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Microwave Spectrum, Structure, and Dipole Moment of Sulfuric Acid

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Abstract: The microwave spectra of the normal, ^{34}S, D$_1$, and D$_2$ isotopic species of gaseous sulfuric acid have been assigned. Rotational and centrifugal distortion constants were obtained. A conformation with C_2 symmetry has been identified. Important structural parameters are r(OH) = 0.97 (1) Å, r(SO$_1$) = 1.574 (10) Å, r(SO$_2$) = 1.422 (10) Å, $\angle$H$_1$O$_1$S = 108.5 (15), $\angle$O$_1$SO$_1$' = 101.3 (10)°, $\angle$O$_2$SO$_2$' = 123.3 (10)°. The torsional angle O$_1$SO$_1$H is –90.9 (10)° and the two SO$_2$ planes form an angle of 88.4 (1)°. The dipole moment was determined to be 2.725 (15) D. A comparison of the derived structural parameters with related species is presented, and the possibility of the undetected existence of other stable conformations of sulfuric acid is discussed.

Introduction

It is well known that the concentration of discrete sulfuric acid molecules above solutions of H$_2$SO$_4$ is negligible under ordinary conditions. Thermodynamic data indicate that concentrated solutions of at least 90% H$_2$SO$_4$ and temperatures of about 80 °C are needed to generate H$_2$SO$_4$ vapor pressures of about 0.1 to 1 Pa.[1]

In spite of its low volatility there has been growing interest in the infrared spectral properties of H$_2$SO$_4$ vapor.[2-6] Such studies have been directed at establishing methods for monitoring its presence in emissions from hot smoke stacks, for example. The information obtained in these efforts may also provide insight on the gas-phase formation process of H$_2$SO$_4$ from SO$_2$[7,8] and, ultimately, the formation of acid aerosols.[9,10]

Earlier infrared (IR) studies[11-13] of the vapors above hot H$_2$SO$_4$ were directed at identifying the fundamental vibrational frequencies and the structure of H$_2$SO$_4$. These showed that it exists mostly as monomeric (HO)$_2$SO$_2$ species with identifiable SO$_2$, S–(OH)$_2$, and OH stretching bands. It was concluded that the heavy atom framework had an approximate tetrahedral configuration with C_{2v} symmetry similar to species such as F$_2$SO$_2$ and (CH$_3$)$_2$SO$_2$. This structure was also consistent with electric deflection experiments which showed that H$_2$SO$_4$ was polar.[14]

Although the orientation of the OH groups is not determined from the IR studies, the usual approach when determining symmetry species and force constants has been to assign overall C_{2v} symmetry to the molecule.[11,15-17] The only molecular orbital

calculation (CNDO/2) also emphasized the C_{2v} symmetry species[8] which has the hydroxyl groups pointing toward and bisecting the terminal SO$_2$ group. The compact C_{2v} conformer corresponds to the t,t isomers in the Discussion.

We report here the microwave spectra of four isotopic species of H$_2$SO$_4$ from which we have determined a detailed structure. The most unusual finding is that the overall symmetry is not C_{2v} but C_2. The OH moieties are rotated approximately 90° from the compact C_{2v} conformation. There is also evidence for a small twist in the heavy atom framework about the C_2 axis so that the frame is also not precisely C_{2v} symmetry. These results and their implications regarding the electronic structure of H$_2$SO$_4$ as well as its structure in the liquid and solid states[18,19] will be discussed below.

Experimental Section

Spectrometer. Portions of the spectrum between 60 and 114 GHz were scanned using a recently constructed, computer-automated, spectrometer. The parallel plate Stark cell is approximately 1 m in length with approximately a 2-mm spacing between plates. The cell was designed so that all internal surfaces could be heated by wrapping the entire cell with heating tapes. Thus, condensation of the material under study, e.g., H$_2$SO$_4$, within the cell is prevented. A more detailed description of the spectrometer and millimeter wave cell has been reported elsewhere[20] and will not be repeated here. Stark modulation techniques were used throughout the course of the experiment. This was augmented by radio-frequency-microwave double resonance (RFMDR) for confirming some of the ^{34}S transitions which occurred in dense regions of the spectrum close to the much stronger ^{32}S transitions.

In a typical experiment, approximately 15 mL of sample was placed in a 20-cm long boat which was inserted into the center of the cell below the waveguide. All parts of the cell except the sample region were then warmed to 130–160 °C. Finally, the sample temperature was slowly raised to ∼100 °C. Continuous pumping with a mechanical pump and liquid nitrogen traps provided a continuous flow of H$_2$SO$_4$ vapor through the plates under these conditions. During the initial stage of heating, spectral lines of SO$_2$ were observed. After a heating period of ∼1 h the intensity of these lines diminished appreciably. One charge of H$_2$SO$_4$ provided 12–16 h of measurement time.

No reliable measurements of the vapor pressure could be made, but the spectral intensity and line widths indicated that total pressure during experiments was similar to those estimated from the thermodynamic data (∼1–3 Pa).[1]

Materials. Reagent grade, 95–98% H$_2$SO$_4$ was used. Sulfuric acid-d_2 (96% in D$_2$O), minimum isotopic purity 99 atom % D, was obtained commericially. This material was used unadulterated for the measurements on the doubly deuterated, D$_2$, species and mixed about 3:2 (D$_2$SO$_4$:H$_2$SO$_4$) when making measurements on the singly deuterated, D$_1$, species (HDSO$_4$).

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Table I. Rotational Transitions of H_2SO_4

transition	ν (MHz)[a]	$\Delta\nu$ (MHz)[b]	transition	ν (MHz)	$\Delta\nu$ (MHz)	transition	ν (MHz)	$\Delta\nu$ (MHz)
$6_{3,3}-5_{2,3}$	60 668.59	-0.06	$10_{3,7}-9_{2,7}$	101 480.86	0.15	$11_{5,7}-10_{4,7}$	111 612.31	0.02
$6_{4,2}-5_{3,2}$	60 861.50	0.06	$10_{4,7}-9_{3,7}$	101 503.07	-0.37	$11_{7,4}-10_{6,4}$	111 617.32	0.12
$6_{1,5}-5_{0,5}$	60 935.35	0.47	$10_{2,8}-9_{1,8}$ }	101 544.66[c]	0.45	$11_{6,6}-10_{5,6}$	111 629.15	0.10
$6_{3,4}-5_{2,4}$	60 939.80	-0.27	$10_{3,8}-9_{2,8}$ }		-0.85	$11_{3,8}-10_{2,8}$	111 661.00	0.61
$6_{2,5}-5_{1,5}$	60 946.00	0.27	$10_{6,5}-9_{5,5}$	101 574.71	-0.16	$11_{4,8}-10_{3,8}$	111 667.05	-0.37
$6_{4,3}-5_{3,3}$	61 060.32	-0.22	$10_{1,9}-9_{0,9}$ }	101 594.99[d]	-0.09	$11_{2,9}-10_{1,9}$ }	111 719.42[c]	0.14
$6_{5,1}-5_{4,1}$	61 317.72	0.34	$10_{2,9}-9_{1,9}$ }			$11_{3,9}-10_{2,9}$ }		-0.19
$6_{5,2}-5_{4,2}$	61 353.12	-0.27	$10_{7,3}-9_{6,3}$	101 775.30	-0.12	$11_{1,10}-10_{0,10}$ }	111 757.44[d]	-0.05
$6_{6,0}-5_{5,0}$ }	61 730.83[c]	1.26	$10_{7,4}-9_{6,4}$	101 852.61	-0.07	$11_{2,10}-10_{1,10}$ }		
$6_{6,1}-5_{5,1}$ }		0.00	$10_{8,2}-9_{7,2}$	102 221.46	0.13	$11_{7,5}-10_{6,5}$	111 817.39	0.18
$8_{3,5}-7_{2,5}$	81 056.65	0.18	$10_{8,3}-9_{7,3}$	102 227.85	0.08	$11_{8,3}-10_{7,3}$	112 126.95	0.07
$8_{5,3}-7_{4,3}$	81 066.90	-0.02	$10_{9,1}-9_{8,1}$ }	102 619.00[c]	0.02	$11_{8,4}-10_{7,4}$	112 156.53	-0.08
$8_{4,5}-7_{3,5}$	81 212.24	0.09	$10_{9,2}-9_{8,2}$ }		-0.22	$11_{9,2}-10_{8,2}$ }	112 546.15[c]	1.66
$8_{1,7}-7_{0,7}$ }	81 268.65[c]	-0.09	$10_{10,0}-9_{9,0}$ }	103 008.75[e]	-0.09	$11_{9,3}-10_{8,3}$ }		-0.20
$8_{2,7}-7_{1,7}$ }		-0.79	$10_{10,1}-9_{9,1}$ }			$11_{10,1}-10_{9,1}$ }	112 937.95[e]	-0.20
$10_{5,5}-9_{4,5}$	101 080.17	-0.05	$11_{6,5}-10_{5,5}$	111 209.35	0.00	$11_{10,2}-10_{9,2}$ }		
$10_{6,4}-9_{5,4}$	101 267.30	-0.11	$11_{5,6}-10_{4,6}$	111 268.10	0.16	$11_{11,0}-10_{10,0}$ }	113 327.41[e]	0.12
$10_{4,6}-9_{3,6}$	101 294.00	-0.46	$11_{4,7}-10_{3,7}$	111 533.90	0.12	$11_{11,1}-10_{10,1}$ }		
$10_{5,6}-9_{4,6}$	101 475.20	-0.12						

[a] Frequencies were typically measured to 0.1–0.2 MHz. [b] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. [c] These transitions were unresolved and therefore not included in the fit. [d] This transition exists as a degenerate pair. Only one of the pair is included in the fit. [e] This transition exists as a degenerate pair. The one that is spin favored is included in the fit, i.e., $K_{\text{oblate}} = \text{odd}$.

Table II. Rotational Transitions of D_2SO_4

transition	ν (MHz)[a]	$\Delta\nu$ (MHz)[b]	transition	ν (MHz)	$\Delta\nu$ (MHz)	transition	ν (MHz)	$\Delta\nu$ (MHz)
10_6-9_5[c]	97 156.77	-0.20	$11_{5,7}-10_{4,7}$	105 597.56	0.18	$12_{4,8}-11_{3,8}$	113 865.35	-0.05
			$11_{6,5}-10_{5,5}$ }	106 419.74[d]	0.28	$12_{4,9}-11_{3,9}$	114 105.67	0.04
10_7-9_6	97 976.85	-0.06	$11_{6,6}-10_{5,6}$ }		-0.11	$12_{5,7}-11_{4,7}$	114 835.88	0.31
10_8-9_7	98 795.26	0.03	11_7-10_6	107 240.90	-0.14	$12_{5,8}-11_{4,8}$	114 859.00	-0.05
$10_{10}-9_9$	100 429.25	0.05	11_8-10_7	108 060.10	0.06	$12_{6,6}-11_{5,6}$ }	115 680.30[d]	-0.06
$11_{2,9}-10_{1,9}$	103 388.28	0.11	11_9-10_8	108 877.82	0.03	$12_{6,7}-11_{5,7}$ }		-1.08
$11_{3,8}-11_{2,8}$	103 669.04	-0.06	$11_{10}-10_9$	109 694.63	-0.01	12_7-11_6	116 504.26	-0.07
$11_{1,10}-10_{0,10}$	103 892.26	0.09	$11_{11}-10_{10}$	110 510.68	0.02	12_8-11_7	117 324.25	-0.03
$11_{2,10}-10_{1,10}$	104 159.26	-0.10	$12_{2,10}-11_{1,10}$	112 833.80	-0.23	12_9-11_8	118 142.65	0.09
$11_{3,9}-10_{2,9}$	104 276.14	-0.03	$12_{3,9}-11_{2,9}$	112 918.47	0.13	$12_{10}-11_9$	118 959.65	-0.10
$11_{4,7}-10_{3,7}$	104 665.66	-0.17	$12_{1,11}-11_{0,11}$	113 414.85	0.40	$12_{11}-10_{10}$	119 776.02	-0.02
$11_{4,8}-10_{3,8}$	104 817.44	0.13	$12_{2,11}-11_{1,11}$	113 610.77	-0.34			
$11_{5,6}-10_{4,6}$	105 586.16	0.13	$12_{3,10}-11_{2,10}$	113 645.35	-0.19			

[a] Frequencies were typically measured to 0.1–0.2 MHz. [b] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. [c] When K_{oblate} is omitted, the transition exists as a degenerate doublet. Only one of the pair is included in the fit, with preference given to the more intense component when alternating spin statistics are involved ($K_{\text{oblate}} = \text{even for } D_2SO_4$). [d] These transitions were unresolved and thus not included in the fit.

Results

Spectral Assignment. Assignment of the spectrum was guided by frequency predictions based on various structural models. Consideration of the IR data and plausible structural parameters suggested that H_2SO_4 would be a near-spherical top with rotational constants clustered near 5 GHz. Because of the asymmetry in the two kinds of SO bonds and OSO angles, the three rotational constants were predicted to vary between 4.7 and 5.3 GHz. Changes in the torsional angles of the two OH groups did not markedly affect the rotational constants. However, this did have pronounced effects on the selection rules. Depending on the OH orientation, μ_a, μ_b, or μ_c selection rules or combinations could be expected. Regardless of the selection rules, most of the predictions provided spectra with dense transition regions at integer multiples of 10 GHz.

Two transition regions were found in the spectral search near 101.5 and 111.5 GHz which were clearly the dense regions predicted from these models. The pattern of the most intense lines in those regions and the direction and rate of frequency shift of their Stark effects were characteristic of μ_c selection rules. It was also apparent from intensity alternations between transitions differing by one unit in the K_0 value that the molecule possessed a C_2 symmetry axis. The transitions with odd K_0 values were three times more intense than those with even K_0 values in accord with the statistical weights for a C_2 symmetry axis along the c inertial axis.

The assigned transitions are shown in Table I. The derived rotational and centrifugal distortion constants are listed in Table IV. For fitting of the transitions, the centrifugal distortion model

of Watson was employed using the computer program developed by Kirchhoff.[21,22] Frequency shifts from the predicted rigid rotor positions were small. For the $J = 11 \leftarrow J = 10$ transitions, the centrifugal distortion corrections systematically increased from 4 to 11 MHz as K_p ranged between its minimum and maximum value.

The assigned transitions and the derived constants for the D_1, D_2, and ^{34}S species are listed in Tables II–IV, respectively. The D_1 and D_2 species had quite different asymmetry ($\kappa = -0.46$ and -0.82, respectively) from the normal isotope ($\kappa = +0.03$) resulting in transitions spread over a wider frequency range for a given J' $\leftarrow J''$ region. Nevertheless, the μ_c selection rule was maintained and the assignments proceeded similarly to the normal species. For the D_2 species, the transitions with even K_0 values were now more intense than those with odd K_0 values. Bose–Einstein statistics should give such an alternation in intensity with nuclear spin weights of 2:1.

Alternation of intensity was absent for transitions of the D_1 species. The D_1 species does not possess a symmetry axis, and dipole moment components along two or three inertial axes should be present. Although μ_a and/or μ_b are expected to be small and no transitions were assigned to them, the fast Stark effects observed for a number of the assigned transitions indicated that μ_a was nonvanishing. This arose for transitions with high K_p values where the prolate asymmetry splitting becomes small. These asymmetry doublets are connected by μ_a matrix elements with small energy

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Table III. Rotational Transitions of HDSO$_4$ and H$_2{}^{34}$SO$_4$

transition	ν (MHz)^a	$\Delta\nu$ (MHz)^b	transition	ν (MHz)	$\Delta\nu$ (MHz)	transition	ν (MHz)	$\Delta\nu$ (MHz)
HDSO$_4$			HDSO$_4$			H$_2{}^{34}$SO$_4$		
$10_{4,6}$-$9_{3,6}$	97 748.00	-0.12	$11_{3,8}$-$10_{2,8}$	107 693.10	0.05	$8_{3,5}$-$7_{2,5}$	81 027.80	0.15
$10_{3,7}$-$9_{2,7}$	97 763.40	0.07	$11_{5,6}$-$10_{4,6}$	107 947.53	-0.15	$8_{4,5}$-$7_{3,5}$	81 186.70	-0.27
$10_{2,8}$-$9_{1,8}$	98 234.32	-0.18	$11_{2,9}$-$10_{1,9}$	108 148.55	-0.12	$10_{3,7}$-$9_{2,7}$	101 446.80	0.11
$10_{3,8}$-$9_{2,8}$	98 383.40	0.02	$11_{4,8}$-$10_{3,8}$	108 173.71	-0.01	$10_{4,7}$-$9_{3,7}$	101 470.60	0.01
$10_{4,7}$-$9_{3,7}$	98 416.14	0.02	$11_{3,9}$-$10_{2,9}$	108 225.74	-0.13	$10_{1,9}$-$9_{0,9}$	101 562.60^e	0.00
$10_{1,9}$-$9_{0,9}$	98 488.45	0.18	$11_{1,10}$-$10_{0,10}$	108 356.04	0.20	$10_{2,9}$-$9_{1,9}$		
$10_{2,9}$-$9_{1,9}$	98 499.51	0.15	$11_{2,10}$-$10_{1,10}$	108 360.27	-0.25	$10_{7,3}$-$9_{6,3}$	101 751.70	0.07
$10_{5,5}$-$9_{4,5}$	98 501.91	0.11	$11_{5,7}$-$10_{4,7}$	108 405.25	-0.03	$10_{9,1}$-$9_{8,1}$	102 590.00^d	0.28
$10_{5,6}$-$9_{4,6}$	98 770.70	-0.10	$11_{6,5}$-$10_{5,5}$	108 859.51	0.04	$10_{9,2}$-$9_{8,2}$		-0.07
$10_{6,4}$-$9_{5,4}$	99 346.36	0.09	$11_{6,6}$-$10_{5,6}$	108 946.35	0.08	10_{10}-9_9	102 977.93	-0.05
$10_{6,5}$-$9_{5,5}$	99 379.01	-0.18	$11_{7,4}$-$10_{6,4}$	109 611.50	-0.06	$11_{4,7}$-$10_{3,7}$	111 494.30	-0.07
$10_{7,3}$-$9_{6,3}$	100 058.30	0.21	$11_{7,5}$-$10_{6,5}$	109 618.40	0.29	$11_{5,7}$-$10_{4,7}$	111 576.50	0.01
$10_{7,4}$-$9_{6,4}$	100 059.50	-0.34	$11_{8,3}$-$10_{7,3}$	110 303.90^d	0.01	$11_{2,9}$-$10_{1,9}$	111 683.30^d	0.00
10_8-$9_7{}^c$	100 742.56	0.00	$11_{8,4}$-$11_{7,4}$		-0.24	$11_{3,9}$-$10_{2,9}$		-0.36
10_9-9_8	101 422.04	-0.02	11_9-10_8	110 985.82	0.02	11_{10}-10_9	112 905.62	-0.03
10_{10}-9_9	102 100.13	0.10	11_{10}-10_9	111 664.60	-0.12	11_{11}-10_{10}	113 292.99	-0.05
$11_{4,7}$-$10_{3,7}$	107 406.91	0.18	11_{11}-10_{10}	112 341.79	-0.57			

^{a} Frequencies were typically measured to 0.1-0.2 MHz. ^{b} $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. ^{c} When K_{oblate} is omitted, the transition exists as a degenerate doublet. Only one of the pair is included in the fit, i.e., K_{oblate} = odd for H$_2{}^{34}$SO$_4$. ^{d} These transitions were not resolved and not included in the fit. ^{e} This transition occurs as a degenerate pair; only one of the pair was included in the fit.

Table IV. Rotational and Centrifugal Distortion Constants for Sulfuric Acid

parameter	H$_2{}^{32}$SO$_4$	H$_2{}^{34}$SO$_4$	HD^{32}SO$_4$	D$_2{}^{32}$SO$_4$
A'' (MHz)	5160.606 (36)^a	5159.040 (77)	5122.307 (42)	5042.420 (24)
B'' (MHz)	5024.534 (27)	5023.043 (57)	4831.917 (33)	4651.802 (28)
C'' (MHz)	4881.02 (12)	4881.20 (30)	4725.747 (65)	4613.252 (40)
τ_1 (kHz)	-8.33 (75)	-6.1 (25)	-9.26 (92)	-5.27 (62)
τ_2 (kHz)	-2.77 (25)	-2.01 (84)	-3.11 (30)	-1.80 (21)
τ_3 (MHz)^b	2.7 (11)	0.2 (24)	2.28 (33)	4.31 (28)
τ_{aaaa} (kHz)	-8.98 (64)	-9.5 (15)	-7.35 (80)	-11.13 (41)
τ_{bbbb} (kHz)	-6.78 (47)	-7.19 (75)	-6.97 (55)	-5.19 (40)
τ_{cccc} (kHz)	-12.8 (79)	5 (15)	-9.6 (22)	-6.87 (82)

^{a} The numbers in parentheses are the standard deviations of the fit and refer to the last digits given. ^{b} τ_3 is not an independently determinable parameter but is fixed by setting $R_6 = 0$. See ref 22.

denominators; thus even a small dipole component results in appreciable Stark shifts of transitions involving these levels.

The ^{34}S transitions involving either the large or small K_0 values could be readily assigned. For the former case, near degeneracies occur in the oblate limit connected by μ_c. This led to fast Stark effects and identification at very low Stark modulation voltages when few other transitions appeared or by using RFMDR modulation. The levels with small K_0 generally occurred in sparse spectral regions where no other nearby candidates could be found. The considerable effort required to assign additional ^{34}S transitions did not seem warranted since the available data confirmed that the sulfur was near the center of mass. This circumstance limits the determination of the sulfur position even if higher precision rotational constants were obtained.

A sizable number of weaker transitions remain unassigned in the spectra of all species, the majority of which fall near the assigned transitions. Also, the entire spectrum between the 10 → 11 and 11 → 12 regions for H$_2$SO$_4$ has been scanned at high sensitivity. No readily apparent dense regions or "clusters" were observed although a number of weak transitions were observed as well as several with somewhat greater intensity. Most of these transitions are undoubtedly attributable to excited vibrational states, and a subsequent investigation of these features could be worthwhile. In the IR study, three fundamental frequencies were assigned in the region of 380 to 400 cm^{-1}. Two OH wags (torsions) were also estimated to occur near 265 cm^{-1}, although no direct data are presented for them. These low-lying states are undoubtedly responsible for a number of the weaker satellite transitions observed.

Without further work on these low-lying states, nothing definite can be deduced regarding the potential function for rotation of the OH group. Nevertheless, it is clear that for the assigned transitions there is no evidence for any torsional perturbations, tunneling splittings, or unusual centrifugal distortion effects as-

sociated with them. The observed spectrum of H$_2$SO$_4$ appears like that of a typical semirigid species.

Dipole Moment. The molecular dipole moment was determined as $\mu_c = 2.725$ (15) D from measurements of the frequency shifts vs. applied electric field for the $M = 1$ and $M = 2$ components of the $6_{43} - 5_{33}$ transition. Four different fields were used for each Stark component, thus providing eight measurements of the unknown μ_c. The data were least squares fit to

$$\Delta\nu = (a_c + b_c M^2) E^2 \mu_c^2$$

where $E = V/d$ is the electric field. V is the applied voltage. The value of d, the parallel plate separation, was determined at 100 °C by calibration with the Stark lobe of the $J = 1 \leftarrow J = 0$ transition of CH$_3$F at 51072.16 MHz. The dipole moment of CH$_3$F was taken as $\mu = 1.8585$ (5) D.[23] The constants a_c and b_c are the usual second-order coefficients calculated by a standard program.[24] For the $6_{43} - 5_{33}$ transition they are $a_c = 2.4048 \times 10^{-8}$ and $b_c = -3.8759 \times 10^{-6}$. The fitting process gave $\mu_c = 2.7246$ (50) D. Using 3σ as the uncertainty estimate results in $\mu_c = \mu_{\text{total}} = 2.725$ (15) D.

Structure Calculation. The intensity alternations in the H$_2$SO$_4$ and D$_2$SO$_4$ species unambiguously establish the presence of a C_2 symmetry axis along the c inertial axis. The determination of the overall molecular symmetry as C_{2v} or C_2 can in principle be determined from the planar moments of inertia. Their values are listed in Table V.

If the hydrogen atoms lie in a symmetry plane, then either P_{aa} or P_{bb} should remain unchanged upon deuteration. The listed values suggest that nonvanishing values for all three hydrogen

(23) Wofsy, S. C.; Muenter, J. S.; Klemperer, W. *J. Chem. Phys.* **1971**, *55*, 2014-2019.

(24) Beaudet, R. Ph.D. Thesis, Harvard University, Cambridge, Mass., 1961. Program modified by W. H. Kirchhoff to include higher order terms.

Table V. Moments of Inertia and Planar Moments[a] (u A²)

	H₂SO₄	H₂³⁴SO₄	HDSO₄	D₂SO₄
I_a	97.9302	97.9599	98.6624	100.2255
I_b	100.5823	100.6121	104.5918	108.6416
I_c	103.5396	103.5358	106.9416	109.5494
P_{aa}	53.0959	53.0940	56.4355	58.9827
P_{bb}	50.4438	50.4418	50.5061	50.5667
P_{cc}	47.4864	47.5181	48.1563	49.6588

^{a} $P_{aa} = (1/2)(I_c + I_b - I_a) = \Sigma ma^2$ and similarly for P_{bb} and P_{cc}.

Table VI. Principal Axes Coordinates (A) for H₂SO₄ by Method I[a]

atom[b]	a	b	c
S	0.0	0.0	0.1244
O₁	−0.8370	−0.8820	−0.8651
O₁′	0.8370	0.8820	−0.8651
H₁	−1.6708	−0.4438	−1.0496
H₁′	1.6708	0.4438	−1.0496
O₂	−0.8851	0.8869	0.8069
O₂′	0.8851	−0.8869	0.8069

^{a} Substitution coordinates for S and H using ³⁴S and D₂SO₄ data. Other coordinates obtained by fitting r(OH) = 0.96 A, I_a, I_b, I_c for normal species and $I_{ab} = \Sigma m_i c_i = 0$. ^{b} See Figure 1 for atom numbering.

coordinates are required. However, the observed increase in P_{bb} upon deuteration is not so large as to completely rule out the C_{2v} structure since it might arise partially or entirely from vibration–rotation interactions. A contribution from such an effect is evident since the hydrogen coordinate, b_H, varies when calculated by Kraitchman's method[25] using different isotopic data. A value of 0.3278 Å is obtained from the D₀ and D₁ data while it increases to 0.4438 Å with the D₀ and D₂ data. The poor agreement indicates the presence of some vibration–rotation effects. Deviations of this size are not unusual given the small change in P_{bb} upon deuteration and the fact that such effects are usually largest when involving H-atom substitution.

Fortunately, the values for the other hydrogen coordinates aid in the confirmation of overall C_2 symmetry. The values for a_H and c_H obtained from the D₂ isotope shifts are listed in Table VI. The large value for the c coordinate is inconsistent with a compact C_{2v} form where the OH bond straddles the terminal SO₂ group in a trans, trans configuration (t,t). For such a conformer, the

t,t
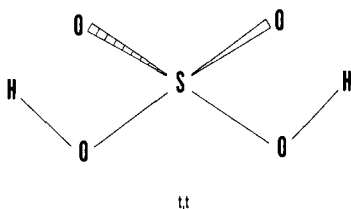
H atoms must lie close to the ab plane resulting in c coordinates of around 0.2 to 0.3 Å. An extended C_{2v} conformer (cis, cis configuration c,c), with the OH groups rotated 180° away from

c,c
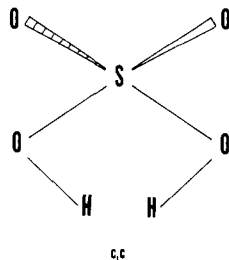
the terminal SO₂ group, also cannot be accommodated plausibly

(25) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17–24.

by the isotopic data. In fact, such a form should result in μ_a selection rules.

With C_2 symmetry, there are eight independent structural parameters for H₂SO₄. The data for the normal and ³⁴S species along with one of the deuterated species provide seven independent moments of inertia. The data for the remaining deuterated species are not sufficiently independent to help uniquely determine the detailed parameters, but they do provide a check on the analysis. Hence there are a variety of procedures which can be employed to determine the atom coordinates and structural parameters.

Table VI lists one set of coordinates. The sulfur and hydrogen coordinates were calculated by the substitution procedure.[25] Nygaard's formulas were used to obtain the H coordinates from the D₂ species isotope shifts.[26] The oxygen coordinates were determined by fixing r(OH) = 0.96 Å and fitting the following equations for the H₂SO₄ species: I_a^0, I_b^0, I_c^0, $I_{ab} = \Sigma m_i c_i = 0$. This procedure is called method I and the resultant structural parameters are listed in Table VII. The structure called I′ was derived the same way except that r(OH) was fixed at 0.98 Å. This change primarily affects the other parameters associated with the OH group.

A slightly different structure results if the same procedure is employed except that the hydrogen coordinates are calculated by Kraitchman's single substitution equations from the D₁ isotope shifts.[25] The hydrogen coordinates become a = 1.6994 Å, b = 0.3278 Å, and c = 1.0460 Å. These coordinates along with the assumption r(OH) = 0.96 results in the structure listed under II.

Structure III was determined from hydrogen and oxygen coordinates obtained by least-squares fitting the nine planar moments of inertia from the D₀, D₁, and D₂ species along with $I_{ab} = \Sigma m_i c_i = 0$.[27] The root-mean-square deviation of the moments fitted was 0.025 u Å². With this procedure, the value of r(OH) was also fixed at 0.96 Å and the sulfur coordinates were set to the values determined by the Kraitchman procedure in order to guarantee convergence.

The structures derived by methods I–III are very similar except for the parameters associated with the H atoms. The differences arise primarily from the ambiguity in assuming a range of values for r(OH) while smaller contributions result from variations arising from the set of isotopic data chosen to locate the hydrogens. It is also informative to estimate the uncertainties introduced because the sulfur atom is near the center of mass. From the Costain rule,[27] the sulfur coordinate is expected to have an uncertainty of about 0.01 Å. Structure IV shows the propagation of the uncertainty in structural parameters when using the same procedure as method I except that the sulfur coordinate (c_S) is increased by 0.01 Å.

The structure in the last column of Table VII takes into account these difficulties in locating the sulfur and hydrogen atoms. It is essentially an average of structures I, I′, and IV with uncertainties sufficient to cover their spread in values. This is considered the best estimate of the structure with the available data.

Discussion

Conformation. The conformation established can be seen from Figure 1. The O₁SO₁H₁ dihedral angle of −90.9° implies that the two planes defined by atoms O₁SO₁ and SO₁H₁ are very nearly perpendicular.[28] In contrast to a compact C_{2v} geometry where both OH groups bisect the terminal SO₂ group, the OH bonds have rotated past the SO₂ and SO₂′ bonds resulting in dihedral angles of 20.8° with them. It is also interesting that the two OSO planes (O₁SO₁′ and O₂SO₂′) are not precisely perpendicular but deviate from this by 1.6°.

Since most work in the literature previously assumed the compact C_{2v} symmetry, it may seem surprising to identify a different stable conformation. Actually there does not appear to

(26) Nygaard, L. *J. Mol. Spectrosc.* **1976**, *62*, 292–293.

(27) The program STRFIT was used. See: Schwendeman, R. H. In "Critical Evaluation of Chemical and Physical Structural Information", Lide, D. R., Jr.; Paul, M. A., Eds.; National Academy of Sciences–National Research Council: Washington, D. C., 1974, pp 94–115.

(28) The reference dihedral angle of 0° occurs for an extended C_{2v} form when both OH bonds are coplanar and point away from the terminal SO₂ group. See also footnote c in Table VII.

Table VII. Structures Calculated for H₂SO₄

| method[a]	I	I'	II	III	IV	pref[b]
r(OH), Å	0.96	0.98	0.96	0.96	0.96	0.97 ±0.01
r(SO₁), Å	1.568	1.568	1.570	1.570	1.579	1.574 ± 0.01
r(SO₂), Å	1.427	1.426	1.424	1.425	1.417	1.422 ± 0.01
∠H₁O₁S, deg	109.1	107.9	108.9	108.8	108.7	108.5 ± 1.5
∠O₁SO₁', deg	101.7	101.7	101.7	101.7	101.0	101.3 ± 1
∠O₂SO₂', deg	122.8	122.8	122.8	122.9	123.9	123.3 ± 1
∠O₁SO₂, deg	108.7	108.7	108.7	108.7	108.5	108.6 ± 0.5
∠O₁SO₂', deg	106.5	106.4	106.5	106.5	106.3	106.4 ± 0.5
τ(H₁O₁SO₂),[c] deg	20.92	21.57	20.77	21.36	19.91	20.8 ± 1
τ(H₁O₁SO₁'),[c] deg	−91.17	−90.49	−91.30	−90.70	−91.58	−90.9 ± 1
τ(P₁P₂),[d] deg	88.45	88.38	88.43	88.45	88.42	88.4 ± 0.1

[a] Consult figure for atom numbers. Consult structure section for description of the calculation methods. In all the calculations, r(OH) was not varied. [b] Preferred structural parameters and uncertainties. [c] Looking down the O₁–S bond, the H₁O₁ projection must be rotated clockwise by 20.92° to be cis to the SO₂ bond and counterclockwise by 91.17° to be cis to the SO₁' bond, for structure I. The convention used in this paper for torsional angles follows ref 36. [d] Angle between O₁SO₁' and O₂SO₂' planes. The small deviation from exactly perpendicular planes brings O₂ and O₂' closer to O₁' and O₁, respectively.

be related work on similar conformational problems for four-coordinate sulfur systems which can be used as a reference point except for the CNDO–MO study described in the Introduction.

The closest analogies to H₂SO₄ are found in several ab initio MO studies predicting conformational energies for some tetrahedral phosphate and carbon systems. Calculations on the dimethyl phosphate anion[29] with geometry optimization resulted in energy differences for the gauche, gauche (g,g), gauche, trans
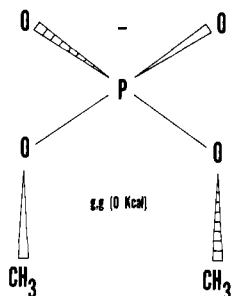
(g,t), and trans, trans (t,t) conformations of less than 1 kcal/mol.
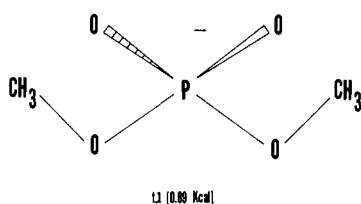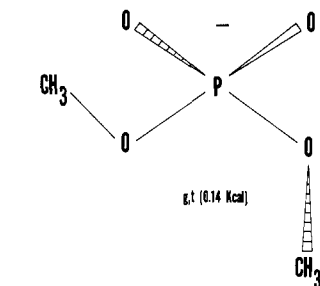
In crystalline dimethylammonium phosphate, the g,g form has been identified for this anion.[30]

The most stable conformation for methanediol is also calculated to be g,g with g,t and t,t destabilized by 4.7 and 11.2 kcal/mol, respectively. The difference between these forms may be briefly described as the result of stabilizing delocalizations of lone pairs (anomeric-like effect) in the g,g form contrasted with destabilizing lone-pair repulsions in the other two forms.[31]

Figure 1. Drawing of sulfuric acid showing the C₂ axis.

Fluoromethanediol with another electronegative group attached to the carbon has two low-energy forms with the g,g no longer the most stable.[32] Calculations on CF₂(OH)₂ are not available,

(29) Gorenstein, D. G.; Luxon, B. A.; Findlay, J. B. *Biochim. Biophys. Acta* **1977**, *475*, 184–190.

(30) Giardi, L.; Garbassi, F.; Calcaterra, M. *Acta Crystallogr., Sect. B* **1973**, *29*, 1826–1829.
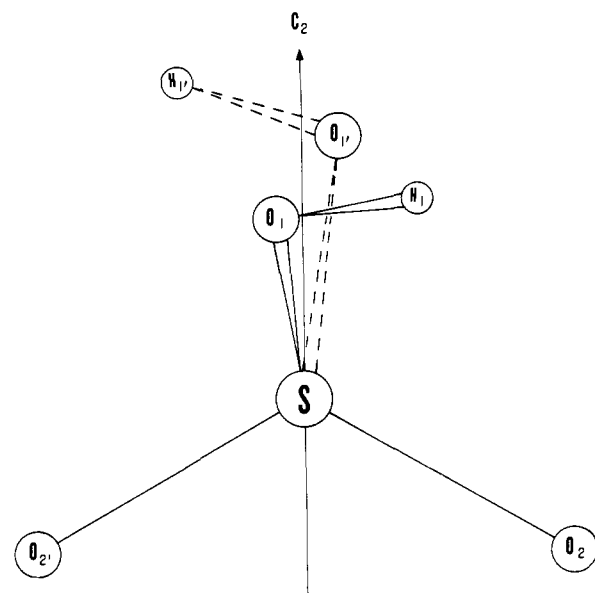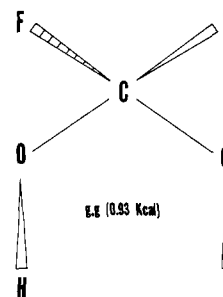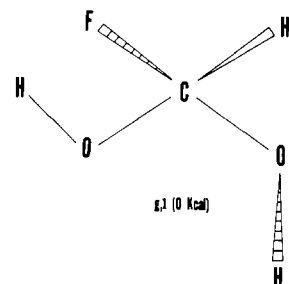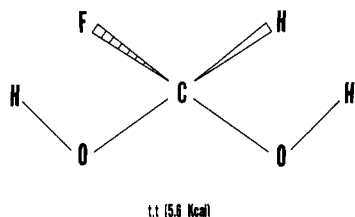
(31) Jeffrey, G. A.; Pople, J. A.; Radom, L., *Carbohyd. Res.* **1972**, *25*, 117–134.

t,t (5.6 kcal)

and it appears difficult to simply extrapolate to its most stable conformation (and presumably to H_2SO_4) given the results on $CH_2(OH)_2$, $CHF(OH)_2$, and $(CH_3O)_2PO_2^-$. Nevertheless, these systems do suggest that interactions from the nonbonding electrons on O(H) atoms must be an important factor in stabilizing the conformation observed for H_2SO_4.

Other Conformations. The difficulty with anticipating conformational energy differences for H_2SO_4 makes it necessary to carefully consider whether the experimental data can accomodate any other low-energy forms, including an even more stable conformer. This can be explored upon consideration of the intensity and complexity of the remaining unassigned lines along with the strength and spectral pattern expected for transitions of other conformers.

Several of the remaining transitions are approximately one-half the intensity of the assigned transitions. The majority are still weaker. Nevertheless, this alone does not rule out the existence of a still lower energy conformation. The intensity of a transition is related to the total energy of the state via the Boltzman expression, but it is also proportional to the dipole moment squared. Hence, if another low-energy conformation has a small dipole moment, it could have a less intense spectrum even though it is more abundant (cf. ref 20).

The conformation expected to have the smallest dipole moment has the compact C_{2v} symmetry (t,t). In this conformation the OH bond dipoles are in the most effective position to partially oppose the net moment from the heavy atom framework. Assuming a bond dipole moment of 1 to 1.5 D for each OH group, a lower limit of 1.3 D is estimated for the total dipole moment. With this lower limit and using 0.5 as an upper limit for the intensity ratio between an unassigned form and the observed conformer, it becomes evident that the observed conformation is either the ground state or within 0.5 kcal/mol of it. In summary, the possibility of other low-energy forms and even a slightly lower conformation cannot be definitively excluded with the present microwave data. Further work on the unassigned transitions could provide a more definitive answer to this question.

Structural Parameters. Apart from the internal rotation angle of the OH group, the values for the other structural parameters in H_2SO_4 are generally close to expected values. For example, the terminal SO bonds and OSO angles are near to those in two similar compounds, viz., F_2SO_2 (1.405 (10) Å, 124.0 (1)°)[33] and $(CH_3)_2SO_2$ (1.43 (1) Å, 121.4 (10)°)[34] while ∠FSF (96.1 (10)°) and ∠CSC (103 (1)°) also bracket the (H)O–S–O(H) angle. The principal inference is that the bonding in H_2SO_4 appears typical

for a compound with polar-covalent bonds. Various MO calculations and models have explored this bonding about sulfur.[35]

The two OSO planes ($O_1SO_{1'}$ and $O_2SO_{2'}$) deviate by 1.6° from being exactly perpendicular. There is less precedence for this and its implications are not readily apparent. Of course, rigorously perpendicular planes are not required since interactions are no longer symmetrical owing to the orientation of the OH groups.

The structure of crystalline H_2SO_4 has very similar features overall, with only minor differences in the detailed structural parameters.[18] The structural parameters are $r(SO_1) = 1.535$ (15) Å, $r(SO_2) = 1.426$ (15) Å, $\angle O_1SO_{1'} = 104$ (1)° and $\angle O_2SO_{2'} = 118.6$ (1)°. The H atoms were not directly located, but a plausible position for them was suggested based on the relative orientations of the SO_4 tetrahedra and the assumption of intermolecular hydrogen bonding to a terminal oxygen in an adjacent molecule. This orients the OH group in roughly the same direction as in the free species. Also analogous to the free H_2SO_4, the local heavy atom symmetry about sulfur was inferred as C_2 from the observed angles about sulfur. Following the numbering in Figure 1, $\angle O_1SO_2$ was 110.5 (10)° and $\angle O_1SO_{2'}$ was 105.9 (10)°.

The structure of liquid H_2SO_4 (100%) has also been estimated from X-ray scattering.[19] It is interesting that two models could fit the data. One model had heavy-atom C_{2v} symmetry with nearly equal $O_1SO_{1'}$ and $O_2SO_{2'}$ angles of 107.9 (14) and 110.4 (14)°, respectively. The second model had heavy-atom C_2 symmetry. Following the numbering in Figure 1, the angles (with standard deviations of 2.2°) were $O_1SO_{1'} = 104.7°$, $O_2SO_{2'} = 112.8°$, $O_1SO_2 = 113.0°$, and $O_1SO_{2'} = 106.6°$. Within experimental error, both had identical SO bond distances of 1.417 (14) and 1.550 (19) Å. The hydrogen atom positions could not be determined and the question of which molecular model is closer to physical reality could not be decided on the basis of the x-ray data. However, one expects liquid H_2SO_4 to be extensively hydrogen bonded because of its high boiling point, and it is attractive to speculate that this could give rise to distortions from C_{2v} symmetry like those observed in the solid phase. Then the structure in the liquid and solid phases would both be similar to the gas-phase conformation. In all three phases, the OH groups would be rotated away from the very polar terminal SO_2 group to positions more favorably oriented for intermolecular hydrogen bonding.

Dipole Moment. Dipole moments in the series F_2SO_2, (HO)$_2SO_2$, and $(CH_3)_2SO_2$ are 1.12(5),[33] 2.72(1), and 4.50(10)[34] D. Presumably, the OH groups contribute in a minor way to the dipole moment of H_2SO_4 because of their orientation. The regular increase in the series is suggestive of similar bonding mechanisms given the electronegativity differences in the attached groups and the large polarity generally associated with terminal SO_2 bonds. The contrast in volatilities for these species supports the assumption that pure, liquid H_2SO_4 must be extensively H-bonded.

(32) Lathan, W. A.; Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 699–703.

(33) Lide, D. R., Jr.; Mann, D. E.; Fristrom, R. M. *J. Chem. Phys.* **1957**, *26*, 734–739.

(34) Jacob, E. J.; Lide, D. R., Jr. *J. Chem. Phys.* **1971**, *54*, 4591–4596.

(35) See the following and references therein: Bartell, L. S.; Su, L. S.; Yow, H. *Inorg. Chem.* **1970**, *9*, 1903–1912.

(36) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations", McGraw-Hill: New York, 1955; p 60.