Weakly bound complexes of sulfur trioxide: The structure of \( \text{ArSO}_3 \) and the dipole moment of \( \text{N}_2\text{SO}_3^\pm \)

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Microwave and radio frequency spectra of \( \text{ArSO}_3 \) and radio frequency spectra of \( \text{N}_2\text{SO}_3^\pm \) are measured by molecular beam electric resonance spectroscopy. Both complexes are symmetric rotors. The spectroscopic constants determined for \( \text{ArSO}_3 \) are \( B = 1449.089(5) \text{ MHz} \), \( D_J = 3.6(6) \text{ kHz} \), and \( \mu = 0.2675(3) \text{ D} \). For \( \text{ArSO}_3 \), \( B = 1439.090(5) \text{ MHz} \). The stretching frequency of the weak \( \text{Ar}-\text{S} \) bond is \( 61.5(5) \text{ cm}^{-1} \), and the force constant is thus \( 0.059(10) \text{ mdyn/Å} \). The \( \text{Ar}-\text{S} \) bond length in \( \text{ArSO}_3 \) is \( 1.350(1) \text{ Å} \). The \( \text{Ar}-\text{S}-\text{O} \) angle is found to be \( 90.5(5)° \), thereby indicating no significant out-of-plane distortion of the \( \text{SO}_3 \) moiety. Preliminary assignment of the \( \text{N}_2\text{SO}_3^\pm \) spectrum yields a dipole moment of \( 0.46(1) \text{ D} \). Electric deflection studies show that \( \text{SO}_3^\pm \) and \( \text{SO}_3^\pm \) are polar species, while \( \text{Xe}_2\text{SO}_3^\pm \) 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 \( \text{SO}_3 \) (the contact process for manufacturing sulfuric acid), by the photochemical oxidation of \( \text{SO}_3 \), and by the nitrogen oxide-catalyzed dark oxidation of damp \( \text{SO}_3 \) (the old lead chamber process). While reactions involving \( \text{SO}_3 \) in the troposphere are not well understood, oxidation reactions between \( \text{SO}_3 \) and free radicals are thought to be important sources of \( \text{SO}_3 \) there.\(^2\) In addition, several negative ion-neutral reactions of probable importance in the ionosphere are known to produce \( \text{SO}_3^- \) and \( \text{SO}_3^\pm \). In both organic and inorganic synthesis, where it is an important sulfinating agent, \( \text{SO}_3 \) is often used in the form of an adduct (or complex) in order to reduce its reactivity.\(^3,5\)

Since \( \text{SO}_3 \) 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. \( \text{X}-\text{ray crystallographic studies have been performed on \text{SO}_3^\pm \text{ complexes of } \text{ArSO}_3^\pm.} \)\(^6\) \( \text{SO}_3 \) \( \text{B}_2\text{O}_3 \), \( \text{(CH}_3\text{)}_2\text{N}^- \text{ and } \text{Si}_2\text{N}_4 \), on graphite insertion compounds involving \( \text{SO}_3 \), and on sulfur trioxide trimer.\(^11\) The latter was found to be a nonplanar, six-membered ring. In the case of \( \text{(CH}_3\text{)}_2\text{N}^- \text{SO}_3 \), 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 \( \text{SO}_3 \) complexes is in sharp contrast to that for adducts of the similarly structured Lewis acid, \( \text{BF}_3 \), for which copious structural data are available through both \( \text{X}-\text{ray crystallographic and microwave spectroscopic studies.} \)

Infrared and Raman spectra of a wide variety of organic and inorganic \( \text{SO}_3 \) complexes,\(^12\)\(^-\)\(^15\) including those involving \( \text{ArSO}_3 \), \( \text{(CH}_3\text{)}_2\text{N}^- \) \( \text{SO}_3 \), and \( \text{SO}_3 \) trimer,\(^16\)\(^-\)\(^19\) have also been recorded. In addition, the Raman spectrum of \( \text{SO}_3\text{Cl}^- \), which is isoelectronic to \( \text{ArSO}_3 \), has been measured in solution and is indicative of \( C_3 \) symmetry for this species.\(^20\) More akin to this work is the determination of the \( \text{IR} \) and Raman spectra of \( \text{SO}_3 \) in \( \text{Xe}_2\text{SO}_3 \) and \( \text{Ar}^{28} \) 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 \( \text{SO}_3^- \cdot \text{NH}_3 \) by Kollman\(^29\) and on \( \text{SO}_3^- \cdot \text{H}_2\text{O} \) by Castleman.\(^30\) The former study finds a relatively large \( \text{SO}_3^- \cdot \text{NH}_3 \) interaction energy, consistent with an acid-base type of interaction, and with the known strength of \( \text{SO}_3 \) as a strong Lewis acid. The latter study explores the structure of the \( \text{SO}_3^- \cdot \text{H}_2\text{O} \) adduct and suggests that the reaction between \( \text{SO}_3 \) and \( \text{H}_2\text{O} \) to form \( \text{H}_2\text{SO}_4 \) 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 \( \text{ArSO}_3 \), the lowest frequency microwave transition of \( \text{Ar}^{28}\text{SO}_3^- \), and two radio frequency transitions of \( \text{N}_2\text{SO}_3^\pm \).

Sulfur trioxide complexes are spectroscopically convenient for several reasons. First, the strong Lewis acidity of \( \text{SO}_3 \) leads to a strong "van der Waals" interaction which results in a relatively large and therefore readily measurable dipole moment. Second, the \( \text{SO}_3 \) 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 \( K = 0, \pm 3, \pm 6, \pm 9, \) 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 \( \text{SO}_3 \) 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 \( \text{ArSO}_3 \) was generated by passing argon (1.5 atm) over frozen \( \text{SO}_3 \) (78 °C) and expanding the mixture through a nozzle hole of ~35 μ diameter (25 °C). A beam containing \( \text{N}_2\text{SO}_3^- \) was simil-
larly produced by flowing a gas mixture of 20% N\textsubscript{2} and 80% Ar over frozen SO\textsubscript{3}, while XeSO\textsubscript{4} beam preparation involved flowing a mixture of 10% Xe and 90% Ar over solid SO\textsubscript{3}. Stabilized sulfur trioxide was obtained commercially\textsuperscript{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\textsubscript{3} and its polymers and the walls of the gas line made this beam source difficult to operate stably.

The corrosive nature of SO\textsubscript{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\textsubscript{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\textsubscript{3} polymers, fragments from each SO\textsubscript{3} polymer due to the multiple loss of oxygens, and, of course, mixed clusters comprised of the carrier gas and SO\textsubscript{3}. When SO\textsubscript{3} was expanded with a mixture of xenon and argon, prominent mass spectral features included, in addition to SO\textsubscript{3} polymers, ArXe, XeSO\textsubscript{4}, fragments of XeSO\textsubscript{4}, and Xe\textsubscript{2}SO\textsubscript{4}. ArSO\textsubscript{3} was, as might be 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\textsubscript{3} ~45% for N\textsubscript{2}SO\textsubscript{3}, ~5% for XeSO\textsubscript{4}, 0% for Xe\textsubscript{2}SO\textsubscript{4}, ~1% for (SO\textsubscript{3})\textsubscript{2}, and ~1% for (SO\textsubscript{3})\textsuperscript{3}. The low percent focusing of XeSO\textsubscript{4} was probably due to ionizer-induced fragmentation of the higher, nonpolar mixed polymers of Xe and SO\textsubscript{3} which had formed preferentially. The relatively high mass of XeSO\textsubscript{4} is an unlikely cause of the low focussability because the expected dipole moment enhancement in XeSO\textsubscript{4} over that of ArSO\textsubscript{3} would tend to cancel inertial effects. In any case, due to the resulting low intensity of focussable beam, presently attempted resonance experiments on XeSO\textsubscript{4} were unsuccessful. Nevertheless, the fact that Xe\textsubscript{2}SO\textsubscript{4} was found to be nonpolar, together with spectroscopic evidence that ArSO\textsubscript{3} and N\textsubscript{2}SO\textsubscript{3} are isomorphous, suggests a trigonal bipyramidal structure for Xe\textsubscript{2}SO\textsubscript{4}. The slight polarity exhibited by both the dimer and trimer of SO\textsubscript{3} is in contrast to the situation for BF\textsubscript{3} where both the dimer and trimer have been found to be nonpolar.\textsuperscript{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\textsubscript{3}, a given rf resonance was found to be equallly strong whether observed at ArSO\textsubscript{3} or at SO\textsubscript{3}, implying that at least 50% of the ArSO\textsubscript{3} complexes fragment in the ionizer.

The details of our flop-in MBER spectrometer have been described elsewhere.\textsuperscript{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\textsubscript{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.,

\[ \Delta W = -\mu EM/4J(J+1), \]

where \( \mu \) 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\textsubscript{3}, only \( K=\pm 3 \) is compatible with the observed first-order Stark effect.\textsuperscript{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 \( J=0 \) and \( K=0 \), viz.,

\[ \Delta W = \frac{\mu^2 E^2}{2BJ(J+1)} \left( \frac{J(J+1)-3M^2}{(2J-1)(2J+3)} \right), \]

thus allowing an initial estimate of 1453 MHz for the rotational constant, \( B \). The \( J=1 \) line (see Fig. 2) and the \( J=2 \) line \textsuperscript{35} microwave lines in Ar\textsuperscript{32}SO\textsubscript{4} were then measured, giving us our best values of \( B \) and the centrifugal distortion constant, \( D \). The \( J=1 \) line in Ar\textsuperscript{34}SO\textsubscript{4}, which allowed us to investigate the out-of-plane distortion of the SO\textsubscript{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 \( M=0 \).

The rf spectrum of N\textsubscript{2}SO\textsubscript{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\textsubscript{3} recorded at 99.67 V/cm with a 10-s time constant.](image)
J = 5, K = ± 3, ΔM = ± 1 quite well, thereby providing a measurement of the dipole moment of N₂SO₃. Consistent with this assignment is the fact that the hyperfine splitting which occurs in a symmetric top with K = ± 3 is at its minimum between J = 4 and J = 5. The results for N₂SO₃ are preliminary and no microwave transitions have yet been observed.

RESULTS

The radio frequency transitions observed in ArSO₃ are given in Table I, while the microwave transitions occurring in ArSO₃ (at zero field) are presented in Table II. Noise-broadened radio frequency transitions for N₂SO₃ 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 ArSO₃ clearly establishes that the argon atom adds along the symmetry axis of the SO₃. In performing the structural analysis we have assumed that the S–O bond length in SO₃ (1.4198 ± 0.0002 Å) 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

![Graph](image)

**FIG. 4.** The ensemble of (R, θ) which is consistent with the measured rotational constants of ArSO₃ and Ar₃SO₃. The structure of the complex is given by the intersection of the two lines. The box around this intersection illustrates the change in θ = 90° when R = 3 Å varies by ± 1 Å.

for both the ³²S and ³⁴S 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 = 3.3 Å, θ = 90.5°. Using a Lennard–Jones potential and treating ArSO₃ as a diatomic molecule, we estimate that the difference in the vibrational averaged R, or more properly, the difference in [(R²)ᵣ₋₃]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 ± 0.3° into θ. It seems likely that significantly greater uncertainty in R and θ is introduced by ignoring other internal dynamics of the ArSO₃ 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 SO₃ submolecule is small in ArSO₃, just as it was in ArBF₃.

An analysis of the centrifugal distortion constant Dₑ provides us with the stretching frequency ω and the stretching force constant kₑ of the Ar–S bond, namely, ω = 61 (5) cm⁻¹ and kₑ = 0.059 (10) mdyn/Å.²⁷

The information we are presently able to extract about N₂SO₃ is considerably less extensive. The observed radio frequency resonances of N₂SO₃, however, unambiguously determine that the molecule is a symmetric rotor and therefore that both nitrogen atoms are colinear with the sulfur atom.

DISCUSSION

Both ArBF₃ and N₂BF₃ have also been shown to be

<table>
<thead>
<tr>
<th>TABLE I. Observed radio frequency transitions in ArSO₃.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (MHz)</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>3.357(5)</td>
</tr>
<tr>
<td>2.025(10)</td>
</tr>
<tr>
<td>1.346(10)</td>
</tr>
<tr>
<td>1.874(3)</td>
</tr>
</tbody>
</table>

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TABLE II. Zero-field microwave transitions in ArSO₃.

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequency (MHz)</th>
<th>J</th>
<th>J'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁵²SO₃</td>
<td>2898.164 (10)</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Ar⁵⁷SO₃</td>
<td>5796.241 (10)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ar⁵³SO₃</td>
<td>2878.166 (10)</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

TABLE III. Observed (noise-broadened) radio frequency transitions in N₂SO₃.

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>E (V/cm)</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.45(5)</td>
<td>99.67</td>
<td>4</td>
<td>±3</td>
</tr>
<tr>
<td>2.30(5)</td>
<td>99.67</td>
<td>5</td>
<td>±3</td>
</tr>
</tbody>
</table>

TABLE IV. Spectroscopic constants for ArSO₃ and N₂SO₃.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B (MHz)</th>
<th>D₂ (kHz)</th>
<th>μ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁵²SO₃</td>
<td>1449.089 (5)</td>
<td>3.6 (6)</td>
<td>0.2676 (3)</td>
</tr>
<tr>
<td>Ar⁵³SO₃</td>
<td>1439.090 (5)</td>
<td>⋯</td>
<td>0.2676 (3)</td>
</tr>
<tr>
<td>N₂⁵³SO₃</td>
<td>⋯</td>
<td>⋯</td>
<td>0.46 (1)</td>
</tr>
</tbody>
</table>

TABLE V. A comparison of SO₃ and BF₃ molecular complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>R (weak bond) (Å)</th>
<th>θ (deg)</th>
<th>μ (D)</th>
<th>ε₀ (cm⁻¹)</th>
<th>k₀ (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArSO₃</td>
<td>3.350 (1)</td>
<td>90.5(5)</td>
<td>0.2676(3)</td>
<td>61(5)</td>
<td>0.059(10)</td>
</tr>
<tr>
<td>ArBF₃</td>
<td>3.325</td>
<td>90.5</td>
<td>0.176</td>
<td>41</td>
<td>0.025</td>
</tr>
<tr>
<td>N₂SO₃</td>
<td>⋯</td>
<td>⋯</td>
<td>⋯</td>
<td>⋯</td>
<td>⋯</td>
</tr>
<tr>
<td>N₂BF₃</td>
<td>2.875</td>
<td>90.5</td>
<td>0.35</td>
<td>⋯</td>
<td>⋯</td>
</tr>
</tbody>
</table>

*Reference 38.*

Despite the structural similarities between ArBF₃ and ArSO₃, and between N₂BF₃ and N₂SO₃, SO₃ and BF₃ complexes differ in terms other than their binding strengths. As mentioned earlier, the dimer and trimer of SO₃ are polar, while those of BF₃ 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 SO₃ and BF₃.

The recent work of Dyke⁶⁰ and Muentert⁶¹ 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.⁶²

It is evident from the large dipole moment of ArSO₃ 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.

Notes:
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31Chemical Specialties Corp., 100 Fairchild Ave., Plainview, New York, 11803.
34In ArBF₃, where there is no restriction on the values that K may have, the rf spectrum was unanalyzable.
35The J = 2 → 1 transition was measured in double resonance by modulating an rf oscillator set to the frequency of the J = 1, ΔM = ± 1 transition and detuning this resonance during the sweep of a locked microwave oscillator.
37The force constant and stretching frequency reported in Ref. 38 for ArBF₃ are in error. The correct values are 0.925 mdynÅ⁻¹ and 41 cm⁻¹, respectively.
40R. Viswanathan and T. R. Dyke (private communication).
41R. Deleon and J. Menter (private communication).