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Microwave Investigation of Sulfuric Acid Monohydrate

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Abstract: The complex H_2SO_4−H_2O has been observed by rotational spectroscopy in a supersonic jet. A-type spectra for 18 isotopic forms have been analyzed, and the vibrationally averaged structure of the system has been determined. The complex forms a distorted, six-membered ring with the water unit acting as both a hydrogen bond donor and a hydrogen bond acceptor toward the sulfuric acid. One of the H_2SO_4 protons forms a short, direct hydrogen bond to the water oxygen, with an H···O distance of 1.645(5) Å and an O−H···O angle of 165.2(4)°. Additionally, the orientation of the water suggests a weaker, secondary hydrogen bond between one of the H_2O hydrogens and a nearby S=O oxygen on the sulfuric acid, with an O···H distance of 2.05(1) Å and an O−H···O angle of 130.3(5)°. The experimentally determined structure is in excellent agreement with previously published DFT studies. Experiments with HOD in the jet reveal the formation of only isotopomers involving deuterium in the secondary hydrogen bond, providing direct experimental evidence for the secondary H···O interaction. Extensive isotopic substitution has also permitted a re-determination of the structure of the H_2SO_4 unit within the complex. The hydrogen-bonding OH bond of the sulfuric acid elongates by 0.07(2) Å relative to that in free H_2SO_4, and the S=O bond involved in the secondary interaction stretches by 0.04(1) Å. These changes reflect substantial distortion of the H_2SO_4 moiety in response to only a single water molecule, and prior to the proton transfer event. Spectral data indicate that the complex undergoes at least one, and probably more than one type of internal motion. Although the sulfuric acid in this work was produced from direct reaction of SO_3 and water in the jet, experiments with $H_2{}^{18}O$ indicate that about 2−3% of the acid is formed via processes not normally associated with the gas-phase hydration of SO_3.

Introduction

Sulfuric acid/water aerosols play a vital role in the heterogeneous chemistry leading to the destruction of stratospheric ozone.[1,2] They have also demonstrated significantly high uptake of nitric acid at temperatures at or near the frost point and are believed to play an important role in the formation of polar stratospheric clouds.[1,3] Because of their importance, numerous experimental and theoretical studies have been aimed at investigating the nucleation of sulfuric acid and water vapor,[4,5] but due to the strong tendency of H_2SO_4 to form hydrates, nucleation rates for aerosols involving sulfuric acid have been notoriously difficult to predict.[4,5] The gas-phase hydration of sulfuric acid is thus of considerable interest with regard to elucidating the details of sulfuric acid aerosol formation in the atmosphere.

Bulk phase spectroscopic measurements on the sulfuric acid−water system date back at least several decades[6] and continue to be a subject of active investigation today.[7] In recent years, spectroscopic and surface analytical techniques have also been applied to H_2SO_4/H_2O thin films,[8] and infrared optical constants have been measured for sulfuric acid−water mixtures as a function of temperature, frequency, and composition.[9] The scattering of water molecules off liquid sulfuric acid surfaces has been studied,[10] and crystal structures for sulfuric acid,[11] its

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(1) Finlayson-Pitts, B. J.; Pitts, J. N., J. *Chemistry of the Upper and Lower Atmosphere. Theory Experiments and Applications*; Academic Press: San Diego, CA 2000.

(2) See, for example: (a) Hallquist, M.; Stewart, D. J.; Baker, J.; Cox, R. A. *J. Phys. Chem. A* **2000**, *104*, 3984. (b) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem*. **1994**, *98*, 5728. (c) Hanson, D. R.; Ravishankara, A. R. *J. Geophys. Res*. **1991**, *96*, *17*, 307. (d) Tolbert, M. A.; Rossi, M. J.; Golden, D. M. *Geophys. Res. Lett*. **1988**, *15*, 847 and references therein.

(3) (a) Carslaw, K. S.; Luo, B. P.; Clegg, S. L.; Peter, Th.; Brimblecombe, P.; Crutzen, P. J. *Geophys. Res. Lett.* **1994**, *21*, 2479. (b) Beyer, K. D.; Seago, S. W.; Chang, H. Y.; Molina, M. J. *Geophys. Res. Lett*. **1994**, *21*, 871. (c) Tabazadeh, A.; Turco, R. P.; Jacobson, M. Z. *J. Geophys. Res.* **1994**, *99*, 12897.

(4) See, for example: (a) Noppel, M. *J. Chem. Phys*. **1998**, 109, 9052. (b) Kusaka, I.; Wang, Z.-G.; Seinfeld, J. H. *J. Chem. Phys.* **1998**, *108*, 6829. (c) Viisanen, Y.; Kulmala, M.; Laaksonen, A. *J. Chem. Phys*. **1997**, *107*, 920. (d) McGraw, R. *J. Chem. Phys.* **1995**, *102*, 2098 and references therein.

(5) (a) Mirabel, P.; Katz, J. L. *J. Chem. Phys*. **1974**, *60*, 1138. (b) Heist, R. H.; Reiss, H. *J. Chem. Phys.* **1974**, *61*, 573. (c) For additional references prior to 1995, see: Laaksonen, A.; Talanquer, V.; Oxtoby, D. W. *Annu. Rev. Phys. Chem*. **1995**, *46*, 489.

(6) See, for example: (a) Walrafen, G. E.; Dodd, D. M. *Trans. Faraday Soc.* **1961**, *57*, 1286. (b) Savoie, R.; Giguére, P. A. *J. Chem. Phys.* **1964**, *41*, 2698. (c) Palmer, K. F.; Williams, D. *Appl. Opt*. **1975**, *14*, 208.

(7) (a) Nash, K. L.; Sully, K. J.; Horn, A. B. *J. Phys. Chem. A* **2001**, *105*, 9422. (b) Tomikawa, K.; Kanno, H. *J. Phys. Chem. A* **1998**, *102*, 6082.

(8) (a) Roberts, J. T. *Acc. Chem. Res.* **1998**, *31*, 415. (b) Biermann, U. M.; Luo, B. P.; Peter, Th. *J. Phys. Chem. A* **2000**, *104*, 783 and references therein.

(9) (a) Niedziela, R. F.; Norman, M. L.; DeForest, C. L.; Miller, R. E.; Worsnop, D. R. *J. Phys. Chem. A* **1999**, *103*, 8030. (b) Tisdale, R. T.; Glandorf, D. L.; Tolbert, M. A.; Toon, O. B. *J. Geophys. Res*. **1998**, *103*, 25353 and references therein.

(10) Govoni, S. T.; Nathanson, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 779.

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monohydrate ($H_3O^+HSO_4^-$),[11] and several higher hydrates[12] have been published. Numerous vapor pressure and uptake measurements involving sulfuric acid solutions have been reported,[13] and hydrated sulfuric acid has even been proposed to form on interstellar dust grains present in circumstellar envelopes.[14a] Aqueous sulfuric acid is also believed to comprise the aerosol particles in the upper layer of the cloud cover over Venus.[14b]

For the isolated hydrates of sulfuric acid, experimental, spectroscopic observations appear limited to cryogenic matrices,[15] and our knowledge of these systems in the gas phase, therefore, has been derived largely from computational results.[16−19] Several studies, in particular, have investigated the structural and energetic properties of isomeric forms of the lower hydrates of the acid and have focused on the transition between neutral and ionic species in the series $H_2SO_4(H_2O)_n$ ($n = 0-7$). On the basis of this work, it appears that the neutral, hydrogen-bonded forms are most stable for low n, but with increasing solvation, the stability of the proton-transferred ion pair increases relative to that of the hydrogen-bonded complex. Indeed, by $n = 5$, the lowest energy form is $(HSO_4^-)(H_3O^+)(H_2O)_4$, albeit by only ~2 kcal/mol.[16] However, even when proton transfer is energetically disfavored, the H_2SO_4 demonstrates a marked ability to act as the proton donor in hydrogen-bonding interactions. For example, in the theoretical structure for the monohydrate, the sulfuric acid hydrogen bonds to the water unit with an exceptionally short hydrogen bond length of only ~1.6−1.7 Å.[16−19]

The study of sulfuric acid monohydrate is also of fundamental significance, as it represents the first stage in the hydration of a simple, common mineral acid. Despite the variety of theoretical calculations which now exist, a definitive gas-phase investigation of the $H_2SO_4-H_2O$ adduct has not been carried out. Accordingly, in this paper, we report the microwave spectrum and structure of the 1:1 complex $H_2SO_4-H_2O$.

Experimental Section

Rotational spectra were recorded on a Balle-Flygare Fourier transform microwave spectrometer,[20] the details of which have been described previously.[21] $H_2SO_4-H_2O$ was produced in situ via the reaction between H_2O and SO_3, using an injection source similar to that which we reported in previous studies on reactive species.[22−24] SO_3 was introduced into the vacuum chamber through the pulsed valve by passing Ar over solid, polymerized SO_3 at a backing pressure of ~2 atm. Water vapor was injected into the expansion by passing Ar gas over a reservoir of liquid water at a backing pressure of 0.165 atm and passing the resulting mixture through a 0.012 in. i.d. needle situated slightly downstream of the nozzle orifice. Ideal conditions for the production of $H_2SO_4-H_2O$ were obtained by clipping the needle to a length of 0.11 in. and carefully placing its end in the central region of the expansion, 0.21 in. below the nozzle orifice. Mixed isotopomers were formed by adding D_2O and H_2O to the reservoir in proportions that optimized the signal under investigation.

Rotational transitions of $H_2SO_4-H_2O$ and its isotopomers were initially identified by their strong correlation with the intensity of the $1_{10} \leftarrow 0_{00}$ transition of H_2SO_4, $HDSO_4$, or D_2SO_4 (predicted and observed using published rotational constants[25]), as well as the nearly symmetric triplet pattern observed for the a-type $J = 2 \leftarrow 1$ rotational transition. This pattern is consistent with the near equivalent $K_p = 1$ splitting about the central $K_p = 0$ transition predicted for a near prolate rotor. The attainment and assignment of spectra of mixed isotopic species was complicated by source conditions, and constant checking on the $1_{10} \leftarrow 0_{00}$ transitions of $HDSO_4$, D_2SO_4, and H_2SO_4 was necessary to ascertain the chemical dependence of each transition. In addition, as the B and C rotational constants are similar for several mixed isotopomers, the a-type spectra were overlapping, initially precluding unique spectral assignments for each of the observed a-type spectral patterns. To overcome this obstacle, the dependence of each transition on the ratio of H_2O/D_2O in the liquid reservoir was tested on several independent occasions to aid in obtaining an initial assignment for each isotopic species. Subsequent confirmation of these assignments came from the ability to predict and observe transitions for a number of isotopomers based on refined structural parameters.

As an additional check of the assignments of each transition to an isotopomer of $H_2O-H_2SO_4$, the Ar carrier gas was replaced with a 70% Ne/30% He mixture. The intensity of the assigned transitions decreased significantly with the use of Ne/He yet the transitions remained observable, ensuring the lack of dependence on Ar. The spectra of all ^{18}O-containing species were obtained by the addition of $H_2{}^{18}O$ (95 atom %, Icon Services) to the liquid reservoir, while the spectrum of the ^{34}S-substituted $H_2SO_4-H_2O$ species was observed in natural isotopic abundance.

The estimated uncertainty in the measured transition frequencies is 2 kHz for the fully protonated forms. For isotopomers containing deuterium, the hyperfine structure was not adequately resolved to determine quadrupole coupling constants. Thus, an average linecenter was estimated, with a corresponding increase of uncertainty, up to about 10 kHz for the fully deuterated derivative.

Results

Spectral Observations. The 18 isotopomers observed in this study are indicated in Table 1, and a listing of assigned transitions is provided as Supporting Information. The atom labeling scheme used in the tables is illustrated in Figure 1a, and a representative spectrum, showing the $J_{K_pK_o} = 2_{12} \leftarrow 1_{11}$ transition of the parent form, is shown in Figure 2. As noted above, in complexes containing deuterium, hyperfine structure was poorly resolved and was not analyzed. For the complexes of HOD, only species with the deuterium in the position closest to the S=O oxygen of the sulfuric acid (O3) were observed.

For isotopomers containing only hydrogen, the a-type transitions appeared as doublets. This is clearly seen for the parent form in Figure 2. The splitting between components of these

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[11] Kemnitz, E.; Werner, C.; Trojanov, S. *Acta Crystallogr.* **1996**, *C52*, 2665.

[12] Mootz, D.; Merschenz-Quack, A. *Z. Naturforsch.* **1987**, *42b*, 1231.

[13] See, for example: (a) Robinson, G. N.; Worsnop, D. R.; Jayne, J. T.; Kolb, C. E.; Swartz, E.; Davidovits, P. *J. Geophys Res*. **1998**, *103*, 25,371. (b) Marti, J. J.; Jefferson, A.; Cai, X. P.; Richert, C.; McMurry, P. H.; Eisele, F. *J. Geophys. Res*. **1997**, *102*, 3725. (c) Zhang, R.; Wooldridge, P. J.; Molina, M. J. *J. Phys. Chem.* **1993**, *97*, 8541 and references therein.

[14] (a) Scappini, F.; Smith, H.; Klemperer, W. *Conf. Proc.−Ital. Phys. Soc.* **2000**, *67* (Workshop − Molecules in Space and in the Laboratory), 55. (b) Encrenaz, T.; Bibring, J.-P.; Blanc, M. *The Solar System*, 2nd Corrected and Revised Edition; Dunlap, S., Translator; Springer: Heidelberg, 1995.

[15] (a) Givan, A.; Larsen, L. A.; Loewenschuss, A.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 827. (b) Bondybey, V. E.; English, J. H. *J. Mol. Spectrosc.* **1985**, *109*, 221.

[16] Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535.

[17] Arstila, H.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **1998**, *108*, 1031.

[18] Bandy, A. R.; Ianni, J. C. *J. Phys. Chem. A* **1998**, *102*, 6533.

[19] Beichert, P.; Schrems, O. *J. Phys. Chem. A* **1998**, *102*, 10540.

[20] Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum*. **1981**, *52*, 33.

[21] (a) Phillips, J. A.; Canagaratna, M.; Goodfriend, H.; Grushow, A.; Almlöf, J.; Leopold, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 12549. (b) Phillips, J. A. Ph.D. Thesis, University of Minnesota, 1996.

[22] Canagaratna, M.; Phillips, J. A.; Goodfriend, H.; Leopold, K. R. *J. Am. Chem. Soc.* **1996**, *118*, 5290.

[23] Ott, M. E.; Leopold, K. R. *J. Phys. Chem. A* **1999**, *103*, 1322.

[24] Fiacco, D. L.; Toro, A.; Leopold, K. R. *Inorg. Chem.* **2000**, *39*, 37.

[25] Kuczkowski, R. L.; Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 2561.

Table 1. Spectroscopic Constants for Isotopic Forms of $H_2SO_4-H_2O$[a]

H1	H2	O1	O2	O3	O4	S	––	H3	H4	O5	state[b]	*B* (MHz)[c]	*C* (MHz)[c]	Δ_J (kHz)[c]	Δ_{JK} (kHz)[c]
1	1	16	16	16	16	32		1	1	16	A	1899.1253(8)	1878.2435(8)	0.94(4)	13.0(4)
											B	1899.1131(8)	1878.2221(8)	0.88(4)	12.4(4)
1	1	16	16	16	16	34		1	1	16	A	1894.8643(8)	1874.243(1)	0.83(5)	*d*
											B	1894.8532(8)	1874.2238(8)	0.86(4)	12.5(4)
1	1	16	16	16	16	32		1	1	18	A	1798.2664(8)	1779.5662(8)	0.85(4)	12.3(4)
											B	1798.2589(8)	1779.5493(8)	0.85(4)	11.9(4)
1	1	16	18	16	16	32		1	1	18	A	1782.3686(9)	1747.5183(9)	0.86(7)	10(1)
											B	1782.3752(9)	1747.4815(9)	0.90(7)	11(1)
1	1	18	16	16	16	32		1	1	18	A	1792.9347(8)	1765.0065(8)	0.86(4)	10.1(4)
											B	1792.9117(8)	1765.0069(8)	0.92(4)	9.6(4)
1	1	16	16	18	16	32		1	1	18	A	1787.0015(8)	1769.942(1)	*d*	*d*
											B	1786.9700(8)	1769.9498(8)	1.01(4)	8.9(4)
1	1	16	16	16	18	32		1	1	18	A	1758.277(1)	1734.3217(8)	0.70(5)	11.7(4)
											B	1758.2798(8)	1734.3004(8)	0.75(4)	11.7(4)
2	2	16	16	16	16	32		2	2	16		1738.950(2)	1724.871(2)	0.8(1)	11(1)
2	2	16	16	16	16	32		2	1	16		1814.473(2)	1800.650(1)	1.27(7)	10.3(6)
2	2	16	16	16	16	32		1	1	16		1853.738(2)	1835.856(2)	0.32(7)	7.5(7)
2	1	16	16	16	16	32		2	1	16		1846.015(1)	1824.795(1)	0.49(6)	14.7(5)
2	1	16	16	16	16	32		2	2	16		1768.390(1)	1748.501(1)	0.84(8)	10.1(8)
2	1	16	16	16	16	32		1	1	16		1884.100(1)	1862.155(1)	0.79(7)	11.8(6)
1	1	16	16	16	16	32		2	1	16		1859.519(1)	1840.540(1)	0.72(6)	11.9(5)
1	2	16	16	16	16	32		2	2	16		1753.289(1)	1736.260(1)	0.95(8)	12.3(8)
1	2	16	16	16	16	32		2	1	16		1830.144(2)	1813.281(1)	0.87(7)	12.6(6)
1	2	16	16	16	16	32		1	1	16		1870.617(1)	1849.075(1)	1.06(7)	11.7(6)
1	1	16	16	16	16	32		2	2	16		1780.986(1)	1762.475(1)	0.85(5)	11.7(5)

[a] Isotopic derivatives are specified by the approximate atomic masses (e.g., 2 for deuterium, 16 for ^{16}O, etc.) according to the atom numbering scheme of Figure 1. [b] Two states were observed only for the fully protonated forms. See text for discussion. [c] Uncertainties are one standard error in the least-squares fit. [d] Not determined.

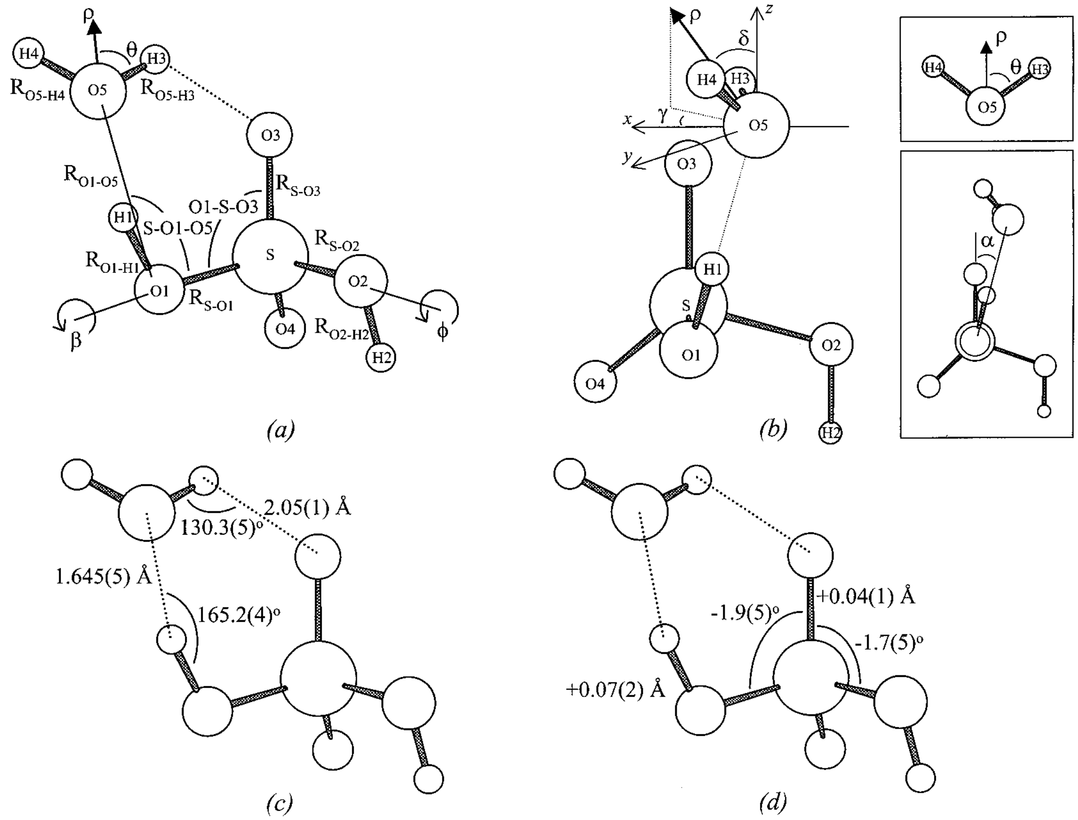

Figure 1. Four views of the sulfuric acid−water complex, emphasizing (a) bond lengths and bond angles within the monomers; (b) intermolecular parameters specifying the relative orientation of the monomers (α is the O5−O1−S−O3 dihedral angle; a positive value of *δ* and a negative value of *γ* are drawn; see text for discussion); (c) chemically interesting features of the experimentally determined structure; and (d) changes in the sulfuric acid monomer structure upon complexation (value in $H_2SO_4-H_2O$ minus value in H_2SO_4 monomer).

doublets was generally on the order of 10−30 kHz in the $J = 1_{01} \leftarrow 0_{00}$ transition, and increased roughly in proportion to $(J'' + 1)$, where J'' specifies the lower state of the transition. The corresponding states are labeled A and B in this paper, with transitions due to state B at the lower frequency. These states, if present, were not discernible for isotopomers containing deuterium, as the splitting is on the same order as that for the hyperfine structure and may, therefore, have been obscured.

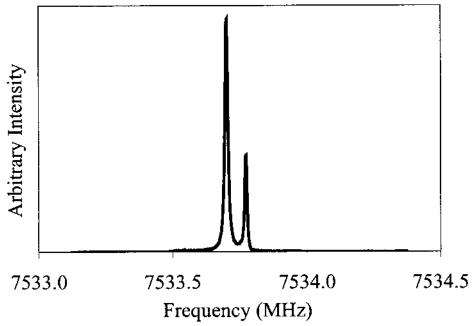

Figure 2. The $2_{12} \leftarrow 1_{11}$ transitions of $H_2SO_4-H_2O$, where the A and B states are apparent. Total data collection time for the spectrum was approximately 39 s.

Moreover, the spectra for mixed species (e.g., those containing $HDSO_4$ and D_2SO_4 with H_2O) were relatively weak, hence the less intense component, if present, may not have been observable in some cases. The intensity ratios for states A and B were not carefully measured, but appeared somewhat variable, ranging from about 3:1 to as much as 16:1 in some spectra. However, these ratios are sensitive to a variety of experimental conditions, including the offset between the molecular frequency and the center frequency of the microwave cavity, and this type of variability is not unprecedented on our spectrometer.

Extensive searches for c-type transitions were also carried out for the parent and fully deuterated forms. These searches were guided by using calculated $H_2SO_4-H_2O$ structures to provide estimates of the A rotational constant. However, instead of a single, assignable c-type line, numerous transitions were observed which were dependent on both SO_3 and either H_2O or D_2O. For example, in experiments with the fully protonated form, a congested pattern of lines spread over an 80 MHz region was observed near the predicted $3_{12} \leftarrow 2_{02}$ transition. Similar results were obtained for the fully deuterated form. For this reason, no c-type transitions were assigned in this work. Separate searches for b-type spectra were not conducted.

In addition to the dense spectra above, a number of other unassigned transitions were observed. These lines also displayed a chemical dependence on SO_3 and either H_2O, H_2O/D_2O, or D_2O, but were not assignable on the basis of rigid rotor predictions. As a sizable assortment of species is likely formed under the experimental conditions detailed above, a large number of additional spectra are not particularly surprising. Moreover, as discussed below, the $H_2SO_4-H_2O$ complex likely undergoes at least one, and perhaps more than one type of internal motion, the spectral signatures of which may add additional non-rigid-rotor transitions to the spectrum. Nevertheless, the rigid-rotor, a-type spectra of all 18 isotopomers investigated were well behaved, and it is the analysis of these transitions that forms the focus of this paper. The frequencies and approximate intensities of all unassigned lines, as well as details of the chemical dependencies of some of them, have been documented elsewhere.[26]

Spectral Fits. The observed a-type transitions for each of the 18 isotopic species studied were fit to Watson's *A*-reduced Hamiltonian for a distortable asymmetric rotor,[27] viz.,

$$H = [(B + C)/2 - \Delta_J \mathbf{J}^2]\mathbf{J}^2 + [A - (B + C)/2 - \Delta_{JK}\mathbf{J}^2 - \Delta_K \mathbf{J}_z^2]\mathbf{J}_z^2 + [(B - C)/2 - 2\delta_J \mathbf{J}^2](\mathbf{J}_x^2 - \mathbf{J}_y^2) - \delta_K[\mathbf{J}_z^2(\mathbf{J}_x^2 - \mathbf{J}_y^2) + (\mathbf{J}_x^2 - \mathbf{J}_y^2)\mathbf{J}_z^2] \quad (1)$$

where *A*, *B*, and *C* are the rotational constants and Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are centrifugal distortion constants. Since the a-type spectra are largely insensitive to *A*, and no b- and c-type transitions were assigned, initial fits were performed with the value of *A* held fixed at 4500 MHz for all 18 isotopomers. This approach resulted in unacceptably large residuals for a number of the isotopic species studied and thus the *A* constant was allowed to float in a series of preliminary fits for each isotopomer. In the final fit for each isotopic species, the *A* constant was then fixed at the value obtained in the preliminary fit, which resulted in much decreased residuals and improved values for *B* and *C*. The values of *B* and *C*, however, were not significantly affected by the choice of *A*. Moreover, the scope of the data set dictated that of the centrifugal distortion constants, only Δ_J, and Δ_{JK} were necessary to fit the spectrum. Thus Δ_K, δ_J, and δ_K were constrained to zero. The residuals from all the final fits were satisfactorily within the experimental uncertainties, and the resulting spectroscopic constants are listed in Table 1. Values of *B* and *C* are seen to be determined with very small standard errors. For the fully protonated forms, for which spectra were split into doublets, separate fits were carried out for each state.

^{18}O Substitution. It is interesting to note from Table 1 that the spectral assignments include isotopomers containing ^{18}O in both S−OH and S═O positions of the sulfuric acid. The latter is somewhat surprising in light of the proposed mechanisms[28−34] for the gas-phase reaction between H_2O and SO_3, which suggest that the water oxygen should retain one of its hydrogens in the final sulfuric acid product. As a check, therefore, the frequency of the $1_{10} \leftarrow 0_{00}$ transition for each of the two possible ^{18}O-substituted forms of the H_2SO_4 monomer was predicted from experimentally determined structural parameters.[25] The transitions for both species were readily located (9940.519 MHz for the S═^{18}O form and 9929.341 MHz for the S−^{18}OH form) and are shown in Figure 3. In addition, to ensure that these transitions were indeed due to H_2SO_4, (rather than lines from other species, fortuitously situated at similar frequencies) the same transition of the ^{34}S partner to each isotopomer was also predicted and observed (9938.278 MHz for ^{34}S═^{18}O; 9925.891 MHz for ^{34}S−^{18}OH). These results provide unambiguous evidence that both ^{18}O derivatives of sulfuric acid are present in the jet. Though not immediately apparent from Figure 3, however, the S−^{18}OH transition was about 30−40 times more intense than that of S═^{18}O, indicating that sulfuric acid formed is at least richer in the expected product. While the formation of the S═^{18}O form

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[26] Fiacco, D. L., Ph.D. Thesis, University of Minnesota, 2001.

[27] Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; John Wiley and Sons: New York, 1984.

[28] Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.

[29] (a) Jayne, J. T.; Pöschl, U.; Chen, Y.; Dai, D.; Molina, L. T.; Worsnop, D. R.; Kolb, C. E.; Molina, M. J. *J. Phys. Chem. A* **1997**, *101*, 10000. (b) Kolb, C. E.; Jayne, J. T.; Worsnop, D. R.; Molina, M. J.; Meads, R. F. *J. Am. Chem. Soc.* **1994**, *116*, 10314.

[30] Lovejoy, E. R.; Hanson, D. R.; Huey, L. G. *J. Phys. Chem.* **1996**, *100*, 19911.

[31] Larson, L. J.; Kuno, M.; Tao, F.-M. *J. Chem. Phys.* **2000**, *112*, 8830.

[32] Hoffman, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 4947.

[33] Reiner, T.; Arnold, F. *J. Chem. Phys.* **1994**, *101*, 7399.

[34] Hoffmann-Sievert, R.; Castleman, A. W., Jr. *J. Phys. Chem.* **1984**, *88*, 3329.

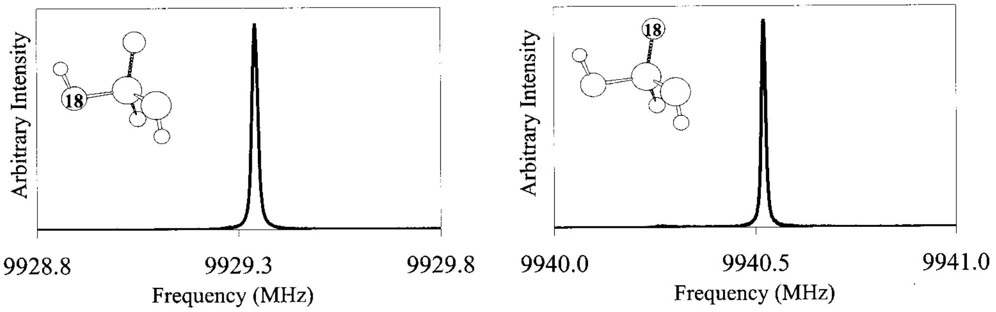

Figure 3. The $1_{10} \leftarrow 0_{00}$ transitions of two isotopomers of ^{18}O-substituted H_2SO_4 formed in the free jet expansion.

is surprising, it is also fortunate, as complexation of the acid with water then allows for a full set of substitution experiments within the sulfuric acid portion of the complex. Further discussion of these observations is given in a later section.

Structure Determination

A preliminary analysis of the rotational constants yielded a structure similar to that obtained from previous ab initio[19] and DFT[16−18] calculations. The complex forms a distorted six-membered ring in which the water unit acts as both a proton acceptor and a proton donor in its interaction with H_2SO_4. The main structural features are highlighted in Figure 1. In the primary interaction, the H_2SO_4 portion of the complex donates a proton to the water unit to form a short, direct hydrogen bond with an O−H distance on the order of 1.6 Å and an O−H−O angle of ~165°. A distance of ~2.1 Å between a hydrogen on the water unit and an S═O oxygen in H_2SO_4 is close to the predicted value of ~2.2 Å.

Twenty four structural parameters are needed to uniquely specify the geometry of the complex. This presents a formidable problem, and although it is common in situations of this type to reduce the number of degrees of freedom by constraining monomer geometries to their free-molecule values, such an approach, in this case, is neither necessary nor appropriate. Because 36 rotational constants have been determined, and since each atom has been substituted at least once, many of the internal degrees of freedom of the monomers are, in principle, determinable. This is fortunate, because calculations indicate that the $H_2O-H_2SO_4$ interaction is strong enough to produce significant deformations of the interacting monomers. For example, in the sulfuric acid unit, the calculated structures[16−19] span a range of 0.02−0.05 Å for the lengthening of the O−H bond involved in the primary hydrogen bond, and a range of 0.03−0.04 Å for the contraction of the corresponding S−O single bond. Likewise, the S═O distance is predicted to increase by as much as 0.01−0.02 Å as a result of the secondary interaction with a water proton. For the water portion of the complex, the calculated H−O−H angle increases by about 1.4°.[18]

While these predicted changes are not enormous in absolute terms, some of them have a significant effect on the moments of inertia of the complex. In particular, with a heavy sulfuric acid, and a light water molecule nearby, the H_2SO_4 unit itself contributes substantially to the moments of inertia of the complex. The result is that changes in its internal structure cannot be ignored, and indeed early attempts to fit only the intermolecular structural parameters without allowing relaxation of the monomer internal degrees of freedom were unsuccessful. Thus, the present situation is unlike that normally encountered for "light", weakly interacting systems in which the monomer distortions are truly small (because the interaction is weak), and the moments of inertia of the complex are dominated by a pseudodiatomic term (to which the monomer internal mass distributions provide only small corrections). In short, the unusually strong interaction in this complex and the concentration of mass in one of the monomer units conspire to render the usual approach untenable.

A subset of the structural parameters used to define the atomic positions is indicated in Figure 1a,b. Figure 1a focuses primarily on bond lengths and bond angles within the monomers, while Figure 1b describes the orientation of the water unit. Only a subset of the parameters used has been indicated to reduce clutter. A full listing appears in Table 2. In Figure 1b, the position of the H_2O unit with respect to H_2SO_4 is determined by placing the oxygen atom in the O1−S═O3 plane at a distance R_{O1-O5} from O1, and forming and angle O5−O1−S. The line joining O1 and O5 is then rotated out of the plane, maintaining the O5−O1−S angle (amounting to a rotation about the S−O1 bond). Thus, α is the O5−O1−S−O3 dihedral angle, with positive α corresponding to rotation of the O5−O1 segment toward the O2 side of the O1−S−O3 plane, as drawn in Figure 1b.

The symmetry of the water unit is broken by allowing the two O−H bond lengths in the water unit to differ (Figure 1a). The orientation of the water is determined by locating the ρ axis (Figure 1b) with respect to the O1−S−O3 plane through two angles labeled by δ and γ as shown in Figure 1b. $\delta = \gamma = 0$ correspond to the orientation when the line designating the height of the O5−H3−H4 triangle coincides with the z axis, which is parallel to the line segment connecting S and O3. Positive δ corresponds to a rotation of ρ toward the sulfuric acid unit in the plane of the page, while positive γ corresponds to a counterclockwise rotation of the water molecule, as viewed from a point on the positive z axis. A negative value of γ is drawn in the figure. Once ρ is in position, two angles are used to locate the position of the water hydrogens: the H−O−H angle and an angle labeled θ, which sets the tilt of the water molecule with respect to the ρ axis.

For the sulfuric acid portion of the complex, the dihedral angle H1−O1−S−O3 is given by β while H2−O2−S−O3 is measured by ϕ. $\beta = 0$ corresponds to the orientation in which H1 is in the O1−S−O3 plane with the O−H1 bond eclipsed to the S−O3 bond, while $\phi = 0$ corresponds to that in which H2 lies in the O2−S−O3 plane, eclipsed to the S−O3 bond. Positive β indicates that the O1−H1 bond must be rotated clockwise to eclipse the S−O3 bond, when viewed down the O1−S axis with O1 closer to the observer. Positive ϕ indicates that the H2−O2

Table 2. Structural Parameters for $H_2SO_4-H_2O$[a]

parameter	exptl	theor[b]	H_2SO_4 monomer[c]	H_2SO_4 distortion[d]
		fitted parameters:		
R_{O1-O5}	2.67(1)	2.64		
S−O1−O5	100.2(6)	99.9		
α	15.3(4)	17.7		
δ	38.7(6)	32.9		
γ	−11.4(8)	0.7		
θ	56(1)	53.7		
R_{O1-H1}	1.04(1)	1.009	0.97(1)	0.07(2)
R_{O2-H2}	0.95[e]	0.975	0.97(1)	
R_{S-O1}	1.567(1)	1.603	1.574(10)	−0.007(11)
R_{S-O2}	1.578(3)	1.636	1.574(10)	0.004(13)
R_{S-O3}	1.464(1)	1.466	1.422(10)	0.042(11)
R_{S-O4}	1.410(4)	1.458	1.422(10)	−0.012(14)
S−O1−H1	108.6[f]	108.4	108.5(15)	
S−O2−H2	108.5[e]	108.0	108.5(15)	
O1−S−O3	106.71(6)	109.1	108.6(5)	−1.9(5)
O2−S−O3	104.71(9)	104.5	106.4(5)	−1.7(5)
O3−S−O4	123.3[e]	122.9	123.3(10)	
O1−S−O4	106.7(4)	107.5	106.4(5)	0.8(9)
O1−S−O2	101.8(2)	102.7	101.3(10)	0.5(12)
β	−13.7(5)	−20.3	−20.9(10)[g]	7.2(15)
φ	−163.4(5)	−165.0	−155.1(10)[g]	−8.3(15)
R_{H3-O5}	0.98(1)	0.971		
R_{H4-O5}	0.98(1)	0.968		
H3−O5−H4	107[f]	107.2		
		calculated from fitted parameters:		
R_{O3-H3}	2.05(1)	2.230		
R_{H1-05}	1.645(5)	1.651		
O1−H1−O5	165.2(4)	165.9		
O5−H3−O3	130.3(5)	122.8		

[a] All distances in Å. All angles in degrees. [b] Values taken from ref 16 or calculated from Cartesian coordinates provided by the authors of ref 16. [c] Reference 25. [d] Value in complex minus value in monomer. [e] Held fixed in fit. [f] Determined from a series of preliminary fits; held fixed in final fit. See text for discussion. [g] The monomer value is calculated from the inertial frame coordinates given in ref 25. A ±1° uncertainty in the monomer values is assumed based on uncertainties reported for other torsional angles reported therein.

bond must be rotated clockwise to eclipse the S−O3 bond when viewed down the S−O2 bond from a point closer to O2. Both angles are indicated in Figure 1a.

A nonlinear least-squares analysis of the observed *B* and *C* rotational constants (36 constants in all) was carried out with use of the 24 structural parameters listed in Table 2. Separate fits were conducted with state A and state B data for the fully protonated forms, and an average was taken to determine the "final" value of each fitted parameter. In the process of fitting the rotational constants, the sensitivity of the data to each parameter was carefully tested. From this process, it was concluded that five of the structural parameters could not be freed in the final fits without resulting in singular matrices which terminated the routine. Thus, their values needed to be constrained in some reasonable way. The five parameters are as follows: (1) S−O1−H1, the angle between the sulfur, O1, and H1; (2) S−O2−H2, the same angle except involving the free H_2SO_4 hydrogen; (3) O3−S−O4, the angle between the two S═O bonds; (4) R_{O2-H2}, the O−H bond distance for the free H_2SO_4 hydrogen; and (5) H3−O5−H4, the water angle.

Appropriate values for the constrained parameters were determined from a comparison of the theoretical structure of $H_2SO_4-H_2O$ with those of the free monomers. As the geometry near the free H_2SO_4 hydrogen appears to remain essentially unchanged upon complexation,[16,17,19] the S−O2−H2 angle was fixed at its free monomer value of 108.5°.[25] Similarly, the angle between the two S═O bonds (O3−S−O4) is not predicted to change from that in free H_2SO_4 and was fixed at the experimental value of 123.3°.[25] On the other hand, although the experimental O2−H2 distance in free H_2SO_4 is 0.97(1) Å, the value of 0.95 Å was found to minimize χ-squared in a series of preliminary fits in which R_{O2-H2} was constrained to various values in the neighborhood of 0.97 Å. Hence, R_{O2-H2} was constrained to 0.95 Å all subsequent fits. The magnitude of the O3−S−O4 angle was also tested in a similar series of preliminary fits and supported the choice of 123.3° noted above.

On the basis of theoretical calculations, both the H_2O and the S−O1−H1 angles are expected to shift somewhat from their free monomer values (1.4° for ∠(HOH)[17] and 0.4−0.5° for ∠(S−O1−H1)[17,18]), and thus appropriate values for these parameters were also obtained from a series of preliminary fits. In the minimization process, the H_2O angle was allowed to vary between 106 and 107°, while the S−O1−H1 angle was allowed to vary between 108.5 and 109.0°. The range for the water angle was chosen by considering the large distortion of this angle predicted by theoretical calculations of the $H_2SO_4-H_2O$ complex. As a verification of the chosen range, values closer to the water angle in free H_2O were tested and indeed resulted in much larger residuals. The optimal values based on these preliminary fits were 107° and 108.6° for the H−O−H and S−O1−H1 angles, respectively.

The final values for all 19 freed parameters are given in Table 2. The quoted uncertainties arise predominantly from those in the H_2O and S−O1−H1 angles, and the quoted values reflect the spread of fitted parameters obtained by using the ranges of these angles described above. Overall, the quality of the structural fit was quite good, with the largest residual among the fitted rotational constants only 560 kHz. The experimentally determined structure of the complex is depicted in Figure 1c, which highlights some of the more chemically interesting features. A table of atomic Cartesian coordinates is provided as Supporting Information.

Discussion

As is evident from the above discussion, the H_2O unit of the sulfuric acid−water complex positions itself so as to form a distorted, nonplanar, six-membered ring with one-half of the H_2SO_4 molecule. In doing so, the water acts as a hydrogen bond acceptor in the complex, forming a short, somewhat direct hydrogen bond characterized by a 1.645(5) Å O⋯H distance (2.663 Å O⋯O distance) and a 165.2(4)° O−H⋯O angle. The orientation of the water also suggests a weaker, secondary interaction between the H_2O proton and a nearby S═O oxygen, with a much longer O⋯H distance of 2.05(1) Å and a highly bent O−H⋯O angle of 130.3(5)°. While weak, however, this interaction appears to provide some real stability for the complex, as is indicated by the lack of deuterium substitution at the free water hydrogen position in the HOD containing species. Such a preference for deuterium substitution in weak hydrogen bonds has been observed in several complexes involving water and is thought to arise from the reduction in zero point energy associated with substitution by a heavier isotope.[35]

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(35) See, for example: (a) Leung, H. O.; Marshall, M. D.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1989**, *90*, 700. (b) Canagaratna, M.; Phillips, J. A.; Ott, M. E.; Leopold, K. R. *J. Phys. Chem. A* **1998**, *102*, 1489.

The experimentally determined structure agrees well with the published computational studies.[16-19] It should be noted, of course, that the experimental parameters represent average values for the ground vibrational state, while the computed results correspond to equilibrium structures. Nevertheless, listed in Table 2 are structural parameters computed by Re et al.,[16] which are seen to reproduce the experimental bond lengths and bond angles typically to within about 0.05 Å and a few degrees, respectively. The results of the other reported computational studies,[17-19] though not listed, are overall of similar quality. We note that in the experimental structure, the two H_2SO_4 hydrogens optimize in a trans configuration, consistent with the lower energy form of the sulfuric acid monomer,[25] and the lowest energy conformation of the complex predicted by Re et al.[16]

The re-determination of many of the monomer structural parameters within the complex also offers an unusual opportunity to examine the degree of structural deformation of a simple acid resulting from the first step in its hydration. The structure of free sulfuric acid has been determined by microwave spectroscopy in the gas phase[25] and direct comparison between complexed and uncomplexed forms, therefore, is possible. Ironically, the uncertainties in the reported monomer structural parameters are somewhat larger than those determined here, quite likely due to the absence of any ^{18}O substitution data in the set of rotational constants analyzed for free H_2SO_4. As a result, changes in only six of the structural parameters are determined to better than the experimental uncertainty (two bond lengths, two bond angles, and the two OH bond torsional angles, β and φ). These changes are listed in Table 2 and highlighted in Figure 1d.

As expected, the most significant changes in the H_2SO_4 structure occur in the region in close proximity to the water molecule. Of particular interest are the 0.07(2) Å bond length increase in the hydrogen bonding OH group and the 0.04(1) Å elongation of the S−O3 bond. The former, clearly, suggests the beginning of proton transfer while the latter may be viewed, in chemical terms, as the earliest stages in the partial loss of double bond character. Such loss is expected as the proton transfers since the S−O3 bond of the bisulfate ion participates in resonance structures with single bond character. While a 0.04 Å change seems small in absolute terms, it is interesting to note that the S−O and S═O bond lengths in free sulfuric acid are 1.574(10) and 1.422(10) Å, respectively. Thus, the 0.04 Å change represents a stretching of the S−O3 bond by approximately 25% of the difference between the single and double sulfur−oxygen bonds in sulfuric acid.

The O5−H1 hydrogen bond distance observed for the $H_2SO_4-H_2O$ marks perhaps the shortest gas-phase hydrogen bond length for a complex involving water, with a value nearly 0.1 Å shorter than that in $HF-H_2O$[36] and 0.134(38) Å shorter than that in HNO_3-H_2O.[35b] The short hydrogen bond distance implies a very strong interaction between H_2SO_4 and H_2O, consistent with the calculated binding energy of 12.5 kcal/mol obtained at the MP2 level in ref 19. This, together with the measurable lengthening of the O1−H1 bond distance, marks the onset of a proton-transfer event, and the $H_2SO_4-H_2O$ complex can reasonably be regarded as an intimation of the earliest stage in the changes that lead to $(H_3O^+)(HSO_4^-)$ ion pair formation. Interestingly, calculations indicate that such ion pairs also form directly during the bulk phase hydration of SO_3.[37] Even with the addition of only one water molecule to $H_2SO_4-H_2O$, however, a further lengthening of the O1−H1 bond by 0.03 Å and an additional shortening of the hydrogen bond distance by 0.127 Å are predicted.[16] Clearly, further high-resolution spectroscopic studies of even slightly higher hydrates of sulfuric acid would be of interest with regard to gas-phase proton transfer.

There is also evidence for internal motion within the complex. The small splittings observed in the a-type spectra of the fully protonated forms are reminiscent of the proton interchange-type motions typical of hydrogen bonded complexes of water.[38] For example, in HNO_3-H_2O,[35b] the $2_{02} \leftarrow 1_{01}$ transition is split by 30 kHz, an amount not too different from the 66 kHz observed for $H_2SO_4-H_2O$. In the former case, this observation was attributed to proton interchange involving a 180° rotation of water either about its C_2 axis or about an axis perpendicular to the HOH plane. Although the intensity ratios for the A and B states do not conform to the 1:3 ratio expected for such motions on the basis of nuclear spin statistics, reservations concerning the variability of the observed ratios noted above leave open as a reasonable possibility that some motion of this nature is operative in the sulfuric acid complex as well. We note, however, that while 180° rotation about the C_2 axis of water directly produces an equivalent configuration, rotation about the perpendicular axis must be accompanied by a simultaneous rotation about the secondary hydrogen bond to leave the complex unchanged. A similar coupling of rotation about a weak hydrogen bond and a water wag has been suggested in $C_2H_4-H_2O$.[39] Another intriguing possibility involves the observation that the complex is chiral at the sulfur and that a fairly simple motion involving an exchange of the roles of the free and bound sulfuric acid protons can interchange the enantiomeric forms. Clearly, there is no shortage of possible tunneling pathways which can account for the observed non-rigid-rotor features in the spectrum. Further analysis, however, is not possible on the basis of the observed a-type spectra alone.

Finally, the observation of ^{18}O incorporation in the S═O positions of the sulfuric acid raises some interesting mechanistic questions about the formation of H_2SO_4 in the jet. Both theoretical[28] and experimental[29,30] studies indicate that the gas-phase reaction of SO_3 and H_2O to produce sulfuric acid may proceed via at least one of two possible reactions, viz.,

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4 + H_2O \tag{2}$$

$$H_2O-SO_3 + H_2O \rightarrow H_2SO_4 + H_2O \tag{3}$$

In either case, calculations indicate participation by a $(H_2O)_2-SO_3$ intermediate, which then undergoes a concerted proton transfer to produce the final sulfuric acid product. The result of such a mechanism is that the added oxygen (which originates in the water) assumes one of the S−OH positions in the H_2SO_4, and does not incorporate into the S═O position of the molecule. Similarly, in the aqueous phase, calculations predict[37] that the initial formation of the new S−O bond is accompanied

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(36) Bevan, J. W.; Kisiel, Z.; Legon, A. C.; Millen, D. J.; Rogers, S. C. *Proc. R. Soc. London* **1980**, *A372*, 441.

(37) Meijer, E. J.; Sprik, M. *J. Phys. Chem. A* **1998**, *102*, 2893.

(38) Fraser, G. T. *Int. Rev. Phys. Chem.* **1991**, *10*, 189.

(39) Andrews, A. M.; Kuczkowski, R. L. *J. Chem. Phys.* **1993**, *98*, 791.

by proton transfer to a neighboring water solvent molecule, directly producing bisulfate ion, and again leaving the water oxygen in a single-bonded position in the molecule. Thus, while the relative intensities of the two ^{18}O substituted forms of the H_2SO_4 monomer (Figure 3) establish that the sulfuric acid produced in the expansion is indeed 30−40 times richer in the expected product, it appears that 2−3% of the sulfuric acid observed in these experiments has formed via alternate or subsequent processes.

The specific nature of these processes is not clear. One possibility may involve chemistry occurring on the stainless steel surfaces of the nozzle and/or injection needle. However, while such a scenario cannot be rigorously excluded, it seems unlikely in view of previous observations that the same molecular source does not scramble protons when forming H_2O-DNO_3 or D_2O-HNO_3 in the jet.[35b] Another possibility involves participation by larger water clusters in the expansion and raises the interesting question as to how large a cluster must be before the proton scrambling prevalent in aqueous phase becomes viable. Interestingly, Tao and co-workers[31] conclude that SO_3-$(H_2O)_4$ is the first cluster to be unstable with respect to formation of $(HSO_4^-)(H_3O^+)(H_2O)_2$, though this, in itself, does not address the question of proton scrambling after initial ion pair formation. It is also worth noting that the $SO_3 + H_2O$ system is well-known to produce sulfuric acid aerosol, and thus, heterogeneous chemistry associated with microdroplets formed during the early phases of the expansion remains another plausible possibility. We have, however, made no attempt to model the nucleation under these conditions.

Summary

The zero point averaged ground-state structure of $H_2SO_4-H_2O$ has been determined from microwave spectroscopy in a supersonic jet, with the sulfuric acid produced in situ from the reaction of SO_3 and water. The system forms a cyclic, doubly hydrogen bonded complex with a very short (1.645 ± 0.005 Å) primary hydrogen bond between one of the sulfuric acid hydrogens and the water oxygen. A second, longer (2.05 ± 0.01 Å), and presumably weaker hydrogen bond is formed between a water hydrogen and one of the doubly bonded oxygens on the sulfuric acid moiety. Though weak, this secondary interaction appears to provide some stability for the complex, as evidenced by the observation that complexes with HOD are only formed in the jet with deuterium in the hydrogen-bonded position. Spectral evidence further indicates that the system undergoes at least one, and quite possibly more than one type of internal motion. The structure obtained from fitting the observed moments of inertia is in excellent agreement with published DFT and ab initio calculations.[16−19]

Sizable changes in the internal structure of the sulfuric acid unit within the complex are observed. These include a 0.07(2) Å elongation of the hydrogen-bonded OH group and a 0.04(1) Å lengthening of the S═O bond involved in the secondary interaction with the water. The ability to measure the structural distortion of a monomer within a complex is unusual, but is made possible in this system due to the appreciable strength of the interaction, the large contribution that the H_2SO_4 itself makes to the moments of inertia of the complex, and the large amount of isotopic data collected. The observed changes reveal a significant effect on the sulfuric acid of only a single water of hydration. Together with the extremely short hydrogen bond, the geometry of the complex intimates the earliest stages of proton transfer, though certainly, the number of solvent molecules is insufficient to stabilize appreciable charge separation. Nevertheless, these results suggest that the infrared spectrum of the monohydrate, as well as any of the higher hydrates of sulfuric acid, might show measurable shifts relative to the free monomer, and should be of considerable interest. Published calculations support this conjecture.[16]

The formation of H_2SO_4 in the jet appears to involve a small contribution from processes not generally associated with the gas-phase reaction of SO_3 and H_2O. Evidence for such pathways comes from experiments with $^{18}OH_2$, in which the ^{18}O is incorporated in the S═O position of free sulfuric acid, and both S═O positions in the $H_2SO_4-H_2O$ complex. While the occurrence of surface reactions in the nozzle cannot be rigorously excluded as a possible explanation, a scenario involving larger clusters seems more likely. The contribution from these additional pathways, however, is small under the conditions used in these experiments, with the bulk of the sulfuric acid produced incorporating the ^{18}O into the S−OH position.

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Supporting Information Available: Tables of transition frequencies and assignments for $H_2SO_4-H_2O$ and its isotopomers and atomic Cartesian coordinates for the fitted structure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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