

# Raman Spectra of Sulphuric Acid Solutions

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#### Raman Spectra of Sulphuric Acid Solutions

A study of the Raman spectra of sulphuric acid for varying concentrations has been made by Nisi,¹ Woodward,² Bell and Fredrickson,³ Rao,⁴ Woodward and Horner.⁵ Woodward and Horner have been the first to report a decided shift in frequency with decreasing concentration. Using the conventional set-up with a spectrograph which gave a dispersion of 15A/mm at 4300A,

we attempted to check this frequency change. All plates were measured by a comparator and checked by a densitometer. The 4339 and 4916A mercury lines were used as standards. Special precautions were taken to obtain 100 percent sulphuric acid. The acid used had a F.P. of 10.3°C. All concentrations are given in volume percent. The frequency differences (cm<sup>-1</sup>) for various concentrations of sulphuric acid are given in Table I (numbers in paren-

TABLE I.

|   | 100%  | 95%                                    | 75%                                 | 50%   | 25%  | 10%                                 |
|---|---|--|-------------------------------------|---|--|-------------------------------------|
| Group I (b) Group II (b) Group III (s) Group IV (s) | $363\pm7 (4)$<br>$556\pm6 (4)$<br>$905\pm1 (8)$ | 395 ±5 (4)<br>557 ±5 (4)<br>906 ±1 (8) | 417±6 (4)<br>575±2 (4)<br>909±5 (4) | $425\pm3 (3)$<br>$582\pm4 (3)$<br>$887\pm4 (3)$ | $425 \pm 7 (3)$<br>$582 \pm 5 (3)$<br>887 (?)<br>$984 \pm 3 (6)$ | 433 (?)<br>595 ±5 (2)<br>974 ±4 (7) |
| Group V<br>Group VI                                 | 1123±9 (2)                                      | $1027 \pm 2 (4)$<br>$1123 \pm 5 (2)$   | 1027 ±2 (6)                         | $1028 \pm 2 (7)$                                | $1041 \pm 4 (6)$   | 1041 ±3 (4)                         |

thesis indicate intensities; s means sharp lines, b broad). The water bands showed up clearly for 25 and 10 percent. No trace of the 1027 cm<sup>-1</sup> line was found for 100 percent acid.

The data obtained from a study of acid sulphate solutions have shown 427, 593, 979, 1051 cm<sup>-1</sup> to be common frequencies, 6 with 1051 as the strongest. Sulphate solutions show 452, 617, 982, 1106 cm<sup>-1</sup> as common frequencies,<sup>7</sup> with 982 as the most intense. Lines which appear below 50 percent and are most intense at 10 percent have been associated with  $S\overline{O}_4$  ions. Those which appear at 95 percent, increase to maximum intensity around 50 percent, and then decrease, have been called HSO<sub>4</sub> lines. Those most intense at 100 percent have been attributed to H<sub>2</sub>SO<sub>4</sub> molecules. From this it would appear that in our data group IV is associated with the  $S\overline{O}_4$  ion, group V with the HSO<sub>4</sub> ion, and group VI with the H<sub>2</sub>SO<sub>4</sub> molecule. This is in agreement with the results of Woodward and Horner. They, too, found an increase in frequency at lower concentrations for group V.

For the other groups, however, they found the following:

Group 1: Three frequencies 381, 417, 452; with 381 strongest for 100 percent, 417 for 50 percent (due to HSŌ4 ion?), and 452 for 10 percent (due to SŌ4 ion). Both 381 and 417 were found at 100 percent, 417 and 452 at 10 percent.

Group II: Three frequencies 555, 595, 617; 555 strongest for 100 percent, 595 for 50 percent (due to  $HSO_4$  ion), and 617 for 10 percent (due to  $SO_4$  ion).

Group III: Two frequencies 910, 896; 910, 100 to 75 percent, 896, 50 to 10 percent.

For group III our results are in agreement with theirs, but in groups I and II our data seem to indicate a gradual shift in frequency, rather than a shift among three different frequencies. This gradual increase in frequency with greater dilution would seem to indicate some sort of gradual change in the molecular arrangement. It may be pointed out that groups I and II at low concentrations contain frequencies which have been found in solutions containing the HSO<sub>4</sub> ion (427 and 593 cm<sup>-1</sup>).

An attempt was made to obtain the Raman spectra of sulphuric acid solutions in anhydrous acetic acid. The results were rather unsatisfactory because of a strong continuous background. The more intense acetic acid lines (889 and 2942 cm<sup>-1</sup>) were found for all concentrations. Only for 50 percent (by volume) were sulphuric acid lines obtained; these were 582 and 1028 cm<sup>-1</sup>.

The anhydrous acetic acid used had a F.P. of 16.3°C. For the pure acid the following Raman lines were obtained (cm<sup>-1</sup>):

| $\tilde{\nu}$       | $\Delta \widetilde{m{ u}}$ | $\tilde{\nu}$       | $\Delta 	ilde{m{ u}}$ |
|---------------------|----------------------------|---------------------|-----------------------|
| $24444 \pm 1 (3)$   | 2944                       | $22055 \pm 1 (3)$   | 883                   |
| $24408 \pm 1 \ (2)$ | 2945                       | $21767 \pm 1 \ (4)$ | 2938                  |
| $24079 \pm 7(3)$    | 626                        | $21701 \pm 7 (1)$   | 1294 (?)              |
| $23809 \pm 1 (1)$   | 896                        | $21663 \pm 7 \ (1)$ | 1275                  |
| $23266 \pm 7 (1)$   | 1439                       | $21580 \pm 1 \ (2)$ | 1358 or 2936          |
| $22490 \pm 1 (1)$   | 448                        | $21515 \pm 2 (1)$   | 1423                  |
| $22321 \pm 1 (2)$   | 617                        | $21263 \pm 7 (1)$   | 1675                  |

We wish to thank Dr. A. W. Hutchison of the Department of Chemistry for preparing some of the solutions

used, and Dr. L. T. DeVore of the Department of Physics for densitometer measurements of some of the plates.

> RAYMOND M. BELL Myron A. Jeppesen

Department of Physics, Pennsylvania State College, August 18, 1934.

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### The Infrared Absorption Spectrum of Silane

The infrared spectrum of methane has been very extensively investigated and the normal frequencies are well known. It has been shown that the molecule has the form of a regular tetrahedron. Because of its probable similarity to methane it has seemed of interest to study the absorption in the infrared of silane (SiH<sub>4</sub>). With an absorption cell 6 cm long fitted with rocksalt windows the spectrum has been measured to beyond  $11.0\mu$ , by using a Wadsworth spectrometer. Four bands enumerated in the order of their intensities have been located at wave-length positions  $10.5\mu$ ,  $4.58\mu$ ,  $3.187\mu$  and  $5.2\mu$ .

The spectrum appears to be entirely similar to that of methane, the three most intense bands definitely showing P, Q and R branches. Two of these regions, at  $3.187\mu$  and 4.58 u, have also been examined by means of an echellette grating. The first of these falls just in the water vapor absorption region at 3.16µ, which is quite intense during the summer months because of the high humidity. It has been possible by running transmission curves through the cell with and without gas, and by referring to the work of Plyler and Sleator,1 quite successfully to separate the two, especially near the center where no intense water vapor lines exist. The Q branch is very intense and the lines in the P and R branches are separated by a spacing of about 5.5

The  $4.58\mu$  region resembles the other at  $3.187\mu$  a great deal, showing also an extremely intense Q branch. The line separation of the P and Q branches is also about 5.5 cm<sup>-1</sup>

By way of a comparison with the methane spectrum we submit Table I giving the frequency positions of the

Table I. A, observed frequencies in SiH<sub>4</sub> in cm<sup>-1</sup>; B, intensities; C, corresponding frequencies in CH<sub>4</sub> in cm<sup>-1</sup>; D, assignment in Dennison's notation.

| D               | С      | В   | A      |
|-----------------|--------|-----|--------|
| ν4              | 1304   | 50. | 965    |
| 224             | 2600   | 0.1 | 1920   |
| ν3              | 3014   | 20. | 2183.6 |
| v1+v4           | 4217 ) | 1.0 | 3155.9 |
| $\nu_3 + \nu_4$ | 4315 } |     |        |

observed silane bands, their approximate intensities, and what we deem the corresponding frequencies for methane, using the notation of Dennison.

The band found at 3155.9 cm<sup>-1</sup> might correspond either with the frequency  $\nu_1 + \nu_4$  or with  $\nu_3 + \nu_4$ , but probably is to be identified with the former. In this case the inactive frequency  $\nu_1$  should lie at about 2191. The Raman spectrum of SiH4 would definitely settle this question since it is to be expected that  $\nu_1$  would appear very strongly in that spectrum.

The complete spectrum will be discussed in a later communication when the grating curves have been extended to the other bands and a more exhaustive search for the less intense combination bands which will determine the value of the second inactive frequency  $\nu_2$ .

We wish to acknowledge our indebtedness to Professor Warren C. Johnson of the Department of Chemistry at the University of Chicago, who has supplied us with the gas. A grant-in-aid awarded to us by the National Research Council is also acknowledged with appreciation.

> WENDELL B. STEWARD HARALD H. NIELSEN

Mendenhall Laboratory of Physics, Ohio State University, August 20, 1934.

<sup>1</sup> E. K. Plyler and W. W. Sleator, Phys. Rev. 37, 1493 (1931).

#### Note on Electric Moments and Infrared Spectra. A Correction

In connection with a recent article1 under the above title, the writer greatly regrets having overlooked an article<sup>2</sup> by Bartholomé dealing with the above subject as applied to the hydrogen halides. Bartholomé has developed theory, and has made intensity measurements on the  $0\rightarrow1$ bands of HCl, HBr, HI by a new and apparently improved method; he has made no intensity measurements on other bands, but finds the  $0\rightarrow 2$  band of HI qualitatively very weak. Bartholomé finds the intensity of the 0→1 band of HCl to be only about one-fourth as intense as the best previous data (Bourgin) indicated.

Combining Bartholomé's 0→1 intensity with Dunham's 0→2 intensity (which, however, although supposed to be more accurate than Bourgin's 0→1 intensity, was measured by the same method as the latter), one gets instead of Eq. (1) of reference 1 the following:

$$\mu_{\text{HCl}} \times 10^{18} = 1.03 \pm (0.52\xi + [-0.54\xi^2 \text{ or } +1.67\xi^2]).$$

The coefficient of ξ² was calculated by means of Dunham's equations.3 Bartholomé's new data also permit writing equations for HBr and HI:

$$\mu_{\text{HBr}} \times 10^{18} = 0.79 \pm 0.51 \xi + \cdots,$$
  
 $\mu_{\text{HI}} \times 10^{18} = 0.38 \pm 0.25 \xi + \cdots.$ 

The HI band, although weak, is stronger than previous work of Czerny indicated.

Bartholomé's data appear to be consistent with either of the two types of curves (Figs. 1a, 1b) shown in reference 1. Bartholomé gives a figure similar to Fig. 1b, with reasons for preferring this to the Fig. 1a or other types. Bartholomé shows theoretically that  $\mu$  should increase as  $r^3$  for r near zero. His argument that the  $\mu(r)$  curve should rise, near