. The center of the runs gave excellent agreement, the variation being less than $\pm .01 \text{ cm}^{-1}$. The region near 4000 cm^{-1} had a deviation of $\pm .06 \text{ cm}^{-1}$. None of the lines in this region were used in the final analysis so this deviation caused no concern.

Photographs 4,5, and 6 show the complete region measured, these were taken especially for this paper at a much compressed scale. The argon reference lines are marked on either end of the record. Many of the lines are due to atmospheric water absorption, these lines were not measured, being subtracted by comparison with a run of water absorption only. Photographs 7 and 8 show sections of the runs as they were measured. The spectrum was spread out to reduce errors in the width of the pencil lines used to mark the centers of the lines being measured. ($4\frac{1}{2} \text{ cm}$ on the paper represented about one cm^{-1})

GROUND STATE ENERGIES

The ground state rotational constants used are those given by Cross². Although the work was done in 1935 the results are accepted by later workers in the field. The constants were derived from analysis of photographic infrared data and therefore considered reliable.

The values of the constants as given by Cross are

$$\begin{aligned} A &= 10.373 \pm .005 \text{ cm}^{-1} \\ B &= 8.991 \pm .004 \text{ cm}^{-1} \\ C &= 4.732 \pm .003 \text{ cm}^{-1} . \end{aligned}$$

Where A, B, and C are the reciprocal moments of inertia given by

$$A = \frac{\frac{h}{8\pi^2 c}}{I_A}, \quad B = \frac{\frac{h}{8\pi^2 c}}{I_B}, \quad C = \frac{\frac{h}{8\pi^2 c}}{I_C} .$$

I_A , I_B , I_C are given about the axes as shown in Figure 1.

The ground state vibrational levels given in Table I, are also from Cross' work.

CALCULATIONS AND RESULTS

The general method of analysis used by Cross ² was followed. This consists of the following steps. The excited state inertial constants were estimated on the assumption that the observed A-type structure arose from the (011) vibrational band. By comparing the reciprocal moments of inertia of previously analyzed bands, it can be seen that the effect of the ν_2 vibration changes the constants by the following amount.

$$\begin{aligned}\Delta A &= -.10 \text{ cm}^{-1} \\ \Delta B &= -.19 \text{ cm}^{-1} \\ \Delta C &= -.068 \text{ cm}^{-1}\end{aligned}$$

Subtracting these changes from the values already computed for the (111) band ⁷, we get the trial values for A, B and C. With these trial values of A, B and C, a spectrum is calculated. The energy levels were computed with the aid of published energy tables of King, Hainer and Cross.¹¹

For completeness, a typical energy level is calculated below. The energy of a given level is given by

$$E = \frac{A + C}{2} (J^2 + J) + \frac{(A - C)}{2} E(K) \quad (2)$$

For the 4_3 level, we use $A = 10.51$, $B = 9.14$ and $C = 4.62$. J , the rotational quantum number, = 4. $E(K)$ is taken from the published tables. K is defined as

$$K = \frac{2B - A - C}{A - C} \quad (3)$$

Using the above values of A, B and C we get from equation(3)

$$K = +.5348$$

$E(K)$ is found by quadratic interpolation between the values listed in the tables. The values from the tables are for negative K, however

$$E_{\tau}^J(K) = -E_{-\tau}^J(-K) \quad (4)$$

where τ is the sublevel of the J quantum state. There are $2J + 1$ values of τ running from $\tau = -J$ to $\tau = +J$.

We can find the values for positive K as follows. Since K is positive, we use the value of 4_{-3} . For this level the energies from the table are given as

$$E(K) = E(-.4) = -15.63481$$

$$E(-.5) = -15.98528$$

$$E(-.6) = -16.35224$$

so that by relation (4)

$$E(.4) = 15.63481$$

$$E(.5) = 15.98528$$

$$E(.6) = 16.35224$$

Using quadratic interpolation between these three points, we get

$$\Delta = a(x) + b(x)^2 \quad (5)$$

where Δ is the difference between two given $E(K)$ values.

x is 10 times the difference between the K's. To find a and b

$$\Delta_1 = a + b \quad (x = 1)$$

$$\Delta_2 = 2a + 4b \quad (x = 2)$$

Δ_1 is the difference between $E(.4)$ and $E(.5)$; Δ_2 is the

difference between E (.4) and E (.6). Hence

$$.35047 = a + b$$

$$.71743 = 2a + 4b$$

Solving these two equations one gets

$$a = +.342225$$

$$b = +.008245$$

$$E(K) = E(.4) + a(x) + b(x)^2 \quad (6)$$

$$\text{For } K = .5348, \quad x = 1.348 = 10(.5348 - .4)$$

$$E(.5348) = 16.111 \text{ cm}^{-1}$$

From equation (2)

$$E = \left(\frac{A+C}{2}\right)(J^2 + J) + \left(\frac{A-C}{2}\right) E(K)$$

$$E = 198.747 \text{ cm}^{-1} \text{ (for } 4_3 \text{ level)}$$

At this point a classical centrifugal distortion correction is applied. Using the method of Cross ², it is assumed that the molecule is rotating as would a classical rotator having the same values of α , β and γ ; where α , β and γ represent the component of the square of the angular momentum along the A, B and C axis respectively. Hence

$$\alpha + \beta + \gamma = (J^2 + J)$$

Thus the energy may be divided into three components.

$$E = \alpha A + \beta B + \gamma C$$

and

$$\alpha = \frac{\partial E}{\partial A}, \quad \beta = \frac{\partial E}{\partial B} \quad \text{and} \quad \gamma = \frac{\partial E}{\partial C}$$

Since the center of gravity is so near the sulfur atom, the further assumption is made that the rotation takes place about the S atom. Using these assumptions, the total change

in energy due to rotational distortion is shown to be

$$\Delta E = \left[-\frac{E^2}{k_1 r^2} - \frac{(\alpha A \tan \phi - \beta B \cot \phi)^2}{2 k_3 r^2} \right] \times 1.963 \times 10^{-16}$$

where

$$1.963 \times 10^{-16} = hc \text{ (to reduce to dimensions cm}^{-1}\text{)}$$

E = energy as calculated from equation (2)

$$k_1 = 4.2 \times 10^5 \text{ dynes cm}^{-1} \text{ (molecular force constant)}$$

$$k_3 = 4.1 \times 10^4 \text{ dynes cm}^{-1} \text{ (molecular force constant)}$$

$$r = 1.361 \text{ \AA}$$

$$\phi = 46^\circ 30'$$

α, β , and γ may be expressed in terms of

$$E = \frac{A+C}{2} (J^2 + J) + \frac{A-C}{2} E(K).$$

The simplest of these is β . By definition

$$\beta = \frac{\partial E}{\partial B}$$

Differentiating the above equation gives

$$\frac{\partial E}{\partial B} = \frac{\partial E}{\partial K} \frac{\partial K}{\partial B} = \frac{A-C}{2} \frac{\partial E(K)}{\partial K} \cdot \frac{\partial K}{\partial B}$$

$$\text{and } K = \frac{2B - A - C}{A - C} \quad \frac{\partial K}{\partial B} = \frac{2}{A - C} \text{ from relation (3),}$$

therefore

$$\beta = \frac{\partial E}{\partial B} = \frac{\partial E(K)}{\partial K}$$

From equation (6) for E(K) one can also obtain

$$\beta = a + 2b(x) \text{ (actual equation used to find } \beta \text{)}$$

Performing similar differentiations, collecting terms and simplifying gives

$$\alpha = \frac{\partial E}{\partial A} = \frac{J^2 + J}{2} + \frac{E(K)}{2} - \beta \left(\frac{K+1}{2} \right)$$

$$\gamma = \frac{\partial E}{\partial C} = \frac{J^2 + J}{2} - \frac{E(K)}{2} - \beta \left(\frac{1-K}{2} \right)$$

Summing these values for α, β , and γ , one gets

$$\alpha + \beta + \gamma = (J^2 + J) \text{ as previously stated.}$$

For the 4_3 level, $\beta = 3.6$, $\alpha = 15.3$ and $\gamma = 1.1$.

After calculation of the energy levels for a rigid rotator (only values up to $J = 10$ were calculated, this is the limit of the published tables) and application of a classical correction for centrifugal distortion, a trial spectrum was calculated, using the published ground state² and the calculated energy levels for the excited state. The transition energies in cm^{-1} were calculated from the equation

$$E_{\text{cal}} = \nu_0 + E(J_T^1) - E(J_T) \quad (8)$$

where E_{cal} is the calculated wave number of the transition, ν_0 is the band center, $E(J_T^1)$ is a rotational energy level of the excited state, and $E(J_T)$ is a rotational energy level of the ground state.

Table II lists the rotational energy levels used in the final analysis of the band. Column one gives the energy level, column two the symmetry, column three the energy of the ground state and column four the energy of the excited state (011).

The symmetries of the rotational levels and the selection rules are those formulated by Dennison.¹³ An operation of 180° rotation with respect to the C axis is indicated by the first sign and an operation of 180° rotation with respect to the A axis by the second sign. A + in either column indicates that the wave function is symmetric for this operation and a - indicates that the wave function is antisymmetric for the operation.

For type A bands, the selection rules are

$$\Delta J = 0, \pm 1$$

and

$$+ - \leftrightarrow --$$

$$- + \leftrightarrow ++$$

For type B bands, the selection rules are

$$\Delta J = 0, \pm 1$$

and

$$++ \leftrightarrow --$$

$$+- \leftrightarrow -+$$

No type C band can occur for plane triatomic molecules as there can be no restoring force for out of plane vibrations.

With the complicated observed bands, it is not only necessary to calculate the position of the transitions, but one also needs to have some idea of their relative intensities before the calculated spectrum can be compared with the observed spectrum. The relative intensities of the lines can be calculated with the aid of tables published by Cross, Hainer, and King¹¹. The approximate intensity of a transition is given by

$$I = e^{-\frac{E}{kT}} \nu g |M^2| \quad (9)$$

where E is the rotational energy level of the ground state;

ν is the frequency of the transition in cm^{-1} ; g is a nuclear spin factor, ($g = 3$ when τ is odd in the ground state and $g = 1$ when τ is even in the ground state); k is the Boltzmann constant; T is the Kelvin temperature; and $|M^2|$ is the "line

strength" or probability of the transition. The values of $|M^2|$ are obtained from the published tables. Using $K = +.5$ will give intensities with sufficient accuracy for this work and eliminates the need for interpolation.

The calculated positions and intensities were plotted from $\pm \nu_0$, ν_0 as yet being unknown. This was then compared with the observed spectrum. The "collected Q"branches of the observed and calculated spectra were matched, and ν_0 assigned. From comparison of locations and intensities a number of transitions were assigned to the observed spectrum. For each assigned transition, an equation of the form

$$\Delta E = \Delta \nu_0 + a \alpha + b \beta + c \gamma \quad (10)$$

was set up, where ΔE is the difference between the observed and calculated value of the transition energy in cm^{-1} . $\Delta \nu_0$ is a change in the band center, and

$$\alpha = \frac{\partial E}{\partial A} \quad \beta = \frac{\partial E}{\partial B} \quad \gamma = \frac{\partial E}{\partial C}$$

(for explicit expressions, see page 32). a , b , and c are changes in the rotational constants. ($\Delta \nu_0$, a , b , and c are undetermined coefficients.)

To bring the observed and calculated frequencies into agreement, the set of equations obtained from equation (10) was solved for $\Delta \nu_0$, a , b , and c by the least squares method.

These increments were added to the original assumed values and new rotational energy levels were calculated. A new calculated spectrum was prepared and compared with the observed spectrum. Many lines in the calculated band were shifted in

location so that more transitions could now be assigned and another least squares fit carried out. The process should be repeated until the change in the increments is negligible. The number of times depends on the original estimate of the rotational constants and on the correct assignment of lines. In each case here it was done twice.

For a molecule for which the ground states were unknown, equation (10) becomes

$$\Delta E = \Delta \nu_0 + a' \alpha' + b' \beta' + c' \gamma' - a\alpha - b\beta - c\gamma$$

where the primed values are for the excited states and the unprimed for the ground state.

Least Squares

To solve a series of equation of the type

$$\Delta E = \Delta \nu_0 + \alpha a + \beta b + \gamma c \quad \text{by least squares}$$

one first obtains the following set of equations where

$$\sum = \sum_{i=1}^n, \quad n \text{ is the number of equations.}$$

$$\sum \Delta E_i = n \Delta \nu_0 + a \sum \alpha_i + b \sum \beta_i + c \sum \gamma_i$$

$$\sum \Delta E_i \alpha_i = \Delta \nu_0 \sum \alpha_i + a \sum \alpha_i^2 + b \sum \alpha_i \beta_i + c \sum \alpha_i \gamma_i$$

$$\sum \Delta E_i \beta_i = \Delta \nu_0 \sum \beta_i + a \sum \alpha_i \beta_i + b \sum \beta_i^2 + c \sum \beta_i \gamma_i$$

$$\sum \Delta E_i \gamma_i = \Delta \nu_0 \sum \gamma_i + a \sum \alpha_i \gamma_i + b \sum \beta_i \gamma_i + c \sum \gamma_i^2$$

These sums can be computed readily with the aid of a Friden Calculator. A typical result is given below for 23 lines in the A band.

$$\begin{aligned}
-1.26 &= 23\Delta\nu_0 + 146.72 a + 182.09 b + 419.19 c \\
-14.12 &= 146.72\Delta\nu_0 + 1650.70 a + 1999.40 b + 2848.49 c \\
-23.32 &= 182.09\Delta\nu_0 + 1999.40 a + 3006.56 b + 4879.44 c \\
-30.57 &= 419.19\Delta\nu_0 + 2848.49 a + 4879.44 b + 19882.55 c
\end{aligned}$$

The above set of equations was solved using determinates for $\Delta\nu_0$, a , b , and c . These values are given below.

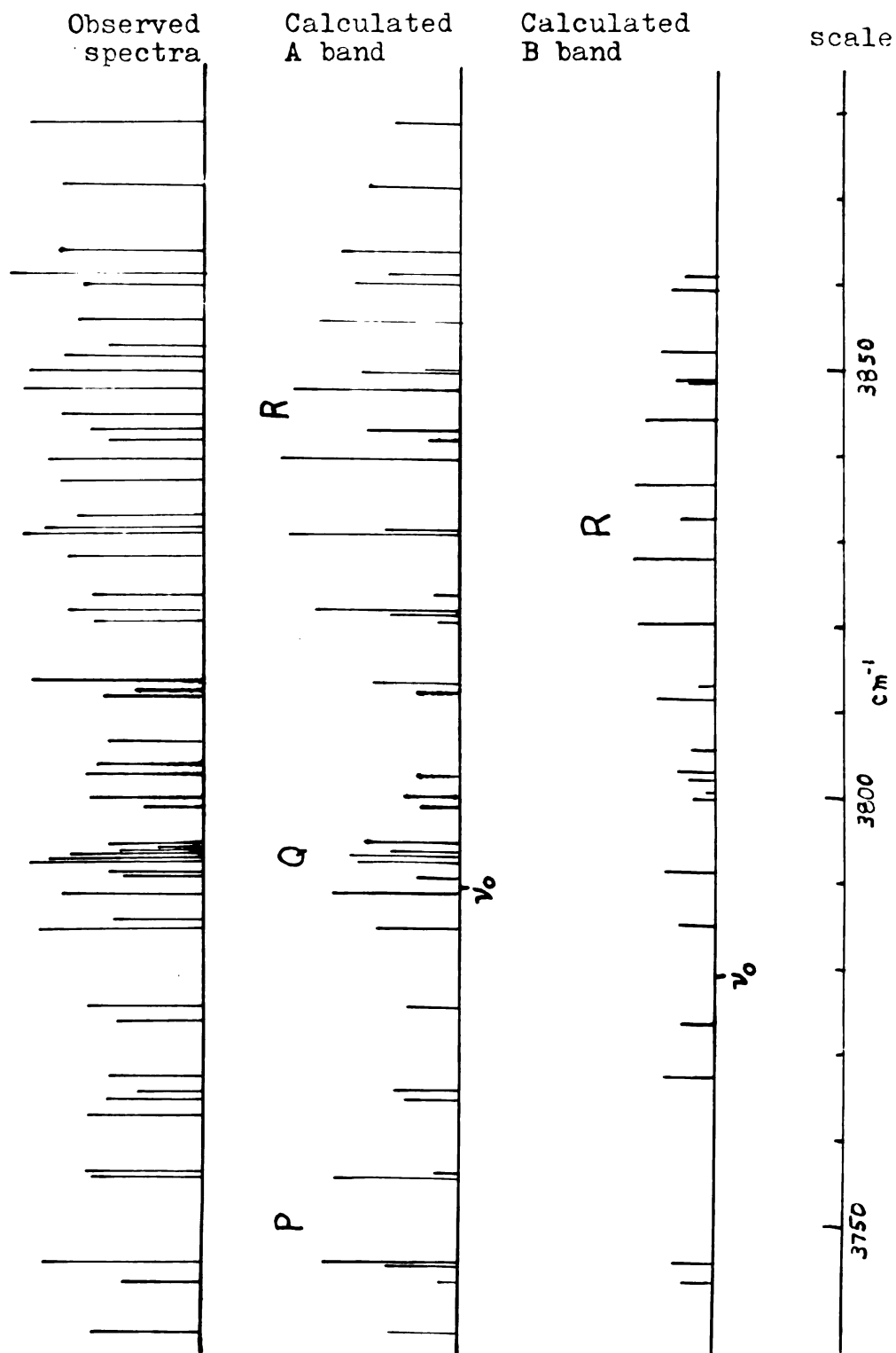
$$\begin{aligned}
a &= + .006 \quad \text{cm}^{-1} & \Delta\nu_0 &= .01 \quad \text{cm}^{-1} \\
b &= - .013 \quad \text{cm}^{-1} \\
c &= + .001 \quad \text{cm}^{-1}
\end{aligned}$$

Table III is a comparison of the observed and calculated spectra. Column one gives the line number assigned in original measurements. Column two gives the observed intensity; it is proportional to the percent absorption of the center of the line and thus not strictly comparable. Column three gives the wave numbers of the observed lines. Column four the assigned transitions; the rotational energy level of the excited state is given first and that of the lower or ground state is given second. Column five lists the calculated wave number of the transitions of the A band (011). Column six lists the calculated wave number of the transitions of a B band (110) to be explained shortly.

Figure 8 shows a line drawing of the observed spectra, with the water absorption removed, compared with the calculated A and B bands.

Only the strongest transitions are drawn to reduce confusion. The B band was calculated for the following reason.

Figure 3. Comparison of observed and calculated spectra.



After as many lines as possible were assigned for the A type band, quite a number of strong lines were still unaccounted for. Since ν_1 and ν_3 are of nearly the same frequency (2635 cm^{-1} and 2651 cm^{-1}), it is logical that a B type band (110) also occurs in this region.

Assuming that most of the additional absorption was due to the (110) band, trial rotational constants were estimated as before. The effect of the ν_3 vibration on the rotational constants is

$$\Delta A = - .19 \text{ cm}^{-1}$$

$$\Delta B = - .034 \text{ cm}^{-1}$$

$$\Delta C = - .046 \text{ cm}^{-1}$$

Using the trial energy levels for the (110) band and the known ground state levels and B type selection rules, a B band was compiled. The procedure is the same as used for the A type band. Table II gives in column five the rotational energy levels for the (110) band used in preparation of Table III. Table III includes, in addition to the A band as mentioned, the transitions of the B band in column six. Figure 8 shows a calculated B band compared with the observed spectrum.

Some difficulty in assigning the band center of the B band was experienced. Because of the H_2O absorption and the small energy available below 3730 cm^{-1} , only the R branch of the B band was observed. The method of matching observed and calculated spectra was as follows. The strongest series calculated for the B band is of the type

$$J_{-J} - (J - 1)_{J-2}$$

That is

$$6_{-6} - 5_{-4}$$

This series was matched to a series of strong observed lines.

Only $\nu_0 = 3779.23$ gave a good fit to the observed spacing and intensities.

CONCLUSION

The absorption in the 3795 cm^{-1} region has been assigned to the bands, (011) and (110). The rotational constants and band centers are given in Table I.

No strong predicted lines were unaccounted for, however some observed lines were not assigned transitions. These unassigned lines are probably for the most part due to transitions of $J > 10$ and the piling up of weak transitions not calculated.

The accuracy of the observed lines are believed to be within $.03\text{ cm}^{-1}$. The mean deviation for the strongest transitions is about $.1\text{ cm}^{-1}$. The classical centrifugal-distortion correction may be responsible for some of the large deviations. Also, many of the listed peak positions cannot be attributed to single transitions. The overlapping of two or more transitions will give an observed peak that will not be the true frequency of any one transition.

The observed intensities of the A and B bands are about the same.

TABLE I
CONSTANTS OF THE H₂S MOLECULE

		(011)	(110)
A	cm ⁻¹	10.517	10.595
B	cm ⁻¹	9.124	8.985
C	cm ⁻¹	4.619	4.603
ν_0	cm ⁻¹	3789.07	3779.23
I _A	g cm ²	2.6613 x 10 ⁻⁴⁰	2.6417 x 10 ⁻⁴⁰
I _B	g cm ²	3.0676 x 10 ⁻⁴⁰	3.1151 x 10 ⁻⁴⁰
I _C	g cm ²	6.0595 x 10 ⁻⁴⁰	6.0806 x 10 ⁻⁴⁰

$$\frac{h}{8\pi^2 c} = 27.989 \times 10^{-40}$$

TABLE II
 ROTATIONAL ENERGY LEVELS (cm^{-1}) OF (000) (011)
 (110) VIBRATION STATES

J_τ	Symmetry	(000)	(011)	(110)
0_0	++	0	0	0
1_1	+-	19.36	19.64	19.58
1_0	--	15.11	15.14	15.20
1_{-1}	-+	13.72	13.74	13.59
2_2	++	58.37	59.19	59.10
2_1	-+	55.20	55.79	55.94
2_0	--	51.06	51.61	51.12
2_{-1}	+-	38.29	38.12	37.99
2_{-2}	++	38.01	37.84	37.62
3_3	+-	117.48	119.09	119.15
3_2	--	115.44	116.87	117.23
3_1	-+	107.24	108.61	107.68
3_0	++	96.36	97.02	96.72
3_{-1}	+-	95.00	95.69	94.97
3_{-2}	--	71.46	70.86	70.58
3_{-3}	-+	71.42	70.83	70.52
4_4	++	197.08	199.75	200.14
4_3	-+	195.92	198.44	199.13
4_2	--	182.56	184.98	183.62
4_1	+-	173.98	175.73	175.23

TABLE II (CONT'D)

J_T	Symmetry	(000)	(011)	(110)
4_0	++	170.27	172.10	170.60
4_{-1}	-+	148.41	148.92	148.24
4_{-2}	--	148.14	148.68	147.87
4_{-3}	+-	114.18	112.94	112.48
4_{-4}	++	114.18	112.94	112.48
5_5	+-	297.29	301.29	302.18
5_4	--	296.66	300.53	301.68
5_3	-+	277.49	281.18	279.58
5_2	++	271.30	274.42	273.83
5_1	+-	263.73	266.95	264.48
5_0	--	244.48	246.39	245.26
5_{-1}	-+	243.47	245.45	243.86
5_{-2}	++	210.30	210.45	209.50
5_{-3}	+-	210.26	210.42	209.44
5_{-4}	--	166.37	164.24	163.60
5_{-5}	-+	166.37	164.24	163.60
6_6	++	417.96	423.41	425.06
6_5	-+	417.52	423.02	424.82
6_4	--	392.57	397.73	396.16
6_3	+-	388.46	393.16	392.59
6_2	++	375.68	380.49	377.07
6_1	-+	359.65	363.30	361.67

TABLE II (CONT'D)

$J\tau$	Symmetry	(000)	(011)	(110)
6_0	--	356.96	360.68	357.81
6_{-1}	+-	325.39	327.24	325.62
6_{-2}	++	325.22	327.08	325.34
6_{-3}	-+	281.70	281.26	280.01
6_{-4}	--	281.69	281.25	280.01
6_{-5}	+-	227.99	224.74	223.91
6_{-6}	++	227.99	224.74	223.91
7_7	+-	558.89	565.98	568.46
7_6	--	558.37	565.57	568.34
7_5	-+	528.26	534.96	533.74
7_4	++	525.55	532.11	531.69
7_3	+-	506.59	513.17	509.03
7_2	--	494.40	499.77	497.66
7_1	-+	488.29	493.87	489.39
7_0	++	459.42	463.21	460.82
7_{-1}	+-	458.71	462.63	459.87
7_{-2}	--	415.98	417.51	415.51
7_{-3}	-+	415.96	417.48	415.46
7_{-4}	++	362.52	361.27	359.71
7_{-5}	+-	362.52	361.27	359.71
7_{-6}	--	299.06	294.50	293.38
7_{-7}	-+	299.06	294.50	293.38

TABLE II (CONT'D)

J_τ	Symmetry	(000)	(011)	(110)
8_8	++	719.67	728.66	
8_7	+-	718.92	728.57	
8_6	--	684.77	692.97	
8_5	+-	682.59	691.22	
8_4	++	657.10	665.78	
8_3	+-	648.35	655.91	
8_2	--	637.49	645.19	649.28
8_1	+-	612.33	618.33	615.11
8_0	++	610.42	616.58	611.84
8_{-1}	+-	569.11	572.88	569.95
8_{-2}	--	568.95	572.77	569.73
8_{-3}	+-	516.03	516.99	514.59
8_{-4}	++	516.03	516.98	514.58
8_{-5}	+-	452.77	450.46	448.57
8_{-6}	--	452.77	450.46	448.57
8_{-7}	+-	379.53	373.43	372.03
8_{-8}	++	379.53	373.43	372.03
9_{-2}	++	688.29	691.82	688.38
9_{-3}	+-	688.29	691.82	688.38
9_{-4}	--	625.36	625.62	622.78
9_{-5}	+-	625.36	625.62	622.78
9_{-6}	++	552.38	548.82	546.54

TABLE II (CONT'D)

J_τ	Symmetry	(000)	(011)	(110)
9_{-7}	$+-$	552.38	548.82	546.54
9_{-8}	$--$	469.39	461.54	459.83
9_{-9}	$-+$	469.39	461.54	459.83
10_{-5}	$+-$	744.11	743.18	740.06
10_{-6}	$++$	744.11	743.18	740.06
10_{-7}	$-+$	661.38	656.34	653.66
10_{-8}	$--$	661.38	656.34	653.66
10_{-9}	$+-$	568.67	558.82	556.75
10_{-10}	$++$	568.67	558.82	556.75

TABLE III
COMPARISON OF OBSERVED AND CALCULATED
SPECTRA IN 2.5μ REGION

*Indicates Overlapping Water Absorption

Line No.	Intensity	Observed Wave No. cm-1	Transition	Calculated Wave No. (011) (110)
.5	.7	4022.69	9 ₋₅ - 8 ₋₇	4022.48
1	1.6	4017.05		
2	1.0	4015.05	9 ₋₃ - 8 ₋₅	4014.84
3	1.0	4011.13		
4	1.1	4010.58		
5	1.4	4007.72		
6	1.1	4007.35	8 ₋₃ - 7 ₋₆	4007.00
7	1.0	4005.98		
8	1.0	4005.32		
9	1.0	4004.79		
9.1	.5	4000.68		
9.2	.5	3999.74	8 ₋₁ - 7 ₋₄	3999.36
			8 ₋₂ - 7 ₋₅	3999.32
9.3	1.0	3998.62		
10	.9	3997.48		
10.6	1.4	3993.34		
11	1.0	3990.10		
12	1.4	3989.02		
13	2.1	3988.08		
14	1.0	3987.43		
15	.8	3987.09		
16	.7	3986.35	8 ₋₂ - 7 ₋₄	3986.44
17	.8	3985.05		
18	1.2	3978.79	7 ₋₃ - 6 ₋₆	3978.56
			7 ₋₂ - 6 ₋₅	3978.59
20	3.6	3973.39		
21*	1.8	3972.47		

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Wave No. (110)
22	2.4	3971.31			
23	3.4	3967.22	7 ₋₃ - 6 ₋₅		3966.70
24	2.8	3965.69			
25*	2.0	3964.87			
26*	3.0	3963.77	7 ₂ - 6 ₋₁	3963.45	
27*	1.2	3961.68	7 ₄ - 6 ₁	3961.53	
28	2.0	3961.04			
29*	4.0	3954.74			
30	1.6	3952.40			
30.1	2.0	3951.60			
31	5.6	3951.13			
32	1.3	3946.12			
35	2.2	3943.48	7 ₁ - 6 ₋₁		3943.24
35.1*	7.0	3942.51	6 ₁ - 5 ₋₂	3942.07	
36	3.0	3939.92	6 ₀ - 5 ₋₃	3939.49	
36.1	3.0	3938.90			
37	2.2	3935.57			
40	3.0	3931.63			
41	2.6	3931.07			
41.1*	4.5	3930.31	7 ₇ - 6 ₅		3930.17
44	4.5	3928.30	7 ₃ - 6 ₁		3928.61
45	2.8	3927.38	8 ₂ - 7 ₃	3927.67	
45.1	2.0	3924.74			

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm-1	Transition	Calculated Wave No. (011)	Wave No. (110)
45.2*	2.6	3924.37	$7_5 - 6_3$		3924.51
45.3*	1.3	3923.39	$8_6 - 7_7$	2923.15	
50	7.0	3921.74	$8_5 - 7_6$	3921.92	
51	2.8	3921.00			
52	5.9	3918.97	$7_4 - 6_4$		3918.35
			$8_3 - 7_4$	3919.43	
53	3.9	3915.66	$5_4 - 4_1$	3915.62	
54	3.7	3914.95			
55	3.4	3914.23			
56	1.4	3911.75	$6_2 - 5_0$		3911.82
			$9_{-2} - 8_{-1}$	3911.78	
57	1.4	3911.14			
58	6.8	3910.35			
59	.8	3909.64	$7_3 - 6_4$	3909.67	
60	1.0	3908.67	$5_{-1} - 4_{-3}$		3908.91
61	3.8	3908.04	$5_1 - 4_{-2}$	3907.88	
			$5_4 - 4_2$	3907.80	
62	3.6	3907.76	$6_6 - 5_4$		3907.63
63	5.3	3907.02	$7_1 - 6_2$	3907.26	
			$10_{-6} - 9_{-5}$	3906.89	
			$10_{-5} - 9_{-4}$	3906.89	
			$6_5 - 5_5$		3906.76
63.1*	9.1	3906.25	$7_5 - 6_6$	3906.07	
			$8_1 - 7_1$		3906.05
64	4.1	3904.79	$6_4 - 5_2$		3904.09
64.1	2.2	3902.73	$8_{-2} - 7_{-1}$	3903.13	
			$8_2 - 7_4$		3902.96
			$8_{-1} - 7_0$	3902.46	
64.2*	5.1	3901.85	$7_2 - 6_2$		3901.21
64.3	2.3	3901.29			

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Calculated Wave No. (110)
68	4.9	3900.35	$7_2 - 6_3$	3900.38	
68.1*	4.0	3899.30	$9_{-4} - 8_{-3}$	3898.66	
			$9_{-5} - 8_{-4}$	3898.66	
			$9_{-2} - 8_{-2}$		3898.65
69*	3.2	3897.95			
70	2.5	3896.69	$8_0 - 7_2$		3896.67
71	9.1	3895.43			
72	2.7	3894.98	$6_3 - 5_3$		3894.33
73	3.8	3893.74	$10_{-5} - 9_{-5}$		3893.93
			$10_{-4} - 9_{-4}$		3893.93
74	6.7	3892.60	$10_{-8} - 9_{-7}$	3893.03	
			$10_{-7} - 9_{-6}$	3893.03	
			$7_0 - 6_1$	3892.63	
74.1	4.0	3891.34	$4_3 - 3_0$	3891.15	
75	3.9	3890.49	$8_{-1} - 7_{-1}$		3890.47
			$8_{-4} - 7_{-3}$	3890.09	
			$8_{-3} - 7_{-2}$	3890.08	
76	6.1	3889.44	$4_0 - 3_{-3}$	3889.75	
			$8_{-2} - 7_0$		3889.54
			$6_4 - 5_5$	3889.51	
77	4.0	3888.71			
78	4.5	3888.43			
79	4.3	3886.94			
79.1*		3885.63	$9_{-5} - 8_{-2}$		3885.98
			$9_{-4} - 8_{-4}$		3885.98
			$6_3 - 5_4$	3885.57	
			$5_5 - 4_3$		3885.49
79.2	7.2	3885.26	$9_{-6} - 8_{-5}$	3885.12	
			$9_{-7} - 8_{-6}$	3885.12	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Calculated Wave No. (110)
79.3	6.5	3884.86	$5_3 - 4_1$		3884.83
80*	5.0	3883.63	$5_4 - 4_4$		3883.83
			$4_3 - 3_{-1}$		3883.36
81	3.1	3882.34			
81.1	1.5	3881.73	$4_4 - 3_1$	3881.58	
81.2*	5.0	3881.03	$7_{-3} - 6_{-2}$	3881.33	
			$7_{-2} - 6_{-1}$	3881.19	
			$6_1 - 5_2$	3881.07	
81.3*	5.0	3880.59	$10_{-7} - 9_{-7}$		3880.51
			$10_{-8} - 9_{-6}$		3880.51
			$7_1 - 6_3$		3880.17
81.4	5.0	3879.67	$7_{-1} - 6_1$		3879.46
82	10.0	3878.55	$10_{-10} - 9_{-9}$	3878.50	
			$10_{-9} - 9_{-8}$	3878.50	
			$4_0 - 3_{-2}$		3878.37
83	3.4	3877.52	$8_{-4} - 7_{-2}$		3877.83
			$8_{-3} - 7_{-3}$		3877.86
			$6_1 - 5_1$		3877.17
			$8_{-6} - 7_{-5}$	3877.01	
			$8_{-5} - 7_{-4}$	3877.01	
84	8.5	3876.78	$10_{-8} - 10_{-9}$	3876.74	
			$10_{-7} - 10_{-10}$	3876.74	
84.5	1.5	3874.98			
84.6*	10.0	3873.70	$5_1 - 4_2$	3873.46	
85	4.4	3873.25	$5_3 - 4_4$	3873.17	
85.1	2.7	3872.76	$9_{-6} - 8_{-6}$		3873.00
			$9_{-7} - 8_{-5}$		3873.00
86	6.8	3872.27	$6_{-2} - 5_{-1}$	3872.68	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Calculated Wave No. (110)
87	8.4	3871.07	9 ₋₈ - 8 ₋₇	3871.08	
			9 ₋₉ - 8 ₋₈	3871.08	
			10 ₋₅ - 10 ₋₈	3870.87	
			10 ₋₆ - 10 ₋₇	3870.87	
87.1*	3	3870.09	7 ₋₃ - 6 ₋₁		3869.30
			7 ₋₂ - 6 ₋₂		3869.52
88	7.6	3868.46	7 ₋₄ - 6 ₋₃	3868.64	
			7 ₋₅ - 6 ₋₄	3868.65	
			9 ₋₆ - 9 ₋₉	3868.50	
			9 ₋₇ - 9 ₋₈	3868.50	
89	5.3	3867.24	5 ₂ - 4 ₃	3867.57	
			3 ₂ - 2 ₋₁	3867.65	
90	5.0	3866.48	10 ₋₉ - 9 ₋₉		3866.59
			10 ₋₁₀ - 9 ₋₈		3866.59
			4 ₂ - 3 ₀		3866.49
91	5.3	3865.79	6 ₀ - 5 ₂		3865.74
			8 ₋₅ - 7 ₋₅		3865.28
			8 ₋₆ - 7 ₋₄		3865.28
92	6.0	3863.93	4 ₄ - 3 ₂		3863.93
			10 ₋₇ - 10 ₋₉		3864.22
			10 ₋₈ - 10 ₋₁₀		3864.22
			5 ₋₁ - 4 ₀	3864.25	
93	8.6	3863.43	8 ₋₈ - 7 ₋₇	3863.44	
			8 ₋₇ - 7 ₋₆	3863.44	
94	1.2	3862.61			
95	5.1	3862.04	9 ₋₄ - 9 ₋₇	3862.31	
			9 ₋₅ - 9 ₋₆	3862.31	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No.	
				(011)	(110)
96	11.0	3861.00	6 ₋₁ - 5 ₋₁		3861.38
			4 ₃ - 3 ₃		3860.88
			5 ₀ - 4 ₁	3861.48	
97	9.2	3859.89	6 ₋₄ - 6 ₋₃	3860.06	
			6 ₋₃ - 5 ₋₂	3860.03	
			6 ₋₂ - 5 ₀		3860.09
			8 ₋₆ - 8 ₋₇	3860.00	
98*	7.0	3859.44	9 ₋₉ - 8 ₋₇		3859.53
			9 ₋₈ - 8 ₋₈		3859.53
			6 ₂ - 5 ₄		3859.64
			3 ₁ - 2 ₋₂	3859.39	
99	5.0	3856.27	4 ₂ - 3 ₃	3856.57	
			9 ₋₆ - 9 ₋₈		3856.38
			9 ₋₇ - 9 ₋₉		3856.38
100	7.2	3855.58	7 ₋₇ - 6 ₋₆	3855.58	
			7 ₋₆ - 6 ₋₅	3855.58	
			9 ₋₂ - 9 ₋₅	3855.53	
			9 ₋₃ - 9 ₋₄	3855.53	
101	8.3	3851.06	5 ₋₂ - 4 ₋₁	3851.11	
			5 ₋₃ - 4 ₋₂	3851.35	
			7 ₋₄ - 7 ₋₇	3851.28	
101.1	4.5	3849.84	9 ₋₄ - 9 ₋₆		3849.63
			9 ₋₅ - 9 ₋₇		3849.63
101.2	10.0	3849.33	5 ₋₁ - 4 ₁		3849.11
			4 ₁ - 3 ₂	3849.36	
			6 ₋₄ - 5 ₋₂		3849.04
			6 ₋₃ - 5 ₋₃		3848.98
102	10.2	3847.47	6 ₋₆ - 5 ₋₅	3847.44	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No.	
				(011)	(110)
102	10.2	3847.47	6 ₋₆ - 5 ₋₅	3847.44	
			6 ₋₅ - 5 ₋₄	3847.44	
			4 ₁ - 3 ₁		3847.22
103	1.3	3845.92	8 ₋₁ - 8 ₋₄	3845.85	
			8 ₋₂ - 8 ₋₃	3845.81	
104	8.1	3844.59	7 ₋₇ - 6 ₋₅		3844.62
			7 ₋₆ - 6 ₋₆		3844.62
			7 ₋₂ - 7 ₋₅	3844.06	
105	6.3	3843.30	2 ₂ - 1 ₋₁	3843.56	
			3 ₃ - 2 ₁		3843.18
106	6.8	3842.73	4 ₋₂ - 3 ₋₁	3842.75	
107	2.4	3842.20	6 ₋₄ - 6 ₋₅	3842.33	
			6 ₋₃ - 6 ₋₆	3842.34	
			9 ₋₂ - 9 ₋₄		3842.25
			9 ₋₃ - 9 ₋₅		3842.25
108	5.5	3841.64	4 ₋₁ - 3 ₀	3841.63	
109	4.2	3840.61	5 ₋₂ - 4 ₋₂		3840.59
			5 ₋₃ - 4 ₋₁		3840.26
110	8.7	3839.20	5 ₋₅ - 4 ₋₄	3839.13	
			5 ₋₄ - 4 ₋₃	3839.13	
			3 ₁ - 2 ₂	3839.31	
111	8.5	3836.77	6 ₋₆ - 5 ₋₄		3836.77
			6 ₋₅ - 5 ₋₅		3836.77
			8 ₀ - 8 ₋₁	3836.54	
112	1.9	3835.76			
113	2.8	3835.39			
114	4.7	3834.07	6 ₋₂ - 6 ₋₃	3834.45	
			2 ₂ - 1 ₋₁	3834.54	
115	4.7	3833.74	3 ₋₁ - 2 ₀	3833.70	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Wave No. (110)
116	7.4	3833.09	8 ₋₁ - 8 ₋₃		3833.15
			8 ₋₂ - 8 ₋₄		3832.93
			5 ₋₂ - 5 ₋₅	3833.15	
			5 ₋₃ - 5 ₋₄	3833.12	
116.5	7.4	3832.59	4 ₋₁ - 3 ₋₁		3832.47
117	9.4	3831.05	3 ₀ - 2 ₁	3830.89	
			6 ₋₃ - 6 ₋₅		3831.25
			6 ₋₄ - 6 ₋₆		3831.25
118	10.2	3830.69	4 ₋₄ - 3 ₋₃	3830.59	
			4 ₋₃ - 3 ₋₂	3830.55	
			4 ₋₂ - 3 ₀		3830.74
119	1.2	3829.64	7 ₂ - 7 ₋₁	3830.13	
120	7.8	3828.65	5 ₋₅ - 4 ₋₃		3828.65
			5 ₋₄ - 4 ₋₄		3828.65
121	1.6	3827.22	6 ₁ - 6 ₋₂	3827.15	
122	5.2	3824.93	3 ₀ - 2 ₀		3824.89
			8 ₁ - 8 ₋₁		3825.23
			5 ₀ - 5 ₋₃	3825.20	
123	7.0	3823.87	7 ₀ - 7 ₋₂		3824.03
124	6.4	3823.59	4 ₋₂ - 4 ₋₃	3823.57	
			7 ₁ - 7 ₀	3823.52	
125	4.0	3822.67	7 ₆ - 7 ₄		3822.62
			6 ₋₂ - 6 ₋₄		3822.88
			5 ₋₂ - 5 ₋₄		3822.36
			5 ₋₃ - 5 ₋₅		3822.30
125.1*	8.0	3821.65	2 ₀ - 1 ₁	3821.32	
			3 ₋₂ - 2 ₋₁	3821.64	
			3 ₋₃ - 2 ₋₂	3821.89	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Calculated Wave No. (110)
126	6.8	3820.24	4 ₋₃ - 3 ₋₃		3820.29
			4 ₋₄ - 3 ₋₂		3820.25
			5 ₂ - 5 ₋₁	3820.02	
127	6.1	3819.46	7 ₇ - 7 ₅		3819.43
			3 ₋₁ - 2 ₁		3819.00
128	6.0	3818.40	8 ₂ - 8 ₀		3818.09
129	3.0	3817.83	7 ₂ - 7 ₀		3817.47
131	5.7	3814.65	3 ₀ - 3 ₋₃	3814.67	
132	10.0	3813.34	3 ₋₁ - 3 ₋₂	3813.30	
			2 ₋₂ - 1 ₋₁	3813.19	
			4 ₋₁ - 4 ₋₃		3813.29
133	4.4	3812.87	4 ₀ - 4 ₋₁	3812.76	
			5 ₋₁ - 5 ₋₃		3812.83
			4 ₋₃ - 4 ₋₄		3812.92
134	4.0	3812.25	2 ₋₁ - 1 ₀	3812.08	
			3 ₋₂ - 2 ₋₂		3811.80
			6 ₃ - 6 ₁		3812.17
135	5.9	3811.44	3 ₋₃ - 2 ₋₁		3811.46
			5 ₁ - 5 ₀	3811.54	
136	4.4	3810.84	3 ₂ - 3 ₋₁	3810.94	
137	.7	3809.83	7 ₁ - 7 ₋₁		3809.92
			6 ₂ - 6 ₁	3809.91	
138	6.6	3808.34	5 ₂ - 5 ₀		3808.58
139	5.5	3806.20	7 ₅ - 7 ₃		3806.38
			4 ₁ - 4 ₋₁		3806.05
140	4.4	3804.49	3 ₀ - 3 ₋₂		3804.49
			4 ₃ - 4 ₁		3804.38
141	6.6	3803.38	2 ₋₁ - 1 ₋₁		3803.50
142	6.8	3802.52	3 ₋₁ - 3 ₋₃		3802.78
			2 ₀ - 2 ₋₁	3802.39	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Wave No. (110)
142.1*		3801.70	2 ₋₂ - 1 ₀		3801.74
			4 ₀ - 4 ₋₂		3801.69
			3 ₋₃ - 2 ₂	3801.53	
143	6.6	3799.44	8 ₆ - 8 ₅	3799.45	
			6 ₄ - 6 ₆		3799.71
			6 ₂ - 6 ₀		3799.34
			7 ₋₁ - 7 ₋₂	3799.72	
143.5	3.0	3798.45	6 ₄ - 6 ₃	3798.34	
			8 ₈ - 8 ₇	3798.81	
			4 ₁ - 5 ₄	3798.43	
			7 ₅ - 7 ₄	3798.48	
144	8.2	3797.56	8 ₇ - 8 ₈	3797.97	
144.1*		3796.60	7 ₇ - 7 ₆	3796.68	
			4 ₄ - 4 ₂		3796.81
			2 ₁ - 2 ₋₁		3796.88
145	6.2	3795.83	7 ₆ - 7 ₇	3795.75	
146	.9	3795.02	5 ₃ - 5 ₁		3795.08
146.1	5.4	3794.54	6 ₆ - 6 ₅	3794.96	
			6 ₅ - 6 ₆	3794.13	
			1 ₀ - 0 ₀		3794.43
147.1	3	3793.91			
147.2	4	3793.72	1 ₁ - 1 ₀	3793.60	
			5 ₅ - 5 ₄	3793.70	
147.3	5	3793.38			
147.4	8	3793.17	2 ₂ - 2 ₁	3793.06	
147.5	9	3792.79	7 ₄ - 7 ₅	3792.90	
			4 ₂ - 4 ₀		3792.58
			3 ₃ - 3 ₂		3792.70
147.6	10	3792.32	5 ₄ - 5 ₅	3792.31	

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated (011)	Wave No. (110)
150	5.5	3791.04	$3_3 - 3_1$		3791.14
151	4.8	3790.42	$4_3 - 4_4$	3790.43	
152	8.3	3788.47	$3_2 - 3_3$	3788.46	
153	2.8	3787.19	$2_2 - 2_0$		3787.27
154	4.9	3786.52	$2_1 - 2_2$	3786.49	
155	5.1	3785.49	$2_0 - 2_1$	3785.48	
			$1_1 - 1_{-1}$		3785.09
156	9.6	3784.94	$1_0 - 1_1$	3784.85	
157	4.6	3781.93	$4_1 - 4_2$	3782.24	
			$7_2 - 7_3$	3782.25	
158	3.6	3781.03			
159*	5.3	3778.72	$3_0 - 3_1$	3778.85	
159.1	2.9	3776.05	$2_{-1} - 2_0$	3776.13	
160	6.7	3775.44	$0_0 - 1_{-1}$	3775.35	
161	5.0	3773.41	$1_{-1} - 1_1$		3773.46
162	4.2	3772.22			
163	4.5	3771.84	$2_0 - 2_2$		3771.98
			$2_{-2} - 2_1$	3771.71	
164	4.8	3771.33	$8_2 - 8_4$		3771.41
165	6.6	3767.70	$4_{-1} - 4_0$	3767.72	
166	5.4	3767.18	$4_0 - 4_2$		3767.27
			$3_{-1} - 3_1$		3766.96
166.1*		3765.64	$4_2 - 4_4$		3765.77
			$1_0 - 2_{-1}$	3765.92	
			$4_0 - 4_3$	3765.25	
167	5.6	3764.89	$3_{-2} - 3_{-1}$	3764.93	
			$1_{-1} - 2_{-2}$	3764.80	
168	3.1	3764.41	$0_0 - 1_0$		3764.12

TABLE III (CONT'D)

Line No.	Intensity	Observed Wave No. cm ⁻¹	Transition	Calculated Wave No. (011)	Wave No. (110)
169	5.2	3763.67	$7_0 - 7_1$	3763.99	
			$2_1 - 3_{-3}$		3763.75
			$3_{-3} - 3_0$	3763.54	
170	6.6	3762.96	$5_{-1} - 5_2$	3763.22	
171	2.9	3761.98	$7_1 - 7_3$		3762.04
			$2_{-1} - 2_1$		3762.02
172	2.4	3761.11	$6_0 - 6_3$	3761.29	
173	2.7	3757.70	$1_1 - 2_0$	3757.65	
174	6.6	3756.14	$5_{-2} - 5_{-1}$	3756.05	
175	6.3	3755.61	$2_{-2} - 3_{-3}$	3755.49	
			$2_{-1} - 3_{-2}$	3755.73	
176	4.3	3748.55			
177	2.5	3747.84	$7_{-2} - 7_{-1}$	3747.87	
178	9.5	3745.77	$3_{-2} - 4_{-3}$	3745.75	
			$3_{-3} - 4_{-4}$	3745.72	
			$2_0 - 3_{-1}$	3745.68	
			$2_{-1} - 3_{-3}$		3745.80
			$7_0 - 7_2$		3745.65
179	4.8	3743.20	$5_{-4} - 5_{-3}$	3743.32	
			$4_{-3} - 4_{-1}$		3743.30
179.5		3742.58	$3_{-2} - 3_3$	3742.45	
180	6.6	3737.63	$3_0 - 4_{-1}$	3737.68	
181	2.5	3729.59			

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