

## The Asymmetric Rotor. VIII. The Hydrogen Sulfide Band at 6300 $\text{cm}^{-1}$

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chromium as Cr<sup>++</sup> (4 unpaired electrons) and shows that three 3*d* orbitals of the chromium atom are involved in the formation of covalent bonds. The chromium atom is presumably attached by essentially covalent bonds to four acetate oxygen atoms. Kimball<sup>10</sup> has given two stable configurations for a tetravalent atom making use of three *d* orbitals, namely, *d*<sup>3</sup>*s* and *d*<sup>3</sup>*p*. The former is tetrahedral and the latter is an irregular tetrahedron. Although the magnetic evidence does not distinguish between these two possible configurations, it seems likely that the former may be favored. All other chromium (II) compounds which have been studied<sup>3</sup> magnetically previously appear to contain either 2 or 4 unpaired electrons per Cr, corresponding to octahedral covalent bonding or ionic bonding, respectively.

<sup>10</sup> G. E. Kimball, J. Chem. Phys. 8, 188 (1940).

The experimental result that the "tris(8-hydroxyquinoline) chromium (II)" reported by Hume and Stone<sup>3</sup> and tris(8-hydroxyquinoline) chromium (III) gave, within the estimated experimental uncertainty of 3 percent, the same magnetic moment for Cr in addition to the same color and empirical formula indicates that these compounds are actually the same, and that the Cr is in the tripositive oxidation state. It seems likely that the 8-hydroxyquinoline oxidizes the Cr (II) during the course of the preparation, although attempts to find the tetrahydro-8-hydroxyquinoline which might be anticipated as a reduction product in our preparation of the reported compound failed, apparently due to difficulties of separation arising from complexing of the reduction product with the Cr (III).

## The Asymmetric Rotor. VIII. The Hydrogen Sulfide Band at 6300 Cm<sup>-1</sup>\*

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The absorption spectrum of hydrogen sulfide in the region 6140 to 6420 cm<sup>-1</sup> has been measured and the rotational fine structure analyzed through the use of published energy tables for the rigid rotor and a classical correction for centrifugal distortion. The excited state constants giving the best fit are *A*\*=10.39, *B*\*=8.90, and *C*\*=4.55 cm<sup>-1</sup>. The band center is located at 6289.5 cm<sup>-1</sup>.

The value of *I*<sub>C</sub>−*I*<sub>A</sub>−*I*<sub>B</sub> and the strong *Q* branch, indicating the non-vanishing electric moment derivative to be along the least inertial axis, show the upper vibrational level to be the (111) state.

### INTRODUCTION

AT the present time the detailed rotational analysis of only one highly resolved absorption band of hydrogen sulfide has been published. This is the (*n*<sub>σ</sub>,*n*<sub>π</sub>,*n*<sub>δ</sub>)=(130) band at 9911 cm<sup>-1</sup>.<sup>1,2</sup> Hainer and King<sup>3</sup> have analyzed by punched card methods the band envelope at 3.7μ as one-half of the ν<sub>σ</sub>-fundamental. Recently Grady, Cross, and King<sup>4</sup> have reported the analysis of two overlapping bands believed to be the (310) at 10194 cm<sup>-1</sup> and the (400) at 10188 cm<sup>-1</sup>. Up to this time no rotational analysis has been made of a

band involving the δ-mode of vibration. This paper will present a rotational analysis of a band envelope at 1.6μ believed to be the (111) band.

### EXPERIMENTAL

Tank hydrogen sulfide (Ohio Chemical and Manufacturing Company) was twice distilled over phosphorous pentoxide and was immediately used for the spectroscopic investigation. Adequate absorption was obtained with a path-length of 106 cm and a pressure of one atmosphere.

This region was investigated with an automatic recording, one meter vacuum spectrograph which was recently described by Badger, Zumwalt, and Giguère.<sup>5</sup>

The spectrum was taken in the first order of a replica grating with 7500 lines per inch, using a lead sulfide cell as the photosensitive element and a slit width of 0.05 mm, corresponding to 0.85 cm<sup>-1</sup> at 2μ.

The band shows well-defined *P* and *R* branches.

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<sup>1</sup> P. C. Cross, Phys. Rev. 47, 7 (1935).

<sup>2</sup> B. L. Crawford, Jr. and P. C. Cross, J. Chem. Phys. 5, 371 (1937).

<sup>3</sup> R. M. Hainer and G. W. King, J. Chem. Phys. 15, 89 (1947).

<sup>4</sup> Grady, Cross, and King, Phys. Rev. 75, 1450 (1949).

<sup>5</sup> Badger, Zumwalt, and Giguère, Rev. Sci. Inst. 19, 861 (1948).

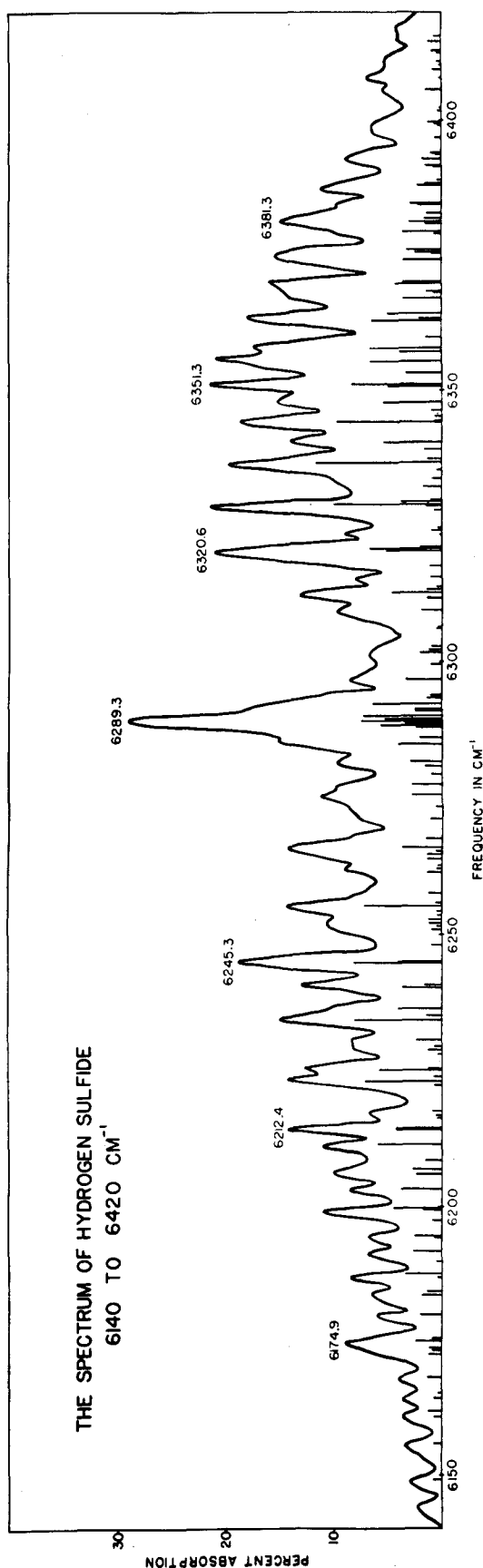


FIG. 1. Calculated and observed band at  $6289.5 \text{ cm}^{-1}$ .

There is an extremely strong absorption located near the center of the band which suggests a collected  $Q$  branch. The experimental resolution seems to be of the order of  $2 \text{ cm}^{-1}$ .

#### VIBRATIONAL ASSIGNMENT

The absorption band at  $1.6\mu$  corresponds to an energy range for which there are six possible vibrational assignments. Dennison<sup>6</sup> has shown that as  $\rho = B/A$  becomes smaller, the  $Q$  branch of type  $A$  bands tends to collect at the center. On the other hand, there is a gap at the center of a type  $B$  band regardless of the value of  $\rho$ . It was thus concluded that this band was an  $A$  type band, i.e., the electric moment oscillates along the least inertial axis. Hence this axis is perpendicular to the symmetry axis,  $n_s$  must be odd and this leaves only two possibilities for the vibrational assignment, (111) and (103). Arguments relating to the relative intensities, to the dependence of the moments of inertia on  $n_s$ , and especially to the value of  $\Delta = I_C - I_A - I_B$  indicate a strong preference for the former. The rotational analysis, however, is independent of the vibrational assignment except for the effect of the symmetry of the excited vibrational state on the selection rules.

#### ANALYSIS

The resolution was not adequate to enable an assignment of specific transitions through the use of the known ground state energies as published with the analysis of the  $9911 \text{ cm}^{-1}$  band.<sup>1</sup> Hence the stochastic procedure of analysis was used.

The energy levels corresponding to an assumed set of inertial parameters for the excited state were readily derived from published tables.<sup>7</sup>

To obtain the relative intensities of the individual lines in the band, it was necessary to combine the published line strengths<sup>8</sup> with appropriate Boltzmann factors determined from the known ground state. These excited state energies, the known ground state energies, and the relative line intensities were then used to synthesize a computed spectrum for comparison with the experimental spectrum.

An initial estimate of the excited state inertial constants was required. The strong transitions in the  $P$  and  $R$  branches are strongly dependent on  $C^*$ , while they are practically independent of  $A^*$  and  $B^*$ . Since the slight convergence of the  $R$  branch indicates that  $C^*$  is slightly less than  $C = 4.732 \text{ cm}^{-1}$ , the value  $C^* = 4.60 \text{ cm}^{-1}$  was used for the first approximation.

The strong transitions of the  $Q$  region are very sensitive to  $A^*$ , being practically independent of  $B^*$  and  $C^*$ , hence the very sharp collected  $Q$  branch requires that  $A^*$  be nearly equal to  $A$  ( $10.37 \text{ cm}^{-1}$ ).

<sup>6</sup> D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

<sup>7</sup> King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).

<sup>8</sup> Cross, Hainer, and King, J. Chem. Phys. 12, 210 (1944).

The transitions involving levels of intermediate energy or  $\tau$ -values are primarily dependent on  $B^*$  although they are more sensitive to the other inertial parameters,  $A^*$  and  $C^*$ , than was true in the previous cases. This dependence can be seen by consulting the table of derivatives previously published.<sup>1</sup> The initial estimates of  $B^*$  were selected such that  $\kappa$  assumed the values of 0.5, 0.4...etc.

The derivative of the transition energies with respect to the inertial constants furnished the means by which these constants could be ascertained accurately with a minimum of calculation. The various inertial constants were readjusted by fitting the transitions most sensitive to each constant until a satisfactory calculated representation of the experimental data was obtained.

To maintain consistency with the original ground state energies, a classical centrifugal stretching correction was applied to the term values of the energy levels.<sup>1,9</sup>

The above procedure allows  $C^*$  to be fixed very closely.  $A^*$  was fixed by integrating the  $Q$  region over a finite slit width as described by Hainer and King.<sup>3</sup> It was possible to vary  $B^*$  over a considerable range without materially affecting the picture; hence, it is the least accurate of the constants.

Approximately 300 transitions were calculated. These are plotted along with the observed spectrum in Fig. 1. Transitions of less than 1.0 in arbitrary intensity units were omitted in the plot unless they contributed materially to the picture. In these units the maximum line intensity is 7.5 and the number of lines with intensity greater than 1.0 is 150. In evaluating the calculated spectrum the effect of an integration of the intensities over a finite slit width must be borne in mind. Figure 1

shows the detail to which the calculated spectrum reproduces the observed absorption.

The excited state constants giving the best fit for the observed spectrum are

$$A^* = 10.39 \pm 0.02 \quad B^* = 8.90 \pm 0.04 \quad C^* = 4.55 \pm 0.01 \\ \nu_0 = 6289.5 \pm 0.5 \text{ cm}^{-1}.$$

## DISCUSSION

Mecke<sup>10</sup> first showed that for water vapor the effective moments of inertia did not satisfy the condition  $I_A + I_B = I_C$  which applies to rigid planar bodies. Darling and Dennison<sup>11</sup> have introduced the parameter  $\Delta = I_C - I_A - I_B$  in their treatment of the water vapor band system. They have given an expression for  $\Delta$  of the following form:

$$\Delta = k_\delta(n_\delta + \frac{1}{2}) + k_\sigma(n_\sigma + \frac{1}{2})$$

which makes use of its near-zero dependence on  $n_\tau$ . Hainer and King<sup>3</sup> point out that this should still be true in the case of hydrogen sulfide, and that  $k_\delta \gg k_\sigma$ . The form of this expression shows that the  $\Delta$  for the (111) state should be three times the value of the (000) state. The results

$$\begin{aligned} (000) \quad k_\delta/2 + k_\sigma/2 &= 0.103 \times 10^{-40} \text{ g cm}^2 \\ (111) \quad 3k_\delta/2 + 3k_\sigma/2 &= 0.32 \end{aligned}$$

confirm this prediction. If  $n_\delta$  were greater than one in the excited state, one would reasonably expect an even larger  $\Delta$ . This evidence leaves little doubt that this is the (111) state.

The authors wish to express their appreciation to Professor R. M. Badger for the use of his spectrograph and to Mr. Thomas Hutton for his aid in carrying out the numerous calculations.

<sup>9</sup> This correction is readily evaluated for individual energy levels and hence has some advantage over methods which involve tedious calculations.

<sup>10</sup> R. Mecke *et al.*, Zeits. f. Physik **81**, 313, 445, 465 (1933).

<sup>11</sup> B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).