Weakly bound complexes of sulfur trioxide: The structure of ArSO₃ and the dipole moment of N₂SO₃[a]

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Microwave and radio frequency spectra of $ArSO_3$ and radio frequency spectra of N_2SO_3 are measured by molecular beam electric resonance spectroscopy. Both complexes are symmetric rotors. The spectroscopic constants determined for $Ar^{32}SO_3$ are $B = 1449.089(5)$ MHz, $D_J = 3.6(6)$ kHz, and $\mu = 0.2676(3)$ D. For $Ar^{34}SO_3$, $B = 1439.090(5)$ MHz. The stretching frequency of the weak Ar–S bond is $61.(5)$ cm^{-1}, and the force constant is thus $0.059(10)$ mdyn/Å. The Ar–S bond length in $ArSO_3$ is $3.350(1)$ Å. The Ar–S–O angle is found to be $90.5°(5)$, thereby indicating no significant out-of-plane distortion of the SO_3 moiety. Preliminary assignment of the N_2SO_3 spectrum yields a dipole moment of $0.46(1)$ D. Electric deflection studies show that $(SO_3)_2$ and $(SO_3)_3$ are polar species, while Xe_2SO_3 is not.

INTRODUCTION

Sulfur trioxide is a strong Lewis acid which is of chemical as well as industrial and environmental interest.[1] It may be prepared by the heterogeneous catalytic oxidation of SO_2 (the contact process for manufacturing sulfuric acid), by the photochemical oxidation of SO_2, and by the nitrogen oxide-catalyzed dark oxidation of damp SO_2 (the old lead chamber process). While reactions involving SO_3 in the troposphere are not well understood, oxidation reactions between SO_2 and free radicals are thought to be important sources of SO_3 there.[2] In addition, several negative ion-neutral reactions of probable importance in the ionosphere are known to produce SO_3^- and SO_3.[3] In both organic and inorganic synthesis, where it is an important sulfonating agent, SO_3 is often used in the form of an adduct (or complex) in order to reduce its reactivity.[4,5]

Since SO_3 is among the most important of manufactured chemicals, and since the reactivity of many of its adducts is well characterized, it is surprising that so little structural information is available about the complexes of sulfur trioxide. X-ray crystallographic studies have been performed on SO_3 complexes of As_2O_3,[6] Sb_2O_3,[7] $(CH_3)_3N$,[8] and S_4N_4,[9] on graphite insertion compounds involving SO_3,[10] and on sulfur trioxide trimer.[11] The latter was found to be a nonplanar, six-membered ring. In the case of $(CH_3)_3N \cdot SO_3$, which is the most interesting of these complexes to us, the nitrogen–sulfur distance was unfortunately not determined. In general, the state of structural information about SO_3 complexes is in sharp contrast to that for adducts of the similarly structured Lewis acid, BF_3, for which copious structural data are available through both x-ray crystallographic and microwave spectroscopic studies.

Infrared and Raman spectra of a wide variety of organic and inorganic SO_3 complexes,[12–22] including those involving As_2O_3,[23] $(CH_3)_3N$,[24] and SO_3 trimer,[25,26] have also been recorded. In addition, the Raman spectrum of SO_3Cl^-, which is isoelectronic to $ArSO_3$, has been measured in solution and is indicative of C_{3v} symmetry for this species.[27] More akin to this work is the determination of the IR and Raman spectra of SO_3 in Xe[26] and

Ar^{28} matrices, respectively. Structural distortions, which are possibly due to the Jahn–Teller effect, were inferred in both studies.

Finally, theoretical studies have been conducted on $SO_3 \cdot NH_3$ by Kollman[29] and on $SO_3 \cdot H_2O$ by Castleman.[30] The former study finds a relatively large SO_3–NH_3 interaction energy, consistent with an acid-base type of interaction, and with the known strength of SO_3 as a strong Lewis acid. The latter study explores the structure of the $SO_3 \cdot H_2O$ adduct and suggests that the reaction between SO_3 and H_2O to form H_2SO_4 proceeds via this complex.

In this work we report the first radio frequency–microwave studies of sulfur trioxide complexes. Using the technique of molecular beam electric resonance (MBER) spectroscopy, we have measured the radio frequency spectrum and the two lowest frequency microwave transitions of $Ar^{32}SO_3$, the lowest frequency microwave transition of $Ar^{34}SO_3$, and two radio frequency transitions of N_2SO_3.

Sulfur trioxide complexes are spectroscopically convenient for several reasons. First, the strong Lewis acidity of SO_3 leads to a strong "van der Waals" interaction which results in a relatively large and therefore readily measurable dipole moment. Second, the SO_3 complexes studied thus far have been symmetric rotors. Third, the threefold symmetry of these complexes, together with the absence of off-axis nuclear spins, forbids the occurrence of K levels other than $K = 0$, ± 3, ± 6, ± 9, etc. Not only does this concentrate molecular populations into fewer states, thus enhancing the signal-to-noise ratio, but it also produces the relatively uncommon spectroscopic situation in which the rf spectrum is easily interpretable. Thus, these special features of the spectroscopy of SO_3 complexes, when taken together, allow information to be obtained immediately from the rf spectrum and later confirmed and refined through the microwave spectrum.

EXPERIMENTAL

A beam containing $ArSO_3$ was generated by passing argon (1.5 atm) over frozen SO_3 (– 78 or 0 °C) and expanding the mixture through a nozzle hole of ~ 35 μ diameter (25 °C). A beam containing N_2SO_3 was simi-

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larly produced by flowing a gas mixture of 20% N_2 and 80% Ar over frozen SO_3, while $XeSO_3$ beam preparation involved flowing a mixture of 10% Xe and 90% Ar over solid SO_3. Stabilized sulfur trioxide was obtained commercially[31] and used without further purification. No evidence of the stabilizer was observed in our mass spectra. A complicated relationship between the concentrations of both SO_3 and its polymers and the walls of the gas line made this beam source difficult to operate stably.

The corrosive nature of SO_3 is worthy of note. It reacts rapidly and violently with mechanical pump oil, but somewhat more slowly with silicone diffusion pump oil. Even though SO_3 did not appreciably attack the stainless steel containers in which it was stored, it eventually enlarged the diameter of our monel nozzle hole and corroded the inside cast-iron surface of our mechanical pump.

Signals were detected with a magnetic mass spectrometer which employed a Weiss-type electron bombardment ionizer with an ionization current of ~ 100 mA at 200 V. The mass spectra obtained were rich with SO_3 polymers, fragments from each SO_3 polymer due to the multiple loss of oxygens, and, of course, mixed clusters comprised of the carrier gas and SO_3. When SO_3 was expanded with a mixture of xenon and argon, prominent mass spectral features included, in addition to SO_3 polymers, ArXe, $XeSO_3$, fragments of $XeSO_3$, and Xe_2SO_3. $ArSO_3$ was, as might have been predicted, absent under these circumstances.

In electric deflection studies the percent focusing around a movable beam obstacle when 20 kV was applied to the quadrupolar A field was ~ 40% for $ArSO_3^+$, ~ 45% for $N_2SO_3^+$, ~ 5% for $XeSO_3^+$, 0% for $Xe_2SO_3^+$, ~ 1% for $(SO_3)_2^+$, and ~ 1% for $(SO_3)_3^+$. The low percent focusing of $XeSO_3^+$ was probably due to ionizer-induced fragmentation of the higher, nonpolar mixed polymers of Xe and SO_3 which had formed preferentially. The relatively high mass of $XeSO_3$ is an unlikely cause of the low focusability because the expected dipole moment enhancement in $XeSO_3$, over that of $ArSO_3$, would tend to cancel inertial effects. In any case, due to the resulting low intensity of focusable beam, presently attempted resonance experiments on $XeSO_3$ were unsuccessful. Nevertheless, the fact that $Xe_2SO_3^+$ was found to be nonpolar, together with spectroscopic evidence that $ArSO_3$ and N_2SO_3 are symmetric tops, suggests a trigonal bipyramidal structure for Xe_2SO_3. The slight polarity exhibited by both the dimer and trimer of SO_3 is in contrast to the situation for BF_3 where both the dimer and trimer have been found to be nonpolar.[32]

The extent of ionizer-induced fragmentation may, under favorable circumstances, be determined by "tagging" a given species through one of its rf or microwave transitions. In the case of $ArSO_3$, a given rf resonance was found to be equally strong whether observed at $ArSO_3^+$ or at SO_3^+, implying that at least 50% of the $ArSO_3$ complexes fragment in the ionizer.

The details of our flop-in MBER spectrometer have been described elsewhere.[33] Radio frequency and micro-

wave spectra were normally taken by modulating the radiation and scanning through the appropriate frequency with the mass spectrometer detector tuned to the parent mass peak of the complex of interest. The output of the detector was fed first into an electrometer and then into a lock-in amplifier. Signal averaging was performed as necessary.

The structure of $ArSO_3$ was solved in a systematic fashion. Three strong radio frequency lines were initially observed, the frequencies of which were found to vary linearly with electric field. These were analyzed in terms of the first-order (symmetric top) expression for the Stark energy, viz,,

$$\Delta W_1 = - \mu E M K / J(J+1) , \tag{1}$$

where μ is the dipole moment and E is the electric field. The ratio of these frequencies at a given voltage determined the assignments $J = 3, 4$, and 5.

Since $J < 6$, and since only integral multiples of 3 are allowed for K in $ArSO_3$, only $K = \pm 3$ is compatible with the observed first-order Stark effect.[34] In order for these transitions to obey "beam selection rules," we envision the angular momentum vector as being driven from positive to negative Stark states in successive equienergetic steps of $\Delta M = \pm 1$. The $J = 3$, $K = \pm 3$, $\Delta M = \pm 1$ transition (Fig. 1) was used to extract the value of the dipole moment. Next, the $J = 1$, $K = 0$, $\Delta M = \pm 1$ line was recorded and found to track quadratically with electric field. As K must be zero for $J < 3$, this transition was interpreted according to the usual expression for the second-order Stark effect with $J \neq 0$ and $K = 0$, viz.,

$$\Delta W_2 = \frac{\mu^2 E^2}{2BJ(J+1)} \frac{J(J+1) - 3M^2}{(2J-1)(2J+3)} , \tag{2}$$

thus allowing an initial estimate of 1453 MHz for the rotational constant, B. The $J = 1 \rightarrow 0$ (see Fig. 2) and the $J = 2 \rightarrow 1$[35] microwave lines in $Ar^{32}SO_3$ were then measured, giving us our best values of B and the centrifugal distortion constant, D_J. The $J = 1 \rightarrow 0$ line in $Ar^{34}SO_3$, which allowed us to investigate the out-of-plane distortion of the SO_3 submolecule, was measured using natural abundance sulfur-34. Individual components were identified by their Stark coefficients and in all cases were found to be $M = 0 \rightarrow 0$.

The rf spectrum of $N_2{}^{32}SO_3$ is complicated by nitrogen hyperfine structure. Thus, in order not to resolve the hyperfine splittings, we purposely broadened the rf radiation. Two such broadened lines were observed (Fig. 3) and found to track linearly with electric field. They fit an assignment of $J = 4$, $K = \pm 3$, $\Delta M = \pm 1$ and
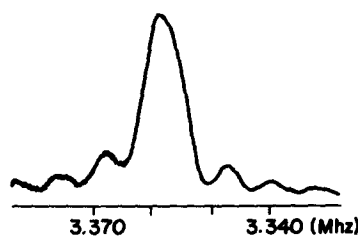

FIG. 1. The $J = 3$, $K = \pm 3$, $\Delta M = \pm 1$ transition in $ArSO_3$ recorded at 99.67 V/cm with a 10-s time constant.
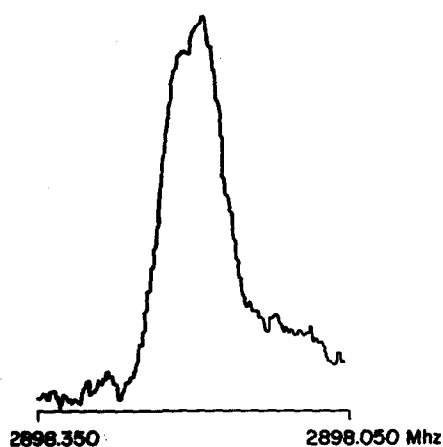
3.370   3.340 (Mhz)

$J = 5$, $K = \pm 3$, $\Delta M = \pm 1$ quite well, thereby providing a measurement of the dipole moment of N_2SO_3. Consistent with this assignment is the fact that the hyperfine splitting which occurs in a symmetric top with $K = \pm 3$ is at its minimum between $J = 4$ and $J = 5$. The results for N_2SO_3 are preliminary and no microwave transitions have yet been observed.

RESULTS

The radio frequency transitions observed in $ArSO_3$ are given in Table I, while the microwave transitions occurring in $ArSO_3$ (at zero field) are presented in Table II. Noise-broadened radio frequency transitions for N_2SO_3 are listed in Table III. The spectroscopic constants for each of the species studied are presented in Table IV.

STRUCTURAL INTERPRETATION

The symmetric top spectrum of $ArSO_3$ clearly establishes that the argon atom adds along the symmetry axis of the SO_3. In performing the structural analysis we have assumed that the S–O bond length in SO_3 (1.4198 ±0.0002 Å)[36] remains unchanged upon complexation. Such an approximation seems justified as the van der Waals interaction is weak compared with normal covalent bonding interactions. Moreover, our conclusions are relatively insensitive to small changes in the S–O bond length.

The problem is thus reduced to one of determining the Ar–S distance R and the Ar–S–O angle θ. To do so, we seek a unique pair of R and θ values which simultaneously reproduce the measured rotational constants
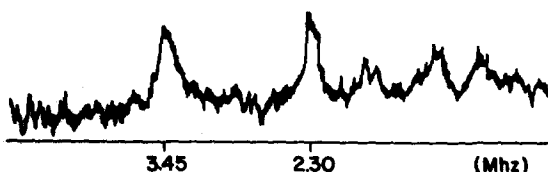
for both the ^{32}S and ^{34}S species. Figure 4 displays the loci of R's and θ's which reproduce each individual B value. The point of intersection gives the best geometry consistent with our model, viz., $R = 3.350$ Å, $\theta = 90.5°$. Using a Lennard-Jones potential and treating $ArSO_3$ as a diatomic molecule, we estimate that the difference in the vibrational averaged R, or more properly, the difference in $[\langle 1/R^2 \rangle_{vib}]^{-1/2}$ is of the order of 0.0001 Å. This is somewhat larger than the error introduced by uncertainty in B. As shown in Fig. 4, this introduces an uncertainty of $\pm 0.3°$ into θ. It seems likely that significantly greater uncertainty in R and θ is introduced by ignoring other internal dynamics of the $ArSO_3$ molecule, and so the values quoted above represent only the best fit to our perhaps simplistic model. Errors quoted in Table V are somewhat more conservative. In any case, the essential feature of this analysis is that out-of-plane distortion of the SO_3 submolecule is small in $ArSO_3$, just as it was in $ArBF_3$.

An analysis of the centrifugal distortion constant D_J provides us with the stretching frequency ω and the stretching force constant k_s of the Ar–S bond, namely, $\omega = 61(5)$ cm^{-1} and $k_s = 0.059(10)$ mdyn/Å.[37]

The information we are presently able to extract about N_2SO_3 is considerably less extensive. The observed radio frequency resonances of N_2SO_3, however, unambiguously determine that the molecule is a symmetric rotor and therefore that both nitrogen atoms are colinear with the sulfur atom.

DISCUSSION

Both $ArBF_3$ and N_2BF_3 have also been shown to be

TABLE I. Observed radio frequency transitions in $Ar^{32}SO_3$.

Frequency (MHz)	E (V/cm)	J	K
3.357(3)	99.67	3	± 3
2.025(10)	100	4	± 3
1.346(10)	100	5	± 3
1.874(3)	1000	1	0

TABLE II. Zero–field microwave transitions in $ArSO_3$.

Species	Frequency (MHz)	J	J'
$Ar^{32}SO_3$	2898.164 (10)	0	1
$Ar^{32}SO_3$	5796.241 (10)	1	2
$Ar^{34}SO_3$	2878.166 (10)	0	1

TABLE III. Observed (noise–broadened) radio frequency transitions in N_2SO_3.

Frequency (MHz)	E (V/cm)	J	K
3.45(5)	99.67	4	± 3
2.30(5)	99.67	5	± 3

TABLE IV. Spectroscopic constants for $ArSO_3$ and N_2SO_3.

Molecule	B (MHz)	D_J (kHz)	μ (D)
$Ar^{32}SO_3$	1449.089 (5)	3.6 (6)	0.2676 (3)
$Ar^{34}SO_3$	1439.090 (5)	···	0.2676 (3)
$N_2{}^{32}SO_3$	···	···	0.46 (1)

TABLE V. A comparison of SO_3 and BF_3 molecular complexes.

Complex	R (weak bond) (Å)	θ (deg)	μ (D)	ω_s (cm^{-1})	k_s (mdyn/Å)
$ArSO_3$	3.350 (1)	90.5(5)	0.2676(3)	61(5)	0.059(10)
$ArBF_3$[a]	3.325	90.5	0.176	41	0.025
N_2SO_3	···	···	0.46(1)	···	···
N_2BF_3[a]	2.875	90.5	0.35	···	···

[a]Reference 38.

TABLE VI. Argon–sulfur bond distances in several weakly bound molecular complexes.

Complex	Ar–S Distance (Å)
$ArOCS$[a]	4.10
ArH_2S[b]	3.99
$ArSO_2$[c]	3.66
$ArSO_3$[d]	3.35

[a]Reference 39.
[b]Reference 40.
[c]Reference 41.
[d]This work.

symmetric top complexes.[38] They are compared with $ArSO_3$ and N_2SO_3 in Table V. Even though the structural parameters in $ArSO_3$ and $ArBF_3$ are very similar, a comparison of their dipole moments and force constants shows that $ArSO_3$ is a considerably stronger complex. Likewise, a comparison of dipole moments indicates that the bonding in N_2SO_3 is probably stronger than that in N_2BF_3. This propensity of SO_3 to form strong complexes is probably due to its strength as a Lewis acid. This work thus indicates that SO_3 is a stronger Lewis acid than BF_3.

Despite the structural similarities between $ArBF_3$ and $ArSO_3$, and between N_2BF_3 and N_2SO_3, SO_3 and BF_3 complexes differ in terms other than their binding strengths. As mentioned earlier, the dimer and trimer of SO_3 are polar, while those of BF_3 are nonpolar. This, of course, indicates differing structural symmetries and therefore implies the operation of somewhat different intermolecular, if not chemical, forces in the polymers of SO_3 and BF_3.

The recent work of Dyke[40] and Muenter[41] permits us to compare argon–sulfur distances in several complexes. The available distances are listed in Table VI. It is clear that a unique argon–sulfur distance does not exist. Thus, the concept of a well-defined van der Waals radius for sulfur appears to be unrealistic. While this is argued on the basis of structures of binary complexes, it is certainly not clear that simplifications should occur in condensed phases. It is unlikely that models based on close packing of hard spheres using a van der Waals radius are meaningful for sulfur containing systems.[42]

It is evident from the large dipole moment of $ArSO_3$ that the short argon–sulfur bonding length in this species is not simply due to a small *rigid* sulfur unit, but rather to the electronic structure of the species. In this sense the van der Waals radius of sulfur will probably be a function of both its chemical environment and the binding partner. The data listed in Table VI indicate that the simplest view of the argon–sulfur bond distance is in terms of the Lewis acidity of the sulfur moiety. The Lewis acidity correlates with the oxidation state of the sulfur.

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