Concerning the Q Branch and Analysis of the Hydrogen Sulfide Band at 10100A

Paul C. Cross

Articles you may be interested in

However, from the similarity of the results in the other cases it appears reasonable to conclude that there is a rather definite spectrum characteristic of the O–H group of which the hydrogen atom is engaged in a hydrogen bond. In the substances studied these bonds appear to be quite similar and the distinction between hydrogen and hydroxyl bonds appears to be somewhat artificial. From the rather moderate shift in the O–H frequency in the formation of the bond it appears that the binding of the hydrogen to the oxygen atom to which it originally belonged has not been greatly affected and consequently that the internuclear distance is probably only slightly larger than the normal O–H separation.

RICHARD M. BADGER
SIMON H. BAUER
Gates and Crellin Laboratories of Chemistry,
California Institute of Technology,
Pasadena, California,
March 5, 1937.

* The investigations here briefly mentioned are part of a program of research made possible by a Grant-in-Aid of the National Research Council to one of us (R. M. B.) and will be reported in detail in papers to appear shortly.
[1] Hilbert, Wulf, Hendricks and Liddel, J. Am. Chem. Soc. **58**, 548 (1936).
[2] Bernal and Megaw, Proc. Roy. Soc. London, **A151**, 384 (1935).
[3] W. W. Coblentz, *Investigations of Infra-Red Spectra* (Carnegie Institution, 1906).
[4] F. H. MacDougall, J. Am. Chem. Soc. **58**, 2585 (1936).
[5] Errera and Mollet, Nature **138**, 882 (1936).

Concerning the Q Branch and Analysis of the Hydrogen Sulfide Band at 10100A

Following an unsuccessful attempt to obtain more than seventeen lines in the hydrogen sulfide band at 10100A, Carvin[1] has recently questioned the validity of the previous measurement and analysis of this band.[2]

Carvin cites specifically the four strongest lines of the Q branch and one line of the P branch as definitely missing. Four of these lines were measured on all fourteen plates of the earlier work, while the fifth was measured on twelve of the fourteen plates. These lines were still observable, though greatly broadened, at pressures as high as 4 atmospheres.

An attempt is made here to reproduce portions of two of the best plates of the series upon which the original report and analysis were based. Enlargements of the original plates on process film were contact-printed on process film, and the latter printed on contrast paper. Practically all the lines reported as of intensity 2 or more are visible on these prints, as well as many of intensity 1, but considerable detail is lost in the halftone reproduction (Fig. 1). Since the original plates (Eastman type 1Q) were used beyond the region in which they are most suitable, they show a marked gradation in intensity which renders quite difficult their reproduction with high contrast. In addition, the slight irregularities in intensity resulting from unevenness of the supersensitization in ammonia are so enhanced as to offset a considerable portion of the gain in clarity afforded by the contrast-reproduction process.

The author wishes also to make use of this opportunity to present the evidence which convinces him that the analysis is unquestionably correct. In Fig. 2(b) are shown the observed lines which gave the clue to the analysis, and on the same scale the calculated positions of the transitions assigned to these lines. (The calculated values are from an unpublished work of Crawford and Cross in which this band is treated by the correct centrifugal distortion theory developed by Wilson.[3] The assignments are the same as in
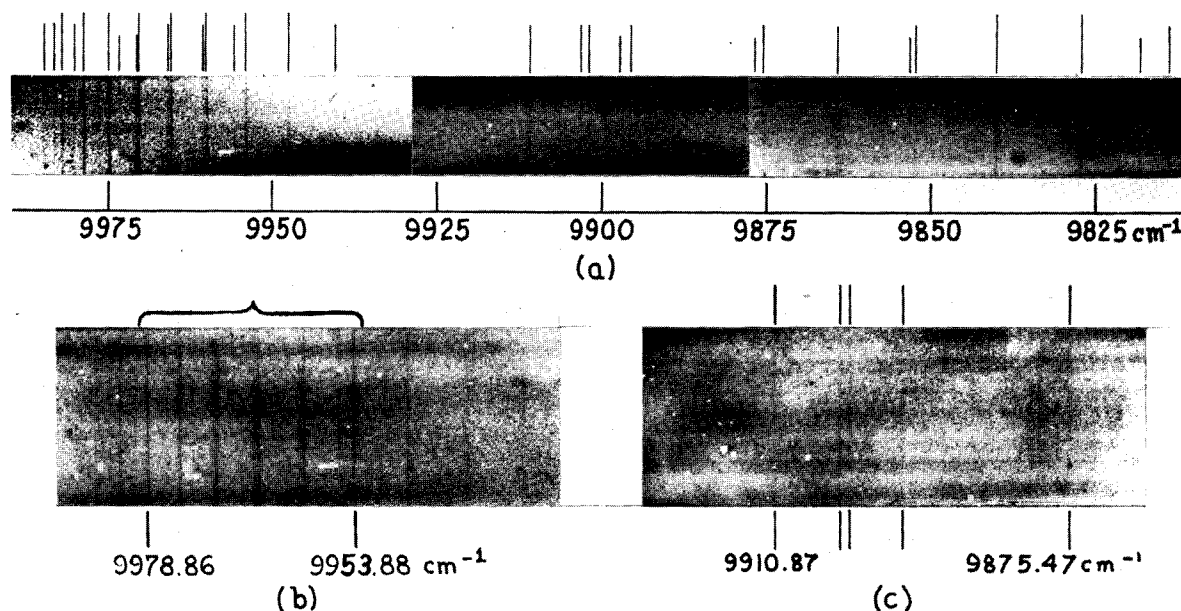

FIG. 1. Absorption band of hydrogen sulfide at 10100A. (a) shows the R, Q and P branches (the latter to 9812 cm^{-1} only) together with the lines given in the original report as having intensities of 5, 4, or 3. (b) shows the R branch, with the brace indicating the group of lines whose satisfactory assignment confirms the correctness of the original analysis. (c) shows the region of the band center, containing the lines of the Q branch from which the original analysis was primarily derived. Special attention is called to the lines reported by Carvin to be "definitely missing."
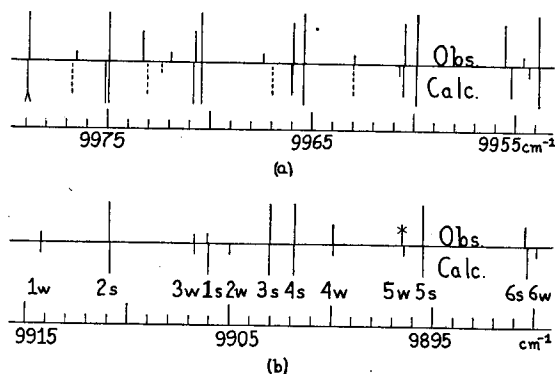
FIG. 2. Comparison of observed and calculated transitions. (a) Region marked by the brace in Fig. 1 (b). The heights of the observed lines are proportional to their intensities (reference 2). Calculated lines originating in levels antisymmetric with respect to the hydrogens are given length 3, while those from symmetric levels are given length 1. Unresolved pairs are given length 4. The full lines indicate transitions of the type $j_{-j+i} \rightarrow (j+1)_{-j-1+i}$, with $i=0$, 1, 2, or 3. Dotted lines represent transitions for which $i > 3$, and are included for the sake of completeness. Detailed assignments may be found in reference 2. (b) Q branch lines of the type $j_j \leftrightarrows j_{j-1}$. Intensities indicated as in Fig. 2 (a). s and w refer to the strong and weak components, respectively, of the pair of lines for a given value of j. The line marked with an asterisk was not given in the original report of this band, but has been located on the reproductions required for this communication.

the former analysis using the classically corrected Wang equation, and only slight changes in the calculated positions are introduced.) Certainly the agreement is all that could be desired. When this region was satisfactorily explained, the unusual "doublet" structure of certain lines in the R branch was automatically accounted for. The observed and calculated lines of this region (marked by the brace in Fig. 1(b)) are shown in Fig. 2(a).

PAUL C. CROSS

Stanford University,
 Stanford University, California,
 March 31, 1937.

[1] F. D. Carvin, J. Chem. Phys. 5, 159 (1937).
[2] P. C. Cross, Phys. Rev. 47, 7 (1935).
[3] E. B. Wilson, Jr., J. Chem. Phys. 4, 260 (1936), and by private communication of unpublished details of the centrifugal expansion treatment.

The Valence Angle in Hydrogen Sulfide

In a recent publication, Sprague and Nielsen[1] have presented data on the infrared spectrum of H_2S which is interpreted as favoring a valence angle of about 85° rather than 92° as previously reported from the rotational analysis of the band at 10100A.[2] The 92° angle may be established by applying the following intensity considerations to the Q branch of this band.

In complete analogy to the case of the H_2 molecule, the rotational wave functions for the H_2S molecule may be divided into two classes: those symmetric and those antisymmetric with respect to interchange of the hydrogen nuclei.[3] In the ground state of H_2S, the antisymmetric states have a statistical weight factor three times that of the symmetric states, and hence lines originating in antisymmetric ground states are approximately three times as strong as analogous lines originating in symmetric states. With an angle of 92°, interchange of the hydrogen nuclei is effected by a rotation through 180° about the axis of intermediate moment of inertia, and the symmetry character of a given rotational state is given by the product of

Dennison·s symmetries (a) and (b).[4] Applied to the Q branch at 10100A, this reasoning yields the intensity pattern plotted in Fig. 2 of the preceding letter, in agreement with the observed intensities.

If the angle were 85°, interchange of the hydrogen nuclei would be effected by a rotation through 180° about the axis of least moment of inertia, and the symmetry character would be given by the second of Dennison·s symmetries, (b). This would require that both transitions of the type $j_j \leftrightarrows j_{j-1}$ be strong for odd values of j and weak for even values of j, in complete disagreement with the observed intensities.

The argument for the 85° angle is partially based on what the authors consider to be an erroneous interpretation of the band at 3.7μ.[5] The suggestion of Sprague and Nielsen that the band center lies near 2685 cm^{-1} yields an average spacing incompatible with the previously derived moments of inertia.[2] Furthermore, the sharpness and high intensity of the lines near 2685 cm^{-1} cannot be reconciled with the typical appearance of rotational bands, either with or without a collected Q branch. On the other hand, the spacing, convergence, and intensities of the observed lines are in satisfactory agreement with the R branch of either ν_σ (ν_3) or ν_π (ν_1) calculated from the known constants for the normal state and constants approximately 1.3 percent smaller for the excited state. (The factor of 1.3 percent was suggested by a rough interpolation between the normal state and the excited state of the 10100A band.) This calculation would place the band center between 2600 and 2620 cm^{-1}; the apparent weakness of the absorption in this region would indicate the absence of a collected Q branch, and hence would require that this band be assigned to ν_π. However, the present unsettled status of the P branch[1, 5-7] makes it very unsafe to draw any definite conclusions based on the apparent absence of a collected Q branch.

Sprague and Nielsen also base their argument on the apparent collected Q branch in the 8.0μ band, which must certainly be assigned to δ_π (ν_2). The oscillation of the electric moment in this vibration is along the symmetry axis, which would accordingly be the axis of least moment of inertia. The authors believe that an alternative explanation of the appearance of this band may be found in the pronounced changes in the least and intermediate moments of inertia which would be expected in this mode of vibration. These changes would produce a pattern markedly different from that of the simplified charts given by Dennison.[3]

These factors, together with certain discrepancies in the data so far reported, make a complete vibrational analysis difficult at this time.

BRYCE L. CRAWFORD, JR.
PAUL C. CROSS

Stanford University,
 Stanford University, California,
 April 12, 1937.

[1] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. 5, 85 (1937).
[2] P. C. Cross, Phys. Rev. 47, 7 (1935).
[3] D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).
[4] D. M. Dennison, Rev. Mod. Phys. 3, 324 (1931).
[5] H. H. Nielsen and E. F. Barker, Phys. Rev. 37, 727 (1931).
[6] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. 43, 375 (1933).
[7] C. R. Bailey, J. W. Thompson and J. B. Hale, J. Chem. Phys. 4, 625 (1936).