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$(\text{N}_2\text{O})_2 \cdot \text{SO}_2$: Rotational spectrum and structure of the first van der Waals trimer containing sulfur dioxide

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The trimer $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ has been studied by Fourier transform microwave spectroscopy. The rotational constants for the normal species are $A = 1369.1014(11)$ MHz, $B = 1115.5816(11)$ MHz, and $C = 730.5790(4)$ MHz. Five isotomers of the complex have been studied, allowing a determination of its structure. The configuration aligns the centers-of-mass of the three monomers in an approximate equilateral triangle. The monomers twist relative to this plane so that the two N_2O 's are intermediate between T-shaped and crossed rather than the usual slipped-parallel planar. The SO_2 is oriented so that its oxygens are straddling one N_2O (similar to the $\text{N}_2\text{O} \cdot \text{SO}_2$ dimer), while its sulfur is closest to the oxygen end of the other N_2O . The dipole moment of $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ was measured, giving $\mu_a = 0.606(1)$ D, $\mu_b = 1.256(2)$ D, $\mu_c = 0.058(2)$ D, and $\mu_{\text{total}} = 1.396(2)$ D. A semiempirical model has been used to predict the trimer structure, and comparison is made with this model as well as with the dimer $\text{N}_2\text{O} \cdot \text{SO}_2$. © 2000 American Institute of Physics. [S0021-9606(00)01520-8]

I. INTRODUCTION

Although there have been many high resolution spectroscopic studies of dimer systems, trimers and larger clusters have been less frequently investigated. Since comparisons can be made between clusters and their dimer analogues, it is of interest to build up a larger set of carefully studied trimer structures. This allows testing of theories which describe intermolecular forces and helps to understand the changes that occur in progressing from dimers to larger clusters and ultimately condensed phases. Since microwave spectroscopy allows the determination of structural parameters, it is an attractive tool for studies of trimer configurations. The large amount of isotopic data needed for a complete structural analysis, however, is often an obstacle in the study of these systems. A lack of sufficient isotopic species can result in several structures that fit the experimental data equally well. The problem is reduced for trimers that primarily involve linear molecules and/or rare gas atoms. Since fewer parameters are needed to locate the constituent monomers, it has been possible to obtain structures that are of a quality similar to that of previous dimer studies. Comparison of trimer configurations with those of related dimers is also convenient, since the dimers of many common linear molecules have been extensively studied. The examination of trimers involving nonlinear molecules becomes more complicated. More parameters are needed to define the structure of the trimer accurately, and the arrangement of the monomers can be much more complex. This also makes comparisons with related dimer systems, if known, more involved.

In the current paper, the first microwave study of a trimer containing the bent molecule SO_2 is reported. The structure of the complex $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ has been determined, and comparisons are made with the dimers $(\text{N}_2\text{O})_2$ (Ref. 1) and $\text{N}_2\text{O} \cdot \text{SO}_2$.² A semiempirical interaction model was used to predict possible structures for $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ and $(\text{SO}_2)_2$

$\cdot \text{N}_2\text{O}$. Comparison of the success of this model at predicting the current trimer with its less accurate behavior on similar dimers provides interesting insight into its strengths and weaknesses.

II. EXPERIMENT

The rotational spectrum of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ was measured using the Balle–Flygare³ Fourier transform microwave spectrometers at the University of Michigan.⁴ The 5.5–9.5 GHz region was searched using the autoscan feature of the Michigan spectrometers.⁵ This very wide search range resulted in a large number of transitions that required both sample components. Many transitions remained after the assignment of the spectrum of $\text{N}_2\text{O} \cdot \text{SO}_2$,² and it was possible to assign most of these to a species that was assumed to be a trimer containing both N_2O and SO_2 . The rotational constants of the assigned spectrum were consistent with various model structures for either $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ or $(\text{SO}_2)_2 \cdot \text{N}_2\text{O}$ that were obtained using a semiempirical program described later. Preliminary assignment of the fully ^{15}N substituted isotopomer of the complex was accomplished using unassigned transitions from searches for $^{15}\text{N}_2\text{O} \cdot \text{SO}_2$. The rotational constants for this species were still consistent with either of the possible $\text{N}_2\text{O}/\text{SO}_2$ trimer combinations; however, they showed a small preference for models that contained two N_2O molecules and one SO_2 . Isotope shifts were used to predict the spectra of $^{15}\text{N}_2\text{O} \cdot ^{14}\text{N}_2\text{O} \cdot \text{SO}_2$ and $^{14}\text{N}_2\text{O} \cdot ^{15}\text{N}_2\text{O} \cdot \text{SO}_2$, and the assignment of both isotopomers close to these predictions confirmed that the carrier of the spectrum was $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$.

A gas sample consisting of about 1% of each of the sample components in “first run” He/Ne (9.5% He, 90.5% Ne) with a backing pressure of 2–3 bar was expanded through a modified Bosch fuel injector valve or a General Valve Series 9 nozzle into the spectrometer cavity. The

nozzle was aligned perpendicular to the axis of microwave propagation to eliminate Doppler doublets. Linewidths of about 30 kHz full-width at half-maximum were observed, and transition frequencies were reproducible to within 4 kHz. There was no evidence of splitting due to the four quadrupolar nitrogen nuclei in the complex, although the transitions of the isotopomers containing $^{14}\text{N}_2\text{O}$ were considerably weaker than those containing only $^{15}\text{N}_2\text{O}$. Transitions of the mixed $^{15}\text{N}_2\text{O}/^{14}\text{N}_2\text{O}$ isotopomers were also not visibly split.

The dipole moment of $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ was measured. The electric field was generated by the application of up to ± 7 kV to two parallel steel mesh plates located just outside the Fabry–Perot cavity of the spectrometer. The plates measure about $50\text{ cm} \times 50\text{ cm}$ and are spaced about 30 cm apart. The electric field was calibrated using the $J = 1 - 0$ transition of carbonyl sulfide at 12 162.98 MHz and assuming a dipole moment of 0.7152 D.⁶

The spectra of four isotopomers of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ were measured in addition to the normal species. For the measurement of $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$, $^{15}\text{N}_2\text{O} \cdot ^{14}\text{N}_2\text{O} \cdot \text{SO}_2$, $^{14}\text{N}_2\text{O} \cdot ^{15}\text{N}_2\text{O} \cdot \text{SO}_2$, and $(^{15}\text{N}_2\text{O})_2 \cdot ^{34}\text{SO}_2$, enriched $^{15}\text{N}_2\text{O}$ (99% ^{15}N , Isotec) was used, and for the assignment of $(^{15}\text{N}_2\text{O})_2 \cdot ^{34}\text{SO}_2$, enriched $^{34}\text{SO}_2$ (90% ^{34}S , Icon) was also used. A 50:50 mixture of $^{15}\text{N}_2\text{O}$ and $^{14}\text{N}_2\text{O}$ was used to assign the mixed N_2O isotopic species.

III. RESULTS

A. Spectra

Both a - and b -type transitions were observed for the five isotopomers. Frequencies of the 46 transitions measured for the normal isotope are in Table I along with the residuals from a fit of these lines to a Watson A-reduction Hamiltonian in the I' representation. Frequencies for the other isotopomers are available as supplemental material.⁷ The spectroscopic constants for the assigned species [$(^{14}\text{N}_2\text{O})_2 \cdot \text{SO}_2$, $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$, $^{15}\text{N}_2\text{O} \cdot ^{14}\text{N}_2\text{O} \cdot \text{SO}_2$, $^{14}\text{N}_2\text{O} \cdot ^{15}\text{N}_2\text{O} \cdot \text{SO}_2$, and $(^{15}\text{N}_2\text{O})_2 \cdot ^{34}\text{SO}_2$] are given in Table II. The fairly large differences between the normal species centrifugal distortion constants and those for the $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ and $(^{15}\text{N}_2\text{O})_2 \cdot ^{34}\text{SO}_2$ species can be explained by a large correlation between the Δ_{JK} and Δ_K constants and a smaller correlation between these constants and δ_K . When one of these constants was fixed for fits of the $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ species, the others converged to values similar to those of the normal isotopomer, but the quality of the fit was not as high. This was probably because the fixed constant had a fairly large contribution to the transition frequency. A fit using the Watson S-reduction Hamiltonian was of similar quality to the A-reduction fit and also showed high correlation between D_{JK} and D_K .

Attempts at assigning the $(^{15}\text{N}_2\text{O})_2 \cdot \text{S}^{18}\text{O}_2$ species using 97% ^{18}O enriched SO_2 were unsuccessful. Lines belonging to the $^{15}\text{N}_2\text{O} \cdot \text{S}^{18}\text{O}_2$ dimer were about a factor of 10 weaker than the normal dimer. Since the normal trimer lines are about two orders of magnitude weaker than the strongest dimer lines, the S^{18}O_2 lines may have been too weak to observe. The cause of these problems involving S^{18}O_2 is unknown. It is possible that ^{18}O and ^{16}O exchange readily from

TABLE I. Transition frequencies for $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$.

$J'_{Ka'Kc'}$	$J''_{Ka''Kc''}$	Frequency/MHz	Obs-Calc/ MHz
3 ₁₂	2 ₁₁	5904.0641	0.0032
3 ₃₁	2 ₂₀	7661.4899	-0.0011
3 ₃₀	2 ₂₁	7980.0246	0.0022
3 ₂₁	2 ₁₂	8299.2614	-0.0079
4 ₀₄	3 ₁₃	6328.6880	-0.0025
4 ₁₄	3 ₁₃	6332.9576	0.0023
4 ₀₄	3 ₀₃	6350.3397	0.0021
4 ₁₄	3 ₀₃	6354.6058	0.0034
4 ₁₃	3 ₂₂	7058.0525	-0.0017
4 ₂₃	3 ₂₂	7197.0219	-0.0012
4 ₁₃	3 ₁₂	7452.8596	0.0005
4 ₂₃	3 ₁₂	7591.8259	-0.0021
4 ₂₂	3 ₂₁	8196.0130	-0.0052
4 ₃₂	3 ₂₁	9165.0839	-0.0016
4 ₄₁	3 ₃₀	10 481.6097	0.0053
4 ₃₁	3 ₂₂	10 527.2685	0.0124
4 ₄₀	3 ₃₁	10 613.4085	0.0005
4 ₂₂	3 ₁₃	11 649.2828	-0.0001
5 ₀₅	4 ₁₄	7799.4656	-0.0005
5 ₁₅	4 ₁₄	7800.2223	-0.0005
5 ₀₅	4 ₀₄	7803.7326	0.0017
5 ₁₅	4 ₀₄	7804.4889	0.0014
5 ₁₄	4 ₂₃	8716.1871	-0.0076
5 ₂₄	4 ₂₃	8752.4806	-0.0007
5 ₁₄	4 ₁₃	8855.1526	-0.0109
5 ₂₄	4 ₁₃	8891.4443	-0.0059
5 ₂₃	4 ₂₂	9957.3743	-0.0042
5 ₃₃	4 ₂₂	10 426.1083	0.0080
5 ₄₂	4 ₃₁	12 103.6321	-0.0121
5 ₅₁	4 ₄₀	13 261.9637	-0.0071
5 ₅₀	4 ₄₁	13 308.2107	0.0081
6 ₀₆	5 ₁₅	9262.1682	0.0031
6 ₁₆	5 ₁₅	9262.2918	0.0009
6 ₀₆	5 ₀₅	9262.9221	0.0004
6 ₁₆	5 ₀₅	9263.0436	-0.0040
6 ₁₅	5 ₂₄	10 238.2039	0.0112
6 ₂₅	5 ₂₄	10 246.1632	-0.0020
6 ₁₅	5 ₁₄	10 274.4945	0.0152
6 ₂₅	5 ₁₄	10 282.4544	0.0026
7 ₀₇	6 ₁₆	10 723.2229	-0.0016
7 ₁₇	6 ₀₆	10 723.3717	0.0013
7 ₂₆	6 ₂₅	11 715.0731	-0.0057
7 ₁₆	6 ₁₅	11 721.4729	-0.0009
7 ₂₆	6 ₁₅	11 723.0536	0.0023
8 ₀₈	7 ₁₇	12 183.9324	-0.0046
8 ₁₈	7 ₀₇	12 183.9623	0.0022

water present in the sample manifold or some other process may have lowered the stated enrichment.

B. Dipole moment

Stark effects for a total of fourteen M components from four transitions of $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ were measured. The observed Stark coefficients are listed in Table III. This gave the dipole moment components in Table IV of $\mu_a = 0.561(1)$ D, $\mu_b = 1.276(2)$ D, $\mu_c = 0.064(2)$ D, and $\mu_{\text{total}} = 1.396(2)$ D in the $(^{14}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ principal axis system. The largest Stark shifts were in the range of 600–800 kHz for several components, and the greatest μ_c contributions were about 30–50 kHz. Although μ_c -type transitions might be observable, we were unable to detect any after lengthy

TABLE II. Spectroscopic constants for (N₂O)₂·SO₂.

	(¹⁴ N ₂ O) ₂ ·SO ₂	(¹⁵ N ₂ O) ₂ ·SO ₂	¹⁵ N ₂ O· ¹⁴ N ₂ O·SO ₂ ^a	¹⁴ N ₂ O· ¹⁵ N ₂ O·SO ₂ ^b	(¹⁵ N ₂ O) ₂ · ³⁴ SO ₂
A/MHz	1369.1014(11)	1337.1700(3)	1363.4695(10)	1344.1393(23)	1315.6368(6)
B/MHz	1115.5816(11)	1070.4026(2)	1085.5748(10)	1098.8989(18)	1068.6156(6)
C/MHz	730.5790(4)	703.7046(2)	717.1382(4)	716.7940(8)	696.9613(3)
Δ _J /kHz	1.389(24)	1.347(4)	1.294(20)	1.482(53)	1.289(14)
Δ _{JK} /kHz	0.743(89)	-0.066(19)	0.618(79)	0.618 ^c	0.230(52)
Δ _K /kHz	1.104(65)	1.969(2)	1.224(59)	1.076(90)	1.587(37)
δ _J /kHz	0.399(12)	0.392(2)	0.349(9)	0.460(26)	0.376(6)
δ _K /kHz	1.318(45)	0.892(11)	1.035(53)	1.73(18)	0.952(29)
N ^c	46	49	41	21	33
Δν _{rms} /kHz ^d	5.4	1.8	5.3	6.3	2.6

^aN₁ and N₂ substituted.^bN₅ and N₆ substituted.^cNumber of lines in fit.^dΔν_{rms} = (Σ(ν_{obs} - ν_{calc})²/N)^{1/2}.^eFixed at a value from ¹⁵N₂O·¹⁴N₂O·SO₂.

averaging. They were about 1000 times weaker than the μ_b-type transitions and below the sensitivity of the spectrometer.

C. Structure

Ten parameters are required to define the structure of the trimer. The parameters chosen are illustrated in Fig. 1. These parameters include two distances and an angle that define the locations of the centers of mass of the three monomers, an angle and a dihedral angle defining the orientation of each of the N₂O molecules relative to the three centers of mass, and an angle and two dihedral angles defining the orientation of the SO₂ molecule relative to the three centers of mass.⁸

Assignment of four isotopomers and the normal species provided 15 moments of inertia with which to determine the 10 parameters, assuming that the monomer structures remain unchanged [*R*_{N-N} = 1.185 Å, *R*_{N-N} = 1.128 Å; *R*_{S-O} = 1.431 Å, θ_{O-S-O} = 119.3° (Ref. 9)]. Least-squares fitting of these 10 parameters to the moments of inertia led to two structures (Table V) that are consistent with the inertial data. Assignment of the (¹⁵N₂O)₂·³²SO₂ and (¹⁵N₂O)₂·³⁴SO₂ iso-

topomers also allowed the determination of Kraitchman coordinates¹⁰ for the sulfur atom of the SO₂. Since the Kraitchman calculation determined the sulfur coordinates in the principal axis system of (¹⁵N₂O)₂·SO₂, it was necessary to transform the coordinates to the normal isotopomer axis system before comparisons could be made with the inertial fit results.

As seen in Table V, comparing the least-squares fitting of the experimental moments of inertia, Structure I has a lower standard deviation than Structure II. (See Figs. 1 and 2.¹¹) This gives a preliminary indication that Structure I is the actual configuration of the complex. Comparison of the experimental dipole moment components and the projections of the monomer dipole moments onto the principal axes for both structures (Table IV) leads to stronger evidence that Structure II is unlikely. Its dipole moment projection has a significant μ_c component which contradicts experimental evidence. The difference is too large to be accounted for by possible induced dipole moment components. Furthermore, the projected dipole components for Structure I are quite similar to the observed dipole moment components. The principal axis coordinates are given for both configurations in Table VI.

Although Structure II can be eliminated based on the dipole moment data, its appearance as a plausible inertial fit deserves comment. It arises from coordinate sign ambiguities in the moments of inertia. This can be perceived by comparing Fig. 1(a) with Fig. 2. One N₂O is approximately reflected across the *ab* plane. The equilibrium structure of I is prob-

TABLE III. Stark coefficients for the transitions used to calculate the dipole moment of (¹⁵N₂O)₂·SO₂.

J' _{Ka'Kc'}	J'' _{Ka''Kc''}	M	Δν/E ² ^a	Obs-Cal ^a
4 ₃₁	3 ₂₂	0	-0.151	0.001
		1	0.865	-0.031
		2	4.024	-0.018
		3	9.286	0.003
3 ₂₁	2 ₁₂	0	-0.981	0.029
		2	7.346	0.006
4 ₂₃	3 ₁₂	0	0.257	-0.005
		1	0.942	-0.028
		2	3.053	-0.038
		3	6.666	0.040
5 ₃₃	4 ₂₂	1	0.259	-0.007
		2	0.509	-0.014
		3	0.936	-0.018
		4	1.537	-0.020

^aUnits of 10⁻⁵ MHz cm²/V². The calculated coefficients were obtained with the rotational constants in Table II and the (¹⁵N₂O)₂·SO₂ dipole moment components in Table IV.

TABLE IV. Dipole moment components for (N₂O)₂·SO₂, the projections of monomer moments for the two possible structures, and the lowest energy configuration from the ORIENT model.

	Experiment ^a	Structure I	Structure II	ORIENT
μ _a /D	0.561(1)	0.573	0.278	0.439
μ _b /D	1.276(2)	1.316	0.995	1.328
μ _c /D	0.064(2)	0.152	1.091	0.150
μ _{total} /D	1.396(2)	1.443	1.503	1.407

^aμ_a, μ_b, and μ_c components transformed from the principal axes of (¹⁵N₂O)₂·SO₂ to the principal axes of (¹⁴N₂O)₂·SO₂. (¹⁵N₂O)₂·SO₂ principal axis components are μ_a = 0.606 D, μ_b = 1.256 D, μ_c = 0.058 D.

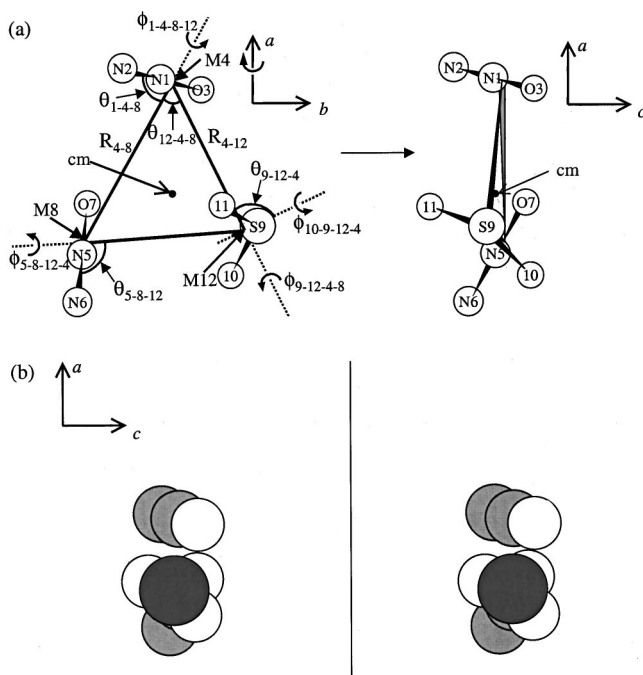


FIG. 1. Structure I from the inertial fit of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ showing the ten parameters used to define the structure. (a) The ab plane is parallel to the page in the left hand view, and the ac plane is parallel to the page in the right hand view. (b) Stereo image of Structure I of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ in the ac plane (Ref. 11).

ably within $\pm 0.05 \text{ \AA}$ and $\pm 5^\circ$ of the N_2O related parameters in Table V (first seven rows) while the parameters associated with SO_2 (next three rows) are less certain, probably within $\pm 10^\circ$. Structure I also resembles a prediction from a semiempirical model which will be discussed presently.

IV. DISCUSSION

Studies over the past few years have indicated that many trimers involving only linear molecules tend to have a barrel-shaped or triangular structure, where the three monomers align themselves roughly parallel to each other with their centers of mass forming a triangle that is approximately per-

TABLE V. Structural parameters for the two possible $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ configurations.

	Structure I ^a	Structure II	ORIENT ^b
$R_{4-8}/\text{\AA}$	3.8558(23)	3.7885(65)	3.749
$R_{4-12}/\text{\AA}$	3.5316(13)	3.591(14)	3.580
$\theta_{12-4-8}/^\circ$	52.494(26)	52.50(36)	51.62
$\theta_{1-4-8}/^\circ$	83.330(85)	86.0(15)	83.49
$\phi_{1-4-8-12}/^\circ$	-129.99(10)	-121.4(20)	-135.32
$\theta_{5-8-12}/^\circ$	97.672(95)	107.0(15)	107.63
$\phi_{5-8-12-4}/^\circ$	-151.19(21)	137.5(22)	-139.20
$\theta_{9-12-4}/^\circ$	90.75(14)	93.8(17)	88.91
$\phi_{9-12-4-8}/^\circ$	163.83(84)	137.7(29)	162.09
$\phi_{10-9-12-4}/^\circ$	-118.66(36)	-112.8(32)	-128.12
s.d. ^d	0.0036	0.0529	...

^aStructure I is preferred.

^bLowest energy configuration from the ORIENT model. See text.

^cThe signs of the dihedral angles are consistent with the definition in Ref. 8.

^dStandard deviation of the inertial fit in amu \AA^2 .

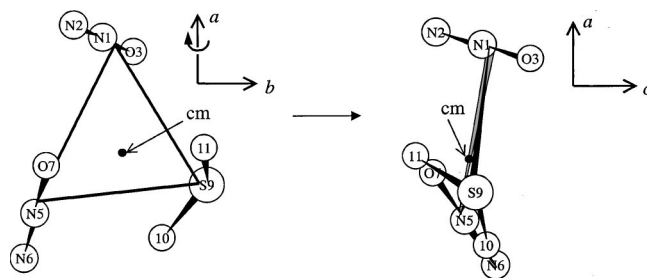


FIG. 2. Views of Structure II of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ in the ab and ac planes.

pendicular to the axes of the molecules.¹²⁻¹⁸ This arrangement presumably maximizes the dispersion interaction while the twisting and turning away from three parallel sticks further balances the electrostatic and repulsive interactions. These experimental results have shown good qualitative, and occasionally quantitative, agreement with structures predicted by a semiempirical model which includes electrostatic, dispersion, and repulsion terms. When the current work began, it was unknown whether a roughly triangular structure with the N_2O molecules approximately parallel to each other would still occur or whether a different structure would take shape. The first attempt at answering this question was made by using the same semiempirical program that has proven successful on trimers involving only linear monomers.

Semiempirical modeling using the ORIENT program¹⁹ employs distributed multipole moments (DMMs) to reproduce the electrostatic interactions in a complex. These DMMs were calculated using the CADPAC suite of programs.²⁰ A TZ2P basis set from the CADPAC library was employed, and calculations were made at the SCF level. The results of the calculations are given in Ref. 2. Analytic dispersion-repulsion terms in the ORIENT model have the form in Eq. (1),

$$U_{\text{exp-6}} = \sum_{i,j} K \exp[-\alpha_{ij}(R_{ij} - \rho_{ij})] - \frac{C_6^{ij}}{R_{ij}^6}. \quad (1)$$

In this equation, K is an adjustable pre-exponential factor that affects the intermolecular distances. It was fixed at the default value of $0.001 E_h$ ($E_h = 1 \text{ hartree} = 219\,474.63 \text{ cm}^{-1}$). The constants α , ρ , and C_6 have been determined by Mirsky²¹ and are given in Table 11.2 of Ref. 22 which also discusses aspects of the model in more detail. It has been assumed, in this case, that the contribution of induction terms was small, and they were omitted from the calculation.

Semiempirical modeling of $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$ led to three structures that are minima on the potential energy surface. The lowest energy structure ($E = -0.010\,41 E_h$, Table V) resembles Structure I. It aligns the N_2O molecules in a non-planar conformation that is intermediate between T-shaped and crossed. The oxygen end of one N_2O points toward the central nitrogen of the other N_2O . The SO_2 molecule is positioned so that the oxygen atoms roughly straddle both of the N_2O molecules. This structure resembles more the pinwheel, planar C_3 structure of one of the two observed CO_2 trimers,^{23,24} where each CO_2 dimer fragment is more T-shaped than slipped-parallel. Two other structures were

TABLE VI. Principal axis coordinates (in Å) for Structures I and II for $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$.^a

	<i>a</i>		<i>b</i>		<i>c</i>	
	Structure I	Structure II	Structure I	Structure II	Structure I	Structure II
N1	2.3445	2.3146	-0.2415	-0.3957	0.0376	0.2595
N2	2.5604	2.5868	-1.0233	-0.9857	-0.7464	-0.6626
O3	2.1177	2.0287	0.5798	0.2241	0.8611	1.2281
M4	2.3307	2.2973	-0.1916	-0.3580	0.0876	0.3183
N5	-1.2133	-1.2465	-1.8536	-1.7886	0.0996	-0.0896
N6	-2.1867	-2.1652	-1.9537	-2.0110	-0.4616	0.5261
O7	-0.1908	-0.2815	-1.7484	-1.5550	0.6892	-0.7363
M8	-1.1512	-1.1879	-1.8472	-1.7744	0.1354	-0.1289
S9	-0.6603	-0.6811	1.7223	1.7134	-0.0771	0.1215
	[0.659] ^b	[0.655]	[1.723]		[0.079]	[0.086]
O10	-1.6608	-1.7622	1.1715	0.7991	0.7852	0.3291
O11	-0.2637	-0.0723	0.9948	1.6428	-1.2438	-1.0930
M12	-0.8115	-0.7631	1.4023	1.4668	-0.1533	-0.1305

^aSee Fig. 1 for atom numbering. Structure I is preferred.

^bAbsolute values of Kraitchman coordinates are in brackets below the corresponding coordinates. The values vary slightly for the two structures, because they were calculated in the $(^{15}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ principal axis system and then transformed to the $(^{14}\text{N}_2\text{O})_2 \cdot \text{SO}_2$ principal axes.

found which have the N_2O molecules aligned roughly parallel to each other (Fig. 3). In these structures, the sulfur atom of the SO_2 and the centers of mass of the N_2O molecules form a triangle which is roughly perpendicular to the N_2O axes. In the lower energy of these two structures ($E = -0.00968 E_h$) the N_2O molecules are aligned with their dipoles opposing each other (antiparallel), and in the higher energy conformation ($E = -0.00960 E_h$) the dipole moments are aligned roughly parallel to each other. While the second conformation appears to optimize the interactions between the N_2O molecules, the first and third configurations seem to optimize interactions between SO_2 and N_2O .

Examination of the two faces of the lowest energy structure which contain one SO_2 and one N_2O molecule shows that one face has a structure similar to that predicted for the $\text{N}_2\text{O} \cdot \text{SO}_2$ dimer by the same semiempirical model.² On the other face the SO_2 straddles the N_2O molecule more symmetrically. Since this structure seems to optimize the interaction between two pairs of monomers while avoiding the unfavorable parallel alignment of the N_2O dipoles, it is sensible that it is lowest in energy. Nevertheless, the large differences from most previously observed trimer structures led us to be wary of initially putting too much trust in this being the experimental structure. Also, semiempirical modeling of SO_2 containing dimers has been relatively unsuccessful,^{2,25,26,27} and this further contributed to our initial caution regarding this structure. The rotational constants of all three structures were sufficiently similar to those found for the normal isotopomer to warrant further consideration of each of them in the absence of isotopic shift data (Table VII).

Analysis of the data from five isotopomers and determination of the dipole moment of the complex led to the conclusion that the experimental structure does resemble the lowest energy theoretical structure. Examination of Table V shows that the distances for Structure I are within about 0.2 Å of the predictions, and most angles are within 5°. A few of the angles are 10°–15° from the prediction, but the qualitative agreement is still quite good.

Comparison of the trimer with the recently studied $\text{N}_2\text{O} \cdot \text{SO}_2$ dimer is interesting, although qualified, since this structure may not be very accurate.² The $\text{N}_2\text{O} \cdot \text{SO}_2$ spectrum is split into doublets due to a tunneling motion; no consideration of this contribution to the moments of inertia was given when determining the structure. Figure 4(a) illustrates the configuration for the dimer consistent with the experimental data. While structural details may be less certain, it is clear that the SO_2 straddles the N_2O axis asymmetrically as illustrated, and that the equilibrium configuration may be even more asymmetric than suggested by Fig. 4(a). In fact, the ORIENT model predicts a considerably more asymmetric structure with one of the S–O bonds nearly parallel to the N–N–O axis.

One face of the trimer [Fig. 4(b)] bears a strong resemblance to the $\text{N}_2\text{O} \cdot \text{SO}_2$ dimer in Fig. 4(a). In fact, the trimer

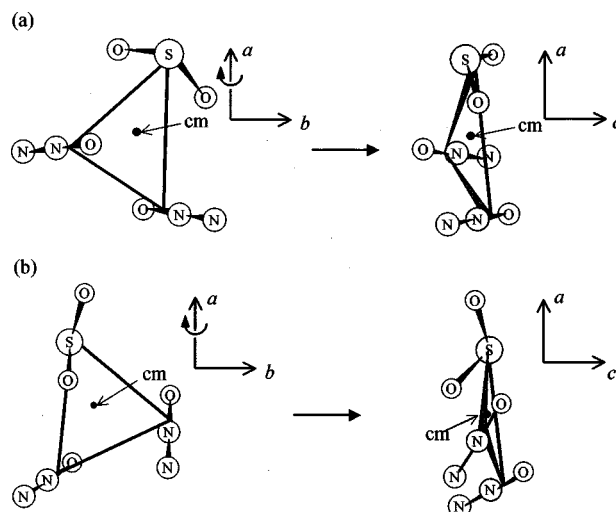


FIG. 3. The second (a) and third (b) higher energy structures predicted by the ORIENT program for $(\text{N}_2\text{O})_2 \cdot \text{SO}_2$. The lowest energy structure resembles Structure I, shown in Fig. 1. See Table VII for the energies of the three configurations.

TABLE VII. Comparison of structural parameters for the three structures predicted with the ORIENT semiempirical model.

	$E = -0.010\ 41\ E_h$ ($-2285\ \text{cm}^{-1}$)	$E = -0.009\ 68\ E_h$ ($-2125\ \text{cm}^{-1}$)	$E = -0.009\ 60\ E_h$ ($-2107\ \text{cm}^{-1}$)
$R_{4-8}/\text{\AA}$	3.749	3.423	3.498
$R_{4-12}/\text{\AA}$	3.580	3.393	3.841
$\theta_{12-4-8}/^\circ$	51.62	66.11	57.78
$\theta_{1-4-8}/^\circ$	83.49	117.23	125.49
$\phi_{1-4-8-12}/^\circ$	-135.32	112.86	-97.42
$\theta_{5-8-12}/^\circ$	107.63	99.52	123.68
$\phi_{5-8-12-4}/^\circ$	-139.20	-127.27	-48.39
$\theta_{9-12-4}/^\circ$	88.91	119.87	69.33
$\phi_{9-12-4-8}/^\circ$	162.09	-123.47	105.69
$\phi_{10-9-12-4}/^\circ$	-128.12	115.03	-174.40
A/MHz	1415.5	1355.4	1547.2
B/MHz	1135.9	1164.7	965.4
C/MHz	739.6	716.8	672.2

might be described as the $\text{N}_2\text{O}\cdot\text{SO}_2$ dimer to which another N_2O nestles such that its central N (slightly positive) is attracted to the terminal O (slightly negative) of the neighboring N_2O , while its terminal oxygen (slightly negative) is attracted to the sulfur (positive). The center-of-mass separation ($M_{12}-M_8=3.28\ \text{\AA}$) and the S_9-N_5 distance of $3.62\ \text{\AA}$ in 4(b) are both in good agreement with the dimer, showing deviations of only $0.05\ \text{\AA}-0.07\ \text{\AA}$ from the $\text{N}_2\text{O}\cdot\text{SO}_2$ values. The $S_9-M_{12}-M_8-O_7$ angle of 4(b) is 10.9° compared to the dimer value of 21.7° . Although these numbers seem close,

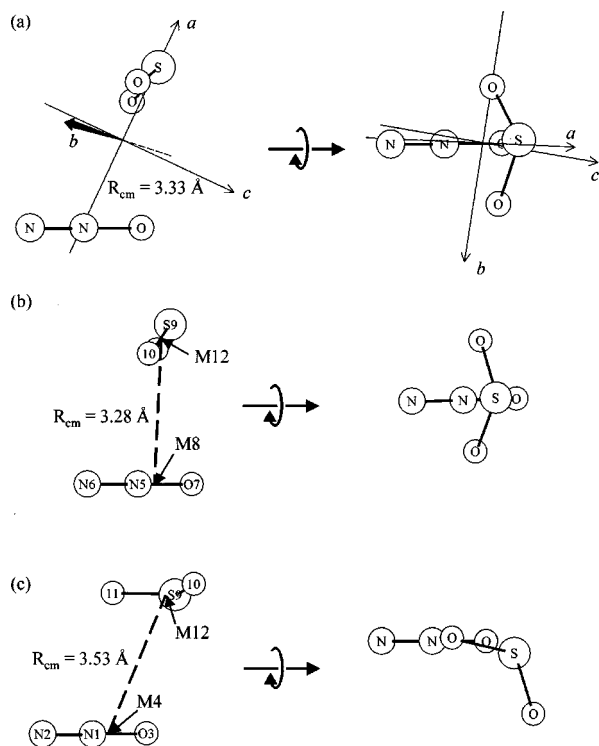


FIG. 4. Experimental structure of $\text{N}_2\text{O}\cdot\text{SO}_2$ dimer (a) and the two $\text{N}_2\text{O}-\text{SO}_2$ faces of $(\text{N}_2\text{O})_2\cdot\text{SO}_2$ (b and c). The views on the left-hand side of the figure place the plane containing the N_2O axis and two centers-of-mass parallel to the page. The views on the right-hand side align this plane perpendicular to the page.

the difference is significant. The $S_9-M_{12}-M_8$ angle of 154.2° , however, is very similar to the dimer angle of 156.6° .

It is interesting that the other $\text{N}_2\text{O}\cdot\text{SO}_2$ face of the trimer [Fig. 4(c)] resembles more strongly the dimer orientation mentioned above predicted by ORIENT with nearly parallel N–O and S–O bonds. The center-of-mass distance, $M_{12}-M_4$, for this portion of the trimer is $3.53\ \text{\AA}$. This compares with a distance of $3.33\ \text{\AA}$ in the isolated dimer. The S_9-N_1 distance for the trimer face is $3.59\ \text{\AA}$. In the dimer the comparable distance is $3.69\ \text{\AA}$. It is interesting that the center-of-mass distance is longer in the trimer, while the distance between the nitrogen and sulfur atoms gets slightly shorter. Perhaps comparison of the angles that orient the SO_2 relative to the N_2O will help elucidate these differences.

In $\text{N}_2\text{O}\cdot\text{SO}_2$ the $S-M_{\text{SO}_2}-M_{\text{N}_2\text{O}}-O$ dihedral angle is 21.7° (Structure I of Ref. 2). The $S-M-M-O$ angle in Fig. 4(c) is $\phi_{9-12-4-3}=41.6^\circ$, a difference of about 20° from the dimer value. Also, the $S-M-M$ angle in the dimer is 156.6° , while the trimer face has an angle, θ_{9-12-4} , of 90.8° . This decrease in the angle between the dimer and the trimer allows the $S-N$ distance to get shorter, while the center-of-mass distance can lengthen slightly. The ORIENT prediction for the dimer gives a dihedral angle of 48.6° and an $S-M-M$ angle of 101.3° , both within 10° of those on the trimer face. It is interesting that this configuration was fairly well reproduced in the trimer, while the actual structure of the dimer appears to be quite different.

The orientation of the two N_2O monomers relative to each other in the trimer is intermediate between a T-shaped and crossed structure. This alignment is completely different from the experimental N_2O dimer structure where the monomers are parallel to each other with opposing dipole moments (slipped parallel structure).¹ It appears that a quadrupole–quadrupole like interaction must dominate the arrangement of these two molecules, with the slightly negative oxygen end of one pointing roughly toward the slightly positive center nitrogen of the other. This bears no resemblance to the known N_2O dimer structure, but a comparison with the HCCH dimer is interesting. The dimer of acetylene is T-shaped and undergoes a geared internal rotation, passing through a slipped-parallel intermediate.^{28,29} In the $(\text{HCCH})_2\cdot\text{OCS}$ trimer the HCCH molecules appear to be intermediate between T-shaped and parallel relative to each other (but nonplanar), and it was proposed that an intermediate configuration in the tunneling process of the dimer was “trapped” in the trimer.³⁰ The $\text{N}_2\text{O}-\text{N}_2\text{O}$ configuration in $(\text{N}_2\text{O})_2\cdot\text{SO}_2$ resembles the $\text{HCCH}-\text{HCCH}$ arrangement in $(\text{HCCH})_2\cdot\text{OCS}$. This raises the question of whether a T-shaped isomer of $(\text{N}_2\text{O})_2$ is possible, although there has been no experimental evidence for this type of structure, yet. Indeed, the observation of this intermediate $\text{N}_2\text{O}-\text{N}_2\text{O}$ configuration in the trimer brings to mind the isoelectronic CO_2 dimer. Although it has now been proven that $(\text{CO}_2)_2$ has a slipped-parallel geometry, it was widely believed for some time that the structure was T-shaped.^{31,32}

A comparison of the $\text{N}_2\text{O}-\text{N}_2\text{O}$ face of the trimer relative to the ORIENT prediction is interesting. The center-of-mass distance between the N_2O molecules is $3.86\ \text{\AA}$, showing relatively good agreement with an ORIENT prediction of

3.75 Å. A comparison of the observed and predicted O–M–M–O dihedral angles shows less quantitative agreement, with an observed angle of 75.3° and a prediction of 52.5°. Although the difference between the prediction and experiment is large in this case, the structures are qualitatively similar, with both showing the intermediate T-shaped/crossed structure described earlier.

V. SUMMARY

The structure of the trimer (N₂O)₂·SO₂ has been determined by microwave spectroscopy. The complex is the first trimer containing the bent molecule SO₂ to be studied by this technique, although many SO₂ containing dimers have been studied,^{2,25–27,33–35} as have many trimers containing only linear molecules or combinations of linear molecules with rare gas atoms or occasionally water.^{13–16,18,36–38} Modeling with a semiempirical program that includes electrostatic, dispersion and repulsion terms was helpful in predicting a structure that was a qualitatively good approximation to the experimental configuration. This model was a useful tool in the assignment of the spectra of both the normal species and isotopomers. It is also interesting to note that the good agreement between the experimental and predicted structures is in contrast to previous results for SO₂ containing dimers. Modeling using the default parameters, as in the current work, has given poor agreement between experiment and predictions for N₂O·SO₂,² CO₂·SO₂,²⁶ and a variety of other SO₂ complexes.³⁹ It is possible that the constraints caused by the greater number of interactions that must be optimized in a trimer system lead to better performance of the semiempirical model on trimers containing SO₂ compared to similar dimers.

Comparison of the trimer structure with the structure of N₂O·SO₂ has shown that one N₂O–SO₂ face of the trimer is quite different from the isolated dimer, while the other N₂O–SO₂ face is quite similar to it. In order to preserve the favorable configuration in one N₂O–SO₂ unit, it was necessary to twist the other unit away from the dimer structure. The N₂O–N₂O face of the trimer does not resemble the isolated N₂O dimer. This suggests that the two sets of N₂O–SO₂ interactions are strong enough to force the N₂O molecules from the slipped parallel arrangement which they have in the isolated dimer to a higher energy T-shaped orientation.

It will be interesting to see if other trimers of two linear molecules with SO₂ have a structure similar to that observed for (N₂O)₂·SO₂ or if they will conform more to the barrel-shaped triangular structure that is common for most linear molecule trimers. Since the dimers of CO₂, OCS, and CS₂ all have a plane of symmetry, which N₂O·SO₂ lacks, these trimers may tend toward more symmetric triangular configurations. Semiempirical modeling of these new trimers will also determine if the success of the ORIENT model on the sulfur dioxide containing (N₂O)₂·SO₂ system is reproducible or purely happenstance.

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