

# Structure and Bonding of the Sulfamic Acid Zwitterion: Microwave Spectrum of $^+\text{H}_3\text{N}-\text{SO}_3^-$

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Received November 27, 1995<sup>⊗</sup>

**Abstract:** The donor–acceptor complex formed from  $\text{NH}_3$  and  $\text{SO}_3$  has been observed in the gas phase by pulsed nozzle Fourier transform microwave spectroscopy. The adduct has the expected  $C_{3v}$  geometry in which the nitrogen is bonded to the sulfur. The N–S bond length is 1.957(23) Å and the NSO angle is 97.6(4)°. The complex is the gas-phase form of the zwitterion which constitutes solid sulfamic acid, but the observed structure differs significantly from the results of previous X-ray and neutron diffraction work on the crystal. In particular, the N–S distance is 0.186(23) Å longer in the gas phase and the NSO angle is 4.9(4)° smaller. The observed structure suggests that the dative bond is only partially formed in the isolated complex. Analysis of the nitrogen quadrupole coupling constant supports this conclusion, indicating that about 0.36 electron is transferred upon formation of the complex. The nature of the gas-phase adduct suggests that significant structural and electronic changes may occur within  $^+\text{H}_3\text{N}-\text{SO}_3^-$  monomer units during the early phases of homogeneous nucleation.

## Introduction

The dative bond has played an important role in structural chemistry since it was first introduced by Lewis in 1923.<sup>1</sup> Since that time, the chemistry of donor–acceptor complexes has been extensively investigated,<sup>2</sup> and even today, the subject continues to attract the attention of workers from a wide variety of disciplines.<sup>3–5</sup> In our laboratory, we have been concerned with complexes of  $\text{BF}_3$ ,<sup>6–10</sup>  $\text{SO}_3$ ,<sup>11</sup> and  $\text{SO}_2$ <sup>12</sup> with electron pair donors and have focussed on several novel aspects of their structure and bonding. We have noted, for example, a wide range of bond lengths and bond angles in these systems, encompassing not only those characteristic of van der Waals interactions and fully formed chemical bonds, but representing a continuum of “partially bonded” structures as well.<sup>6,7,9–11</sup> We have also demonstrated that complexes in the gas phase which lie in the partially bonded regime are subject to extraordinary changes in structure upon condensation to form molecular crystals.<sup>5–8,12</sup>

In the context of this work, a number of features of the prototypical donor–acceptor complex  $^+\text{H}_3\text{N}-\text{SO}_3^-$  have be-

come strikingly familiar. The adduct is the tautomer of sulfamic acid ( $\text{NH}_2\text{SO}_2\text{OH}$ ), whose crystal has been shown by both X-ray and neutron diffraction techniques to be comprised not of the aminosulfonic acid form, but rather of  $^+\text{H}_3\text{N}-\text{SO}_3^-$  zwitterionic units.<sup>13–15</sup> Interestingly, however, while the crystalline system has been well-characterized experimentally, the adduct has had a curious history of eluding theoretical attempts to correctly predict the observed structure.<sup>16,17</sup> Indeed even the most recent studies employing various levels of theory<sup>17,18</sup> have given N–S bond lengths and NSO angles which are consistently about 0.1–0.2 Å longer and 5° smaller, respectively, than those observed in the solid. Suspecting that the level of theory could not account for these discrepancies, Wong, Wiberg, and Frisch extended their own *ab initio* calculations of the free monomer to investigate the effects of a dielectric medium on the structure and bonding of the zwitterion.<sup>18</sup> Using the self-consistent reaction field (SCRF) approach, these authors obtained much better agreement with the solid-state data, suggesting that the apparent discrepancies were not due to computational deficiencies, but rather were manifestations of a genuine medium effect. A similar conclusion has also been reached by Cioslowski and Martinov.<sup>19</sup>

The calculated structure of the gas-phase complex<sup>18</sup> has an N–S distance of about 1.9 Å, which is quite long for a chemical bond between nitrogen and sulfur. Moreover, the calculated NSO angle is only 97.8° (compared with 102.5° in the crystal) and the gas-phase binding energy (19.1 kcal/mol) is about half that obtained in the dielectric medium (32.6 kcal/mol). Thus, the *ab initio* results suggest not only a strong medium effect on the bonding, but the existence of a weakened interaction in the gas phase as well. It is the simultaneous appearance of these two phenomena which is reminiscent of our previous experience

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, May 15, 1996.

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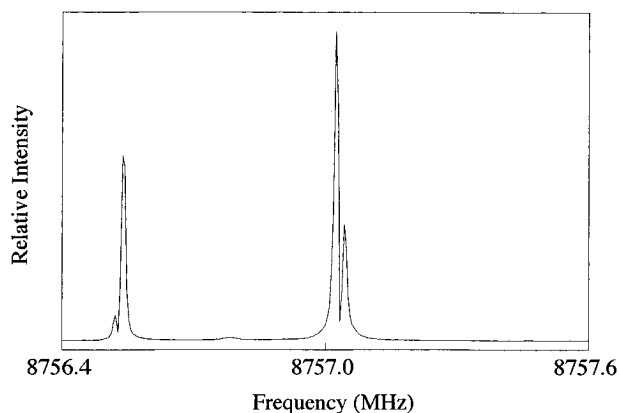
with donor-acceptor complexes<sup>6-12</sup> and has drawn our attention to this system. Although the zwitterion has also been studied in aqueous solution,<sup>20</sup> polar solvents,<sup>21</sup> and under cryogenic conditions,<sup>22</sup> there appears to be no gas-phase experimental work which would provide a suitable comparison with theory. Thus, it is clear that the  $^+H_3N-SO_3^-$  adduct is ripe for a definitive gas-phase structural study.

The  $NH_3-SO_3$  interaction is of interest for a number of other reasons as well. Sulfamic acid, which has been important to chemists for over a century, is widely used in industry and has applications ranging from electrometallurgy to catalysis.<sup>23</sup> Moreover, the  $NH_3-SO_3$  system has recently been suggested as a possible precursor to atmospheric aerosols. In particular, it has been noted that while atmospheric  $NH_3$  is primarily consumed by acidic aerosols and/or cloud water droplets (rather than by  $SO_3$  per se),<sup>24</sup> the  $NH_3 + SO_3$  reaction product, sulfamic acid, may yet be important as it is stable with respect to dissociation.<sup>25</sup> Thus, when the adduct forms, it remains available for further clustering, and even small amounts may represent a significant seed for the growth of atmospheric particulates.<sup>25</sup>  $NH_3$  has also been implicated in a ternary mechanism for sulfate particle formation.<sup>26</sup>

In this paper we report the gas-phase structure of  $^+H_3N-SO_3^-$  as elucidated by pulsed nozzle Fourier transform microwave spectroscopy. The results are in good agreement with theoretical calculations and unambiguously confirm that the complex undergoes substantial changes in the N-S bond length and NSO angle upon crystallization. Examination of the spectroscopic constants indicates that the N-S bond is indeed only partially formed in the gas phase, and the large effect of the crystalline environment, therefore, is in accord with previous results on donor-acceptor adducts. We also speculate that the partially bonded, medium-sensitive nature of the  $NH_3-SO_3$  interaction could significantly impact on the early phases of the homogeneous nucleation involving sulfamic acid. We conclude with a brief comparison to the closely related system  $H_2O-SO_3$ .

## Experimental Section

Rotational spectra of  $^+H_3N-SO_3^-$  were obtained using a newly constructed Balle-Flygare type pulsed-nozzle Fourier transform microwave spectrometer. The technique has been described in detail elsewhere,<sup>27</sup> and the important features of our spectrometer have been summarized in a recent paper.<sup>9</sup> Since  $SO_3$  and  $NH_3$  react to form solid sulfamic acid under bulk conditions, a co-injection nozzle similar to that employed in other laboratories<sup>28</sup> was used to minimize mixing



**Figure 1.** The  $J = 1 \leftarrow 0$ ,  $F = 1 \leftarrow 1$ , and  $F = 2 \leftarrow 1$  transitions of  $^+H_3N-SO_3^-$ . This spectrum resulted from the average of 508 gas pulses and took 67 s to collect.

times. Argon at a pressure of 10 psig was flowed over a sample of solid  $SO_3$  kept at 0 °C, and the resulting mixture was pulsed through a 0.8 mm nozzle orifice. Pure  $NH_3$  at a pressure of approximately 1.0 atm was continuously injected into the expansion through a 0.007 in. ID needle. The needle was inserted into the expansion 1/16 in. below the nozzle orifice and had a 90° bend to direct the ammonia flow along the axis of the expansion. Typically, 10 free induction decays of 256 or 512 data points each were taken per gas pulse, and the time domain signals were averaged over several hundred gas pulses.

Although the co-injection nozzle was designed to minimize reaction between  $SO_3$  and  $NH_3$  before expansion, the nozzle orifice was still prone to clogging due to the formation of solid sulfamic acid. As a result, the chamber housing the microwave cavity was equipped with an airlock which facilitated cleaning of the nozzle without shutdown of the vacuum system. Since the airlock is perpendicular to the cavity axis, all spectra in this study were obtained by pulsing the gas perpendicular rather than parallel to the microwave cavity.

Initial spectral searches were guided by published *ab initio* structure calculations.<sup>18</sup> The spectral peaks due to the  $^+H_3N-SO_3^-$  complex were identified by their dependence on  $NH_3$  flow and the characteristic quadrupole splitting of the  $^{14}N$  nucleus. Further confirmation was obtained by the agreement between the observed and predicted rotational spectra for the corresponding  $^{15}N$  and  $^{34}S$  substituted complexes. The  $^{34}S$ -containing adducts were observed in natural abundance while the  $^{15}N$ -containing species were obtained using isotopically enriched  $^{15}NH_3$ . A sample spectrum is shown in Figure 1. Note that the usual Doppler doubling, which appears clearly in this spectrum, was found to be sensitive to the exact location of the  $NH_3$  injection needle. This effect, together with the appearance of only partially resolved magnetic hyperfine structure on some of the transitions, rendered many of the observed line shapes somewhat irreproducible.

Interestingly, the calculations of Wong et al.<sup>18</sup> have indicated that both the zwitterionic and neutral forms ( $^+H_3N-SO_3^-$  and  $NH_2SO_3H$ , respectively) lie very close in energy in the gas phase, with the latter more stable by only 0.5 kcal/mol. The barrier to interconversion, however, was predicted to be 28.6 kcal/mol, and thus the primary interaction product, which is presumably the zwitterion, is expected to be kinetically stabilized at the ~2 K temperature of the supersonic jet. Although no spectral searches were conducted with the specific intent of locating the neutral form, no transitions attributable to it were found during the course of this study.

## Results

The observed frequencies for the  $J = 1 \leftarrow 0$  and  $2 \leftarrow 1$  transitions of the isotopic species studied are listed in Table 1. Some of the observed nitrogen hyperfine components were further split, presumably by magnetic coupling due to  $NH_3$ , but these splittings were only partially resolved and were not analyzed. The frequencies were readily fit to the usual expression for a symmetric rotor with centrifugal distortion terms

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**Table 1.** Fitted Transition Frequencies for  ${}^+{}^3\text{H}_3\text{N}-\text{SO}_3^-$ <sup>a</sup>

isotopic form	$J''$	$J'$	$F''$	$F'$	$K$	freq (MHz)	obsd - calcd
${}^{14}\text{NH}_3-{}^{32}\text{SO}_3$	0	1	1	1	0	8756.527	-0.002
	0	1	1	2	0	8757.035	-0.001
	0	1	1	0	0	8757.798	0.003
	1	2	2	2	0	17513.350	0.004
	1	2	0	1	0	17513.430	-0.001
	1	2	1	2	1	17513.742	0.004
	1	2	1	2	0	17513.850	-0.003
	1	2	2	3	1	17514.258	-0.005
	1	2	0	1	1	17514.794	0.001
	1	2	1	1	0	8746.499	-0.001
${}^{14}\text{NH}_3-{}^{34}\text{SO}_3$	0	1	1	2	0	8747.006	0.000
	0	1	1	0	0	8747.765	0.001
	1	2	2	2	0	17493.293	0.004
	1	2	0	1	0	17493.369	-0.004
	1	2	1	2	1	17493.677	0.003
	1	2	1	2	0	17493.793	-0.002
	1	2	2	3	0	17493.833	0.002
	1	2	1	1	1	17494.090	-0.005
	1	2	2	3	1	17494.200	0.002
	${}^{15}\text{NH}_3-{}^{32}\text{SO}_3$	0	1			0	8543.194
1		2			0	17086.341	0.000 <sup>b</sup>
1		2			1	17086.651	0.000 <sup>b</sup>
${}^{15}\text{NH}_3-{}^{34}\text{SO}_3$	0	1			0	8532.313	0.000 <sup>b</sup>
	1	2			0	17064.583	0.000 <sup>b</sup>
	1	2			1	17064.891	0.000 <sup>b</sup>

<sup>a</sup> All frequencies in MHz. Estimated uncertainties are 5 kHz or less.<sup>b</sup> The residuals vanish since three frequencies were used to calculate three spectroscopic constants.**Table 2.** Spectroscopic Constants for  ${}^+{}^3\text{H}_3\text{N}-\text{SO}_3^-$ <sup>a</sup>

isotopic form	$B$ (MHz)	$D_J$ (kHz)	$D_{\text{eff}}$ (kHz)	$eqQ({}^{14}\text{N})$ (MHz)
${}^{14}\text{NH}_3-{}^{32}\text{SO}_3$	4378.4797(16)	2.06(23)	-76.79(86)	-1.6882(54)
${}^{14}\text{NH}_3-{}^{34}\text{SO}_3$	4373.4647(15)	2.01(21)	-75.12(73)	-1.6854(58)
${}^{15}\text{NH}_3-{}^{32}\text{SO}_3$	4271.6009(27)	1.96(46)	-77.5(18)	
${}^{15}\text{NH}_3-{}^{34}\text{SO}_3$	4266.1601(27)	1.79(47)	-77.0(18)	

<sup>a</sup> Uncertainties for the  ${}^{14}\text{N}$  species are one standard error in the fit. Uncertainties for the  ${}^{15}\text{N}$  species are derived directly from the 0.005 MHz measurement uncertainty.

and nuclear quadrupole coupling, viz.

$$\nu = 2(J'' + 1)[B - D_{\text{eff}}K^2] - 4D_J(J'' + 1)^3 + \Delta E_Q \quad (1)$$

In this expression  $D_{\text{eff}}$  is an effective distortion constant (discussed in more detail below), and other symbols have their usual meanings.<sup>29</sup>  $\Delta E_Q$ , which vanishes for the  ${}^{15}\text{N}$  species, is the difference in hyperfine energies between the upper and lower states and was calculated using the usual first-order treatment for the  ${}^{14}\text{N}$  nucleus. A least-squares analysis of eq 1 was performed for each isotopic species, and the fitted spectroscopic constants are given in Table 2.

The *ab initio* calculations of Wong et al.<sup>18</sup> indicate that the internal rotation barrier of the complex is about 0.4 kcal/mol. Thus, the reduced barrier height<sup>29,30</sup> is about 10, and even allowing for substantial error in this value, the system lies in the "intermediate barrier" regime described by Lin and Swalen.<sup>30b</sup> The energy levels observed in this work correspond to the A and E levels of the ground torsional state, but may also be approximately described by the quantum number  $m$ , which gives the angular momentum of the  $\text{NH}_3$  about its symmetry axis in the limit of free internal rotation. The A levels correlate with  $m = 0$  and the E levels correlate with  $m = \pm 1$ . The determination of internal rotation barriers for symmetric tops

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generally requires the observation of excited torsional states, or states with  $|m| > 1$ ,<sup>29,30</sup> and since the population of these levels is precluded by the  $\sim 2$  K temperature attained in an argon expansion, the barrier height is not determined in this work.

The oxygen and proton nuclear spin statistics have an observable effect on the spectrum, and are readily understood in the language of free internal rotation. In the limit of infinite separation of the monomer units,  $m$  and  $K - m$  correlate with  $k_{\text{NH}_3}$  and  $k_{\text{SO}_3}$ , respectively, where the  $k$ 's are the ordinary  $K$  quantum numbers for the free monomer units.<sup>29</sup> Since the oxygens are spinless,  $k_{\text{SO}_3}$  is restricted to multiples of three. Moreover, the collisional interconversion of the  $k = 0$  and  $\pm 1$  states of  $\text{NH}_3$  is nuclear spin forbidden, and thus both the  $m = 0$  and  $\pm 1$  states of the complex are populated in the expansion. States with  $|m| > 1$ , however, are not populated, as they have energies substantially higher than  $kT$  in the jet, and may be cooled to  $m = 0$  or  $\pm 1$ . For the rotational transitions observed in this study,  $K$  is necessarily  $\leq 1$  and, since  $K = k_{\text{SO}_3} + k_{\text{NH}_3}$ , the spin statistics require that only states with  $K = m$  are observed. Without this restriction, the  $D_{JKm}Km$  distortion term used by Fraser et al. in the analysis of  $\text{F}_3\text{CH}-\text{NH}_3$  spectra<sup>31</sup> splits the  $K = \pm 1$  transitions into a doublet whose components correspond to  $mK > 0$  and  $mK < 0$ . In the present case, however, with  $m = K$ , only the  $mK > 0$  component is observed.  $D_{\text{eff}}$  in eq 1 is related to the constants of Fraser et al.<sup>31</sup> by  $D_{\text{eff}} = D_{JK} + D_{JM} + D_{JKm}$ , but is about an order of magnitude smaller than that calculated from the individually measured distortion constants for  $\text{F}_3\text{CH}-\text{NH}_3$ . Whether this is due to a fortuitous cancellation in the sum (which occurs to some extent for  $\text{F}_3\text{CH}-\text{NH}_3$ ) or to the presumably higher reduced barrier in the  ${}^+{}^3\text{H}_3\text{N}-\text{SO}_3^-$  complex cannot be determined from the present data.

## Structure Analysis

The existence of a symmetric top spectrum and the results of the  ${}^{15}\text{N}$  substitution experiments confirm the expected geometry of the adduct in which the nitrogen lone pair is directed toward the sulfur along the  $\text{C}_3$  axis of the  $\text{SO}_3$ . Further analysis of the rotational constants is facilitated by a number of simple but reasonable approximations which reduce the set of structural parameters to be determined. Preliminary calculations give an N-S distance of about 2.0 Å, which lies between the 1.7714(3) Å value observed in the crystal and the 2.9 Å value expected for a nitrogen-sulfur van der Waals interaction (see next section). Thus, the true values of  $r_{\text{NH}}$ ,  $r_{\text{SO}}$ , and  $\gamma_{\text{HNH}}$  in the gas-phase complex also almost certainly lie within the rather narrow intervals defined by the unperturbed monomers<sup>32,33</sup> and the crystalline solid. The HNH angle of free  $\text{NH}_3$ <sup>32</sup> differs from that in crystalline sulfamic acid<sup>13-15</sup> by less than 2°, while the N-H and S-O bond lengths differ by only 0.0188 and 0.0225 Å, respectively. These ranges are quite small, and since the N-S bond length in the gas phase is significantly closer to that in the solid state, we constrain  $r_{\text{NH}}$ ,  $\gamma_{\text{HNH}}$ , and  $r_{\text{SO}}$  to their crystallographically determined values<sup>15,34</sup> (1.0344 Å, 108.78°, and 1.4423 Å, respectively).

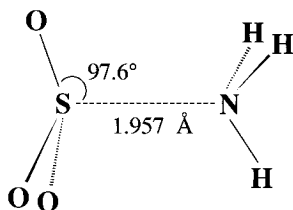
With this simplification, the N-S bond length and the NSO angle are readily determined from the measured rotational constants. Since the bond angle is determined primarily from

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**Table 3.** Structural Parameters for  $^+\text{H}_3\text{N}-\text{SO}_3^-$ 

	experimental		theoretical	
	gas <sup>a</sup>	crystal <sup>b</sup>	gas <sup>c</sup>	SCRF <sup>e,d</sup>
$R(\text{N}-\text{S})$ (Å)	1.957(23)	1.7714(3)	1.912 <sup>c</sup>	1.817
$\alpha(\text{NSO})$ (deg)	97.6(4)	102.46(2)	97.8	101.0
$\Delta R$ (Å)		0.186(23)		0.095
$\Delta\alpha(\text{NSO})$ (deg)		-4.9(4)		-3.2

<sup>a</sup> This work. <sup>b</sup> Reference 15. <sup>c</sup> Reference 18. <sup>d</sup> Dielectric medium,  $\epsilon = 40$ . <sup>e</sup> This value is for the staggered configuration. The calculated value increases to 1.950 Å in the eclipsed conformation, which represents a local maximum on the torsional potential.



**Figure 2.** The structure of  $^+\text{H}_3\text{N}-\text{SO}_3^-$  drawn in the staggered configuration. The intermolecular torsional angle is not determined in this work.

the  $^{32}\text{S}/^{34}\text{S}$  isotope shift, the four rotational constants listed in Table 2 provide a redundant determination of the structure. Using the  $^{14}\text{N}$  data, analysis of the rotational constants gives  $R(\text{NS}) = 1.9566$  Å and  $\alpha(\text{NSO}) = 97.61^\circ$ , while  $^{15}\text{N}$  gives 1.9575 Å and  $97.60^\circ$  for the bond length and bond angle, respectively. The results are in remarkable agreement and the averages of the two bond lengths and bond angles are reported in Table 3. The structure is shown in Figure 2. Note that the rotational constants do not depend on the intermolecular torsional angle (which, therefore, remains undetermined in the analysis), but the system has been drawn in the staggered configuration corresponding to the calculated<sup>18</sup> minimum energy structure.

The dominant source of uncertainty in these results arises from approximations inherent in the structural model, and these are now considered in detail. The first concerns treatment of the adduct as a rigid molecule. Had the system been a weakly bound species, large-amplitude motion of the  $C_3$  axes of the two monomers away from the equilibrium  $C_{3v}$  geometry of the complex would necessitate the application of small corrections in the analysis of the rotational constants. Implicit in the above treatment, however, is that these vibrational amplitudes are vanishingly small. A conservative estimate of their effects can be made by assuming that the angular non-rigidity of the complex is comparable to that in a truly weakly bound system. This will surely overestimate the error incurred, since by several criteria (bond length, bond angle, and *ab initio* binding energy) the system is more strongly bound than a van der Waals complex. But the effects turn out to be small and, as described below, provide our best (or at least safest) estimate of the model-related uncertainty in the structure.

It has been noted previously that in nitrogen-bound van der Waals complexes of  $\text{NH}_3$ , the zero point vibrationally averaged excursion of the  $C_3$  axis of the ammonia away from its equilibrium position is about  $22^\circ$ .<sup>31,35,36</sup> This determination is made from the measured values of the nitrogen nuclear quadrupole coupling constant assuming that complexation does not alter the electronic structure of the ammonia. Repetition

(35) Fraser, G. T.; Leopold, K. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 2577.

(36) More precisely,  $\langle \cos^2 \theta \rangle = \cos^2(22^\circ)$ . The vibrationally averaged structure of the complex is still axially symmetric, with  $\langle \theta \rangle = 0$ .

of the structural analysis using standard equations<sup>6,37</sup> and an average excursion amplitude of  $22^\circ$  produces only minor differences in the calculated results, changing the N-S distance and NSO angle by  $-0.0011$  Å and  $-0.02^\circ$ , respectively.

For the  $\text{SO}_3$  moiety, no corresponding information is available for weakly bound systems due to the absence of nuclear spins. However, the moments of inertia of  $\text{SO}_3$  are nearly equal to those of  $\text{BF}_3$ , and the two molecules are quite similar in their interaction with common binding partners. Thus, an estimate of the vibrational amplitude for weakly bound  $\text{BF}_3$  complexes should provide a similarly conservative upper limit for the vibrational excursions of the  $\text{SO}_3$ . For  $\text{Ar}-\text{BF}_3$ ,  $\text{CO}-\text{BF}_3$ ,  $\text{HF}-\text{BF}_3$ , and  $\text{HCN}-\text{BF}_3$ , the angles are  $15.0^\circ$ ,<sup>38,39</sup>  $13.7^\circ$ ,<sup>38,39</sup>  $13.6^\circ$ ,<sup>9</sup> and  $13.1^\circ$ ,<sup>7</sup> respectively, with an average value of  $13.8^\circ$ . Repetition of the structural calculations for  $\text{H}_3\text{N}-\text{SO}_3$  with this value changes the N-S bond length and NSO angle by only  $-0.019$  Å and  $-0.3^\circ$ , respectively.

Finally, the effect of the assumed monomer geometries on the calculated structure can be tested. If the S-O bond length in  $\text{SO}_3$  is shortened to the 1.4198-Å monomer value,<sup>33</sup> the calculated values for  $R(\text{N}-\text{S})$  and  $\alpha$  change by 0.021 Å and  $0.4^\circ$ , respectively. Similarly, constraining the N-H bond length and the HNH angle of  $\text{NH}_3$  to the values observed in free ammonia<sup>32</sup> results in inconsequential changes of  $-0.003$  Å in  $R(\text{N}-\text{S})$  and  $0.009^\circ$  in  $\alpha$ . The uncertainties quoted in Table 3 are chosen to encompass the sum of all of the model-dependent uncertainties calculated above.

## Discussion

The experimental values of  $R(\text{NS})$  and  $\alpha(\text{NSO})$  determined above unambiguously affirm the conclusion of Wong et al.<sup>18</sup> that the differences between the *ab initio* and crystal phase structures are due to a genuine medium effect. This is readily seen in Table 3, which gives the experimental geometries for both the gas-phase and solid-state zwitterions, together with previously published *ab initio* results. The experimental structure establishes that the NS bond contracts by 0.186(23) Å and the NSO angle widens by  $4.9(4)^\circ$  upon crystallization. The calculated gas-phase bond length is in good agreement with that observed, but is somewhat short, while that in the dielectric medium is somewhat long. The errors add, giving predicted gas-solid structure differences which are about a factor of 2 smaller than those actually observed (0.095 Å vs 0.186 Å for  $R(\text{NS})$  and  $3.2^\circ$  vs  $4.9^\circ$  for  $\alpha(\text{NSO})$ ). The 0.186-Å shortening of the N-S bond is similar to the 0.214(34)-Å contraction which has been observed in  $(\text{CH}_3)_3\text{N}-\text{SO}_2$  upon crystallization.<sup>40,41</sup>

A cursory examination of the structure of the complex indicates that the dative bond is only partially formed in the gas phase. The most obvious indicator, perhaps, is the  $7.6^\circ$  out-of-plane distortion of the  $\text{SO}_3$ , which is halfway between the  $0^\circ$  and  $12.5^\circ$  distortions of the free monomer and the crystalline complex, respectively. Moreover, the gas-phase bond length is 0.22 Å longer than that of an N-S single bond, but 0.94 Å shorter than the predicted van der Waals bond length (2.90 Å). The latter estimate takes into account the strong dependence of the "van der Waals radius" of sulfur on oxidation

(37) Fraser, G. T.; Leopold, K. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 1423.

(38) Janda, K. C.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Am. Chem. Soc.* **1978**, *100*, 8074.

(39) These values are calculated from the original data of ref 38 using the subsequently measured value of  $eqQ(^{14}\text{B}) = 3.002(13)$  MHz: (a) Dreizler, H. Z. *Naturforsch.* **1992**, *47a*, 342. (b) Vormann, K. Dissertation, Kiel, 1991.

(40) Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, K. W., II; Kuczowski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 4732.

(41) van Der Helm, D.; Childs, J. D.; Christian, S. D. *Chem. Commun.* **1969**, 887.

state<sup>42</sup> by employing a comparison of known bond lengths in Ar–BF<sub>3</sub>,<sup>38</sup> N<sub>2</sub>–BF<sub>3</sub>,<sup>38</sup> and Ar–SO<sub>3</sub>.<sup>42,43</sup> The former arises simply from the sum of standard single bond covalent radii of nitrogen and sulfur,<sup>45</sup> which give 1.74 Å.<sup>46</sup> That the isolated system is only partially bonded is further substantiated by the calculations of Wong et al.,<sup>18</sup> which give a binding energy of 19.1 kcal/mol in the gas phase, but 32.6 kcal/mol in a dielectric medium of  $\epsilon = 40$ .

We have noted previously<sup>5,6,8</sup> that large gas–solid structure differences are a characteristic feature of molecules which, like <sup>+</sup>H<sub>3</sub>N–SO<sub>3</sub><sup>–</sup>, are intermediate between weakly bonded complexes and chemically bound species. In effect, with a large dynamic range accessible to the bonding in these systems, and with intramolecular bond energies low enough to be rivaled by crystal lattice energies, the existence of intermolecular interactions produces profound changes in the nature of intramolecular bonds. Thus, the extreme sensitivity of this system to the presence of an environment is not surprising in light of its gas-phase structure.

It is worth noting that the large gas–solid structure differences observed for this complex are likely to have direct implications regarding the nature of sulfamic acid containing clusters, whose formation, as noted above, has been suggested as a possible route to atmospheric particulates. Clearly, the structure and bonding of a sulfamic acid unit is sensitive to the presence of a condensed medium, and thus the physical properties of the free monomer must transform as nucleation takes place. Moreover, it is likely that the largest changes occur at the very small cluster level, i.e. in response to the appearance of nearest neighbors.<sup>48</sup> Thus, we expect that the properties of an <sup>+</sup>H<sub>3</sub>N–SO<sub>3</sub><sup>–</sup> unit change rapidly as clustering proceeds. Indeed, in light of the calculated increase in dipole moment upon bond formation,<sup>18</sup> one might even speculate that the <sup>+</sup>H<sub>3</sub>N–SO<sub>3</sub><sup>–</sup> becomes stickier as a cluster grows. But regardless of the specific outcome of the effect, the system's hypersensitivity to the existence of a medium is certain to have a significant impact on the kinetics and thermodynamics of the elementary reactions leading to particle formation. Thus, it seems likely that any molecular-level understanding of the growth of a sulfamic acid based particle will need to incorporate this effect.

The <sup>14</sup>N nuclear quadrupole coupling constant contains quantitative information about the electronic structure of the complex. Indeed, the –1.6882(54)-MHz value of  $eQq(N)$  measured for <sup>+</sup>H<sub>3</sub>N–SO<sub>3</sub><sup>–</sup> is strikingly different from that observed in weakly bound systems such as CF<sub>3</sub>H–NH<sub>3</sub>,<sup>31</sup> HCCH–NH<sub>3</sub>,<sup>37</sup> and CO<sub>2</sub>–NH<sub>3</sub>,<sup>35</sup> for which the measured values of  $eQq(N)$  are –3.186(8), –3.137(18), and –3.175(4) MHz, respectively. The reduction in  $eQq(N)$  for these systems relative to that in free ammonia is not electronic but rather is

(42) Bowen, K. H.; Leopold, K. R.; Chance, K. V.; Klemperer, W. *J. Chem. Phys.* **1980**, *73*, 137.

(43) The difference in hybridization between N<sub>2</sub> and NH<sub>3</sub> is immaterial. For example, if H<sub>3</sub>N–CO<sub>2</sub><sup>35</sup> and Ar–CO<sub>2</sub><sup>44</sup> are used in place of N<sub>2</sub>–BF<sub>3</sub> and Ar–BF<sub>3</sub>, the predicted N–S bond distance is 2.85 Å.

(44) Steed, J. M.; Dixon, T. A.; Klemperer, W. *J. Chem. Phys.* **1979**, *70*, 4095.

(45) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1972.

(46) Interestingly, examination of the abundant structural data given in ref 47 indicates that nominally single bonded N–S distances most often lie in the 1.6–1.7-Å range. The apparent shortening relative to the sum of single bond covalent radii may be attributable to contributions from multiply bonded resonance structures.

(47) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984.

(48) A perhaps useful point of reference in this connection is provided by recent *ab initio* calculations on H<sub>3</sub>N–BH<sub>3</sub>, which also exhibits a significant (0.093 Å) contraction of the dative bond upon crystallization. For this system, 60% of the change in bond length between the gas phase and solid state is realized upon the conglomeration of only four monomer units! See ref 4.

predominantly projective in origin, i.e., it arises from zero point angular oscillations of the NH<sub>3</sub> moiety relative to the figure axis of the complex, not from bonding.<sup>31,35,37</sup> If such were the case for <sup>+</sup>H<sub>3</sub>N–SO<sub>3</sub><sup>–</sup>, the measured value of  $eQq(N)$  would imply a 39° angular excursion of the NH<sub>3</sub> moiety. Since all the evidence is that the NH<sub>3</sub>–SO<sub>3</sub> interaction is significantly stronger than a van der Waals bond, this degree of angular non-rigidity is unphysical, and a projective interpretation of  $eQq$  is certainly incorrect. In this regard, it is also interesting to note that the calculated dipole moment of the gas-phase complex is 6.61 D,<sup>18</sup> which is 4.5 times the sum of the monomer moments. This further supports the notion that significant electronic changes are incurred upon formation of the N–S bond.<sup>49</sup>

In this light, it is natural to interpret the measured value of  $eQq(N)$  according to the simplistic but widely used analysis of Townes and Dailey.<sup>29</sup> The essence of the approach is that the dominant contribution to the molecular electric field gradient (and hence to  $eQq$ ) arises from valence p electrons on the quadrupolar nucleus. Thus, changes in  $eQq$  upon bond formation reflect the loss of p electrons at the atomic center. If  $\phi_N$  is the approximately sp<sup>3</sup> hybridized donor orbital on the nitrogen and  $\phi_S$  is the acceptor orbital on the SO<sub>3</sub>, expression of the wave function for the dative bond as  $\psi_d = \alpha\phi_N + \beta\phi_S$  readily allows the reduction in the quadrupole coupling constant of the complex relative to that of free ammonia to be given by

$$[(eQq)_{\text{complex}} - (eQq)_{\text{NH}_3}] = -6a_s^2(eQq_{210})(1 - \alpha^2) \quad (2)$$

This is equivalent to the formulas given by Oh et al.<sup>40</sup> and by Lucken,<sup>50</sup> albeit cast in somewhat different terms.  $a_s$  is the coefficient of the nitrogen 2s function in the NH bond wave functions of NH<sub>3</sub>, and  $(eQq_{210})$  is the quadrupole coupling constant for a single 2p<sub>z</sub> electron in atomic nitrogen. The latter has been estimated to be –9.0 MHz,<sup>50</sup> while the former can be obtained from the observed HNH bond angle in ammonia,  $\gamma$ , according to the expression<sup>29b,50</sup>

$$a_s^2 = \cos \gamma / (\cos \gamma - 1) \quad (3)$$

Thus, assuming that the observed reduction in  $eQq$  upon complexation is entirely due to electronic reorganization, the values  $\gamma = 108.78^\circ$ <sup>15</sup> and  $(eQq)_{\text{NH}_3} = -4.08983(2)$  MHz<sup>32b</sup> give  $\alpha^2 = 0.82$ . Since the dative bond is occupied by two electrons, this may be interpreted as a transfer of 0.36 electron away from the nitrogen. Alternatively, the value of  $\alpha^2 = 0.82$  is seen to be about midway between  $\alpha^2 = 1$  (no bond) and  $\alpha^2 = 0.5$  (perfectly equitable electron pair sharing between the moieties). In either viewpoint, the bond appears to be only “partially formed”.

Although the electronic contribution to  $eQq(N)$  is clearly significant, it is perhaps prudent to assess the possible effect of a convolution of electronic and angular zero point motions on the above analysis. In the absence of electronic reorganization, as is normally assumed for *weakly bound* systems, the change

(49) Interestingly, in the complex of NH<sub>3</sub> with SiF<sub>4</sub>,  $eQq(^{14}\text{N})$  has a value of –2.77 MHz (which is much closer to that of a weakly bound complex than the –1.688-MHz value determined here), yet the measured increase in dipole moment upon complexation is 4.14 D! See: (a) Ruoff, R. S.; Emilsson, T.; Jaman, A. I.; Germann, T. C.; Gutowsky, H. S. *J. Chem. Phys.* **1992**, *96*, 3441. (b) Keith, T. A.; Bader, R. F. W. *J. Chem. Phys.* **1992**, *96*, 3447.

(50) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: New York, 1969.

in  $eQq$  relative to that of the free monomer is given by<sup>51</sup>

$$(eQq)_{\text{complex}} = (1/2)(eQq)_0(3 \cos^2 \theta - 1) \quad (4)$$

Here,  $(eQq)_{\text{complex}}$  and  $(eQq)_0$  are the measured quadrupole coupling constants in the complex and the free monomer, respectively,  $\theta$  is the angle that the symmetry axis of the  $\text{NH}_3$  forms with the  $a$ -inertial axis of the complex, and the angular brackets denote averaging over the vibrations of the molecule. In the present case, if we again assume that upper limit for the angular oscillation amplitude corresponds to the  $22^\circ$  value typical of a weakly bound ammonia complex, eq 4 provides a "corrected" value of  $(eQq)_0$  of  $-2.1383$  MHz. This may be interpreted as the " $(eQq)_0$ " of an electronically reorganized  $\text{NH}_3$ , whose value in the complex is reduced still further by a  $22^\circ$  angular zero point oscillation. Using the zero-point corrected coupling constant in the Townes and Dailey analysis above changes the calculated value of  $\alpha^2$  to 0.85, and corresponds to a transfer of 0.30 electron upon formation of the dative bond. Thus, contamination of the quadrupole coupling constant by angular oscillations comparable to even those in a truly weakly bound complex has only a minor impact on the estimated degree of electronic reorganization.

It is pleasing to note that the above analysis, giving about a third of an electron transferred upon complexation, is quite consistent with the calculations of Wong et al.<sup>18</sup> whose *ab initio* calculations indicate a charge transfer of 0.28 electron. We caution, however, that the two quantities are somewhat different, and their comparison is not to be overinterpreted. The *ab initio* numbers arise from a quantum topological analysis which explicitly considers charges on all atoms. Indeed, some of the significant changes in charge which develop as a result of the 0.28 e transfer from  $\text{NH}_3$  to  $\text{SO}_3$  occur on the hydrogens and oxygens. Thus, the simple expression of the dative bond in terms of nitrogen and sulfur atomic orbitals, though standard in the Townes and Dailey analysis, necessarily misses significant features of the charge redistribution in this system. The agreement, nonetheless, is remarkable.

Despite the above caveat, the dative bond appears, from both a theoretical and experimental standpoint, to be only partially formed. It is interesting to note that with the transfer of about a third of an electron, and a covalent bond order of 0.46,<sup>18</sup> the NSO angle lies almost exactly between that of a hypothetical van der Waals complex ( $90^\circ$ ) and that in crystalline sulfamic acid ( $102.46(2)^\circ$ ). In contrast, however, the N–S distance is only about 0.22 Å longer than that of an N–S single bond, yet a full 0.9 Å shorter than that of a van der Waals bond. This would suggest that truly chemical interactions do not develop linearly as the nitrogen proceeds from the van der Waals interaction distance to the N–S single bond distance, but rather that the development of a true bond occurs primarily at relatively short distances. Similar behavior has been noted previously for the formation of dative bonds to  $\text{BF}_3$ .<sup>5,6,52</sup>

In view of the above results, it is also interesting to consider the mechanical rigidity of the N–S bond in the gas phase. If the centrifugal distortion of the complex were dominated by stretching of the intermolecular bond, the stretching force constant,  $k_s$ , would be simply related to the centrifugal distortion constant of the complex,  $D_J$ , according to<sup>31,53</sup>

$$k_s = (4\pi)^4 (M_s R_{\text{cm}})^2 B^4 / 2hD_J \quad (5)$$

Here,  $M_s$  is the pseudodiatomic reduced mass of the complex and  $R_{\text{cm}}$  is the separation between the centers of mass of the  $\text{NH}_3$  and the  $\text{SO}_3$  moieties. In light of the nature of the dative bond in this system, however, it is not obvious that the intermolecular stretch should dominate the observed value of  $D_J$ . Nonetheless, it is interesting to note that naive application of the above formula gives a force constant of about 0.8 mdyn/Å, which is much larger than that of a typical van der Waals bond, yet somewhat smaller than that of most ordinary chemical bonds. For example, the stretching force constant in  $\text{H}_3\text{N}-\text{CO}_2$  is 0.070 mdyn/Å,<sup>35</sup> while most single bond force constants are of the order of several mdyn/Å.<sup>54</sup> Vibrational analysis of solid  $^+\text{H}_3\text{N}-\text{SO}_3^-$  gives an N–S force constant of 2.2 mdyn/Å.<sup>55</sup>

Finally, it is of interest to compare the structure of  $^+\text{H}_3\text{N}-\text{SO}_3^-$  with that recently determined for  $\text{H}_2\text{O}-\text{SO}_3$ .<sup>11</sup> The microwave spectrum of the water complex indicates only a  $2-3^\circ$  out-of-plane distortion of the  $\text{SO}_3$  moiety, in contrast with the  $7-8^\circ$  deformation observed here. Moreover, the intermolecular S–O bond length in  $\text{H}_2\text{O}-\text{SO}_3$  is only about 0.4 Å shorter than a van der Waals bond, while for the  $\text{NH}_3$  adduct, the shortening relative to the predicted van der Waals distance is about 0.9 Å. These observations are in good accord with chemical intuition, since  $\text{NH}_3$  is generally regarded as a stronger Lewis base than  $\text{H}_2\text{O}$ . Indeed, these differences are mirrored in the *ab initio* binding energies of the complexes, which are 7.9<sup>56</sup> and 19.1 kcal/mol<sup>18</sup> for the  $\text{H}_2\text{O}$  and  $\text{NH}_3$  complexes, respectively. The calculated degrees of charge transfer, 0.04 (ref 56) and 0.28 e (ref 18) for the  $\text{H}_2\text{O}$  and  $\text{NH}_3$  complexes, respectively, further parallel this trend.

## Conclusion

The gas-phase structure of  $^+\text{H}_3\text{N}-\text{SO}_3^-$  has been obtained via pulsed-nozzle Fourier transform microwave spectroscopy. The experimental structure is that of a symmetric top in which the nitrogen lone pair bonds to the sulfur with a N–S bond length of 1.957(23) Å and an NSO angle of  $97.6(4)^\circ$ . This study unambiguously confirms previous predictions that the structure of the complex is strongly affected by the presence of a medium. Specifically, the N–S bond length decreases by 0.186(23) Å and the NSO angle increases by  $4.9(4)^\circ$  upon condensation to form crystalline sulfamic acid. The gas-phase structure indicates that the N–S interaction is neither a van der Waals bond nor a fully developed chemical bond. Mechanical and electronic properties of the system support this view. The unusual sensitivity of the complex to the presence of an environment is consistent with previous work on donor–acceptor adducts which has indicated a fundamental connection between large gas–solid structure differences and the existence of partially formed bonds. This feature of the system indicates that the homogeneous nucleation about sulfamic acid is likely to be accompanied by significant structural and electronic changes in monomer units during the early phases of clustering.

**Acknowledgment.** The support of the National Science Foundation is gratefully acknowledged. We also thank Drs. E. R. Lovejoy and D. R. Hanson for a preprint of ref 25.

JA953983M

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