

Rotational spectrum, structure and modeling of the SO₂–CS₂ complex

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The rotational spectra of seven isotopomers of the SO₂–CS₂ van der Waals dimer have been observed with a Fourier transform microwave spectrometer. The rotational constants for the normal species were determined to be $A=2413.2000(3)$ MHz, $B=1105.3803(3)$ MHz and $C=884.9885(2)$ MHz. They are consistent with the SO₂ straddling the CS₂ molecule and C_s symmetry for the complex. The centers of mass of the two monomers are separated by 3.4287(2) Å. Two structures were found that are consistent with this symmetry which differ in the relative tilt of the CS₂ and SO₂. In both structures, the C_2 axis of the SO₂ is aligned close to parallel to the CS₂ molecular axis with the oxygen end of the SO₂ tipped closer to the CS₂. In one structure the deviation from parallel is 9.8(8)° while in the other it is 17.7(11)°. The dipole moment components have been determined to be $\mu_a=0.0137(5)$ D and $\mu_b=1.1961(9)$ D. A semi-empirical model employing electrostatic, dispersion and repulsion interactions was employed to analyze the system and resulted in a reasonable reproduction of the angular geometry. A comparison of the results for the SO₂–CS₂ complex with the closely related SO₂–CO₂ and SO₂–OCS complexes is presented. © 1999 American Institute of Physics. [S0021-9606(99)00314-1]

I. INTRODUCTION

The recent determination of the structures of the SO₂–CO₂ (Ref. 1) and SO₂–OCS (Ref. 2) complexes by rotational spectroscopy revealed some rather significant structural changes on going from a nonpolar linear molecule to a polar one. In SO₂–CO₂, the C_2 axis of the SO₂ was perpendicular to the CO₂ axis (C_{2v} symmetry). In SO₂–OCS, the SO₂ rotated approximately 45° away from the perpendicular (C_s symmetry). It is appropriate to further extend this series with the study of the SO₂–CS₂ dimer, which contains another nonpolar, linear triatomic molecule. This system is particularly attractive in that CS₂ has a molecular quadrupole moment of opposite sign to that of CO₂. For example, Watson *et al.*³ give values for the molecular quadrupole moments (obtained from electric field induced birefringence experiments) as follows: $\Theta(\text{CS}_2)=+3.4\times 10^{-26}$ esu cm² and $\Theta(\text{CO}_2)=-4.3\times 10^{-26}$ esu cm². It is of interest to see what effect this has on the structure of the CS₂ complex with SO₂ and whether the resulting structure will resemble the SO₂–CO₂ or the SO₂–OCS complex more closely.

In this paper we report on the analysis of the rotational spectra of seven isotopomers of the SO₂–CS₂ dimer. A structure in which the SO₂ straddles the CS₂ molecular axis, with the C_2 axis of the SO₂ lying close to parallel to the CS₂ axis, has been determined from fitting the moments of inertia.

A semi-empirical model employing electrostatic, dispersion and repulsion interactions was also used in an attempt to reproduce the experimental structure. An analysis of the model's performance and a comparison of the structure and

bonding of the SO₂–CS₂ complex in light of the SO₂–CO₂ and SO₂–OCS results will be discussed.

II. EXPERIMENT

The rotational spectra of the SO₂–CS₂ dimer and six additional isotopomers were measured with a Balle-Flygare Fourier transform microwave spectrometer⁴ in the frequency range 5.5 to 14.5 GHz. After an initial search of a 1.4 GHz region between 6 and 7.4 GHz in which the 3←2 transitions were predicted, mixing experiments were carried out to eliminate transitions that did not require both components. Stark effect measurements were then made on several of the strongest remaining transitions observed in the initial search region. Stark effect experiments were carried out by the application of an electric field up to ±6 kV to a pair of parallel steel mesh plates measuring approximately 50 cm×50 cm. These plates are situated above and below the Fabry-Perot cavity and are separated by around 30 cm. The electric field was calibrated daily by the measurement of the $J=1\leftarrow 0$ transition of OCS at 12 162.980 MHz and using a dipole moment of 0.7152D.⁵

The SO₂–CS₂ dimer was generated in a supersonic expansion of a gas mixture of approximately 1.5% of each of the two components diluted in "first-run" He/Ne carrier gas (90% Ne, 10% He) at a backing pressure of *ca.* 2.8 atm. This gas mixture was expanded into the evacuated cavity through a modified Bosch fuel injection valve operating at a frequency of about 10 Hz, in a direction perpendicular to the resonator axis. Full width at half maximum of the transitions was estimated to be of the order of 30 kHz and our measured transition frequencies were reproducible to 2 kHz. Only *b*-type transitions were observed during measurement of the spectra and the most intense of the normal species transi-

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TABLE I. Rotational transition frequencies and residuals for the normal isotopomer of SO₂-CS₂.

J'_{kaKc}	J''_{kaKc}	ν_{obs} (MHz)	$\Delta\nu$ (kHz) ^a
2 ₂₁	1 ₁₀	8124.3841	-0.9
2 ₂₀	1 ₁₁	8370.4731	-2.8
3 ₁₃	2 ₀₂	6737.7725	-1.7
3 ₃₀	3 ₂₁	6981.4453	3.9
3 ₃₁	3 ₂₂	7105.4183	-1.3
3 ₂₂	2 ₁₁	9893.8176	-3.2
3 ₂₁	2 ₁₂	10 681.0938	3.9
3 ₃₁	2 ₂₀	13 050.3277	1.2
3 ₃₀	2 ₂₁	13 077.8185	-0.1
4 ₀₄	3 ₁₃	6856.2390	0.1
4 ₃₁	4 ₂₂	6820.6121	2.5
4 ₃₂	4 ₂₃	7171.0368	-0.5
4 ₁₄	3 ₀₃	8340.9527	1.3
4 ₄₀	4 ₃₁	9872.6083	-3.3
4 ₄₁	4 ₃₂	9885.5399	-1.5
4 ₂₃	3 ₁₂	11 549.7985	-2.5
4 ₂₂	3 ₁₃	13 234.1710	0.9
5 ₂₄	5 ₁₅	5984.6148	-1.0
5 ₃₂	5 ₂₃	6553.2885	-1.5
5 ₁₄	4 ₂₃	7163.6906	-3.6
5 ₃₃	5 ₂₄	7297.4264	1.5
5 ₀₅	4 ₁₄	8900.4499	4.0
5 ₄₁	5 ₃₂	9821.1646	6.6
5 ₄₂	5 ₃₃	9871.5112	-4.2
5 ₁₅	4 ₀₄	9922.9880	2.0
6 ₂₄	5 ₃₃	5982.8161	-1.3
6 ₂₅	6 ₁₆	6689.6477	-0.3
6 ₃₄	6 ₂₅	7505.5165	-1.1
6 ₁₅	5 ₂₄	9614.2489	4.0
6 ₄₂	6 ₃₃	9716.9670	-1.2
6 ₄₃	6 ₃₄	9861.8581	2.4
6 ₀₆	5 ₁₅	10 872.2081	-1.8
6 ₁₆	5 ₀₅	11 524.9847	-0.2
6 ₂₅	5 ₁₄	14 554.5512	0.0
7 ₄₄	7 ₃₅	9869.3933	-0.5
7 ₀₇	6 ₁₆	12 776.3257	-0.7
7 ₁₇	6 ₀₆	13 168.1880	-0.5

$$^a\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}.$$

tions, the 2₂₁←1₁₀ and 2₂₀←1₁₁ transitions, had signal-to-noise ratios in excess of 30 in 100 gas pulses.

The ³⁴SO₂ isotopomer and the two singly substituted C³²S³⁴S isotopomers were observed in natural abundance (*ca.* 4%). The 2₂₀←1₁₁ transition for these species typically had a signal-to-noise ratio of *ca.* 7 or more in 1000 gas pulses. Some of the weaker transitions for these species required averaging for several thousand gas pulses in order to achieve a satisfactory signal to noise. The spectrum of the SO₂-¹³CS₂ species was observed using an isotopically enriched sample of ¹³CS₂ (Cambridge Isotope Labs., 97%–99% ¹³C). The S¹⁸O₂-CS₂ isotopomer was observed using an isotopically enriched sample of S¹⁸O₂ purchased from Icon (97% ¹⁸O). Upon least-squares fitting of the moments of inertia for these isotopomers it became apparent that there existed two structures that were consistent with the inertial data. Another isotopomer, ³⁴SO₂-¹³CS₂ (consisting of a sample of the enriched ¹³CS₂ and the ³⁴SO₂ in natural abundance), was therefore assigned in an attempt to clear up the ambiguity.

III. RESULTS

A. Spectra

Only *b*-type transitions were observed for this complex with searches for *a*- and *c*-type transitions being unsuccessful. Further searches for *a*-type transitions in light of the nonzero μ_a dipole component obtained from analysis of the Stark data (see Sec. III B) also proved to be unsuccessful, with averaging for 50 000 gas pulses failing to reveal a transition. The lack of a μ_c dipole component suggests an *ab* plane of symmetry with the SO₂ monomer likely straddling the CS₂ monomer as observed in the SO₂-OCS complex.² The lack of intense *a*-type transitions was initially problematic since attempts at initial assignment assumed a structure in which the μ_a component was sizable. Based on Stark effect data obtained from the transitions at 6737.7725 and 7163.6906 MHz a tentative assignment of these lines as the 3₁₃←2₀₂ and the 5₁₄←4₂₃ transitions was made since these transitions seemed to be the only likely candidates in the regions. Stark shift data from several other strong lines in the 6 to 7 GHz region were important in suggesting further assignments, and a process of trial and error in which various combinations of transitions were added to the above transitions eventually revealed the correct assignment. The fit with a rigid rotor model at this stage proved to be more than sufficient to give reasonably good agreement, even upon the inclusion of lines with $K_a=2$ or 3. This is in contrast to the SO₂-OCS complex in which inclusion of lines with K_a greater than 1 caused large standard deviations.² The good performance of the rigid rotor model greatly simplified the location of further transitions in the rotational spectrum. The 37 measured lines for the normal species were fit to a Watson *A*-reduction Hamiltonian.⁶ Transition frequencies for the normal species along with the residuals for this fit are given in Table I, while the resulting spectroscopic constants are given in Table II for the normal and the six other isotopic species. Isotopic shifts were calculated from a model based upon a structure obtained from a semi-empirical model (to be discussed later) in which the SO₂ straddled the CS₂ molecule; the tilt and separation of the SO₂ molecule were adjusted so as to more closely reproduce the rotational constants and the dipole moment of the normal species. This model provided isotopic shifts which were sufficiently good to locate the isotopomers with a minimum of searching. As noted above, a least-squares fit of the transition frequencies to a rigid rotor model that included no centrifugal distortion constants gave a reasonable fit, suggesting that centrifugal distortion was much less important in this complex than in the SO₂-OCS complex.² We conclude that the SO₂-CS₂ complex likely exhibits considerably less floppiness in its structure.

Several transitions found in the initial search region still remain unassigned although they are considerably weaker and are not suitable for a Stark effect study. These lines likely belong to trimeric and higher order clusters of SO₂, CS₂, rare gases and maybe H₂O, and further studies will attempt to identify these species.

TABLE II. Spectroscopic constants for the seven isotopomers of SO₂-CS₂.

Spectroscopic constant	SO ₂ -CS ₂	³⁴ SO ₂ -CS ₂	SO ₂ -C ³⁴ S ³² S	SO ₂ -C ³² S ³⁴ S
<i>A</i> (MHz)	2413.2000(3)	2411.3806(11)	2365.0998(9)	2357.1336(12)
<i>B</i> (MHz)	1105.3803(3)	1088.1265(11)	1091.8708(10)	1095.7358(12)
<i>C</i> (MHz)	884.9885(2)	873.6646(8)	869.8006(7)	871.1596(8)
Δ_J (kHz)	1.639(4)	1.624(2)	1.61(1)	1.59(2)
Δ_{JK} (kHz)	170.1(1)	164.5(6)	160.4(5)	163.5(6)
Δ_K (kHz)	-177.2(2)	-172.9(9)	-166.8(8)	-171(1)
δ_J (kHz)	0.355(2)	0.352(8)	0.345(7)	0.362(10)
δ_K (kHz)	-219.2(4)	-214.9(2)	-197(2)	-202(2)
P_{cc} (amu Å ²) ^a	47.782	47.785	47.755	47.753
$\Delta\nu_{rms}$ (kHz) ^b	2.81	3.47	2.90	3.36
<i>N</i> ^c	37	22	22	21
	S ¹⁸ O ₂ -CS ₂	SO ₂ - ¹³ CS ₂	³⁴ SO ₂ - ¹³ CS ₂	
<i>A</i> (MHz)	2337.9206(3)	2413.2116(6)	2411.3904(9)	
<i>B</i> (MHz)	1063.4009(4)	1099.5262(8)	1082.2549(11)	
<i>C</i> (MHz)	866.0965(3)	881.2330(7)	869.8754(7)	
Δ_J (kHz)	1.498(5)	1.64(2)	1.57(2)	
Δ_{JK} (kHz)	169.0(2)	167.8(4)	162.6(7)	
Δ_K (kHz)	-176.9(2)	-174.9(3)	-167.2(7)	
δ_J (kHz)	0.304(3)	0.351(9)	0.335(10)	
δ_K (kHz)	-264.2(7)	-217(1)	-211(2)	
P_{cc} (amu Å ²) ^a	53.950	47.782	47.785	
$\Delta\nu_{rms}$ (kHz) ^b	1.96	2.76	2.47	
<i>N</i> ^c	29	24	21	

^a P_{cc} is the out of plane second moment.^b $\Delta\nu_{rms} = [\sum(\nu_{obs} - \nu_{calc})^2/N]^{1/2}$.^c*N* is the number of fitted transitions.

B. Dipole

Thirteen *M* components from the 3₁₃←2₀₂, 4₃₁←4₂₂ and 5₁₄←4₂₃ transitions were least squares fitted to determine the dipole moment components for this complex (Table III). As was suspected from the initial failure to locate any *a*-type transitions, the μ_a component of the dipole moment was found to be very small, $\mu_a = 0.0137(5)$ D, while μ_b

TABLE III. Stark coefficients and dipole moment components for SO₂-CS₂.

Transition	<i>M</i>	$\Delta\nu/\epsilon^2$ ^a	Obs.-Calc. ^a
3 ₁₃ -2 ₀₂	0	2.339	-0.003
	1	17.623	-0.022
	2	63.603	0.050
4 ₃₁ -4 ₂₂	1	-2.694	-0.015
	2	-4.926	-0.006
	3	-8.752	-0.098
	4	-13.829	0.053
5 ₁₄ -4 ₂₃	1	-2.835	0.035
	2	-3.983	0.045
	3	-5.897	0.062
	4	-8.394	0.267

$$\mu_a = 0.0137(5) \text{ D}$$

$$\mu_b = 1.1961(9) \text{ D}$$

$$\mu_c = 0.00(5) \text{ D}^b$$

$$\mu_{tot} = 1.1962(9) \text{ D}$$

^aObserved Stark coefficients and residuals in units of 10⁻⁶ MHz/(V cm⁻¹)².^b μ_c fixed at zero during fitting.

= 1.1961(9) D. This gives $\mu_{total} = 1.1962(9)$ D, some 0.43 D less than the dipole moment of the SO₂ monomer.⁷ The small μ_a component could be accurately determined because of high sensitivity of the Q branch transition in the set to this component.

C. Structure

The *ab* plane of symmetry that is suggested by the absence of *c*-type transitions can be verified by calculation of the out of plane second moments for the normal isotopic species. The value of the second moment $P_{cc} [= \sum m_i c_i^2 = 0.5(I_a + I_b - I_c)]$ is calculated to be 47.782 amu Å², in good agreement with the value of 47.8(4) amu Å² for P_{bb} in the SO₂-CO₂ complex¹ and similar to the value of $P_{cc} = 48.350$ amu Å² in the SO₂-OCS complex.¹² This provides convincing evidence that the oxygen atoms of SO₂ are indeed straddling the symmetry plane. Values of P_{cc} for all of the isotopomers studied are listed in Table II. Using litera-

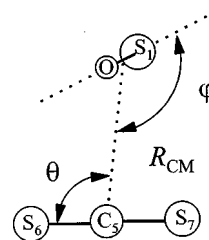


FIG. 1. Structure of the SO₂-CS₂ complex in the *ab* symmetry plane showing the fitted structural parameters. The center of mass of the SO₂ is labeled M₄ but is suppressed in the figure for simplicity.

TABLE IV. Fitted structural parameters for possible structures I and II in the SO₂-CS₂ complex.

Parameter	Literature value ^a	Adjusted value ^a		ORIENT ^b
		I	II	
R_{CM} (Å)	3.4273(10)	3.4287(1)	3.4287(2)	3.377
θ (°)	92.6(9)	92.7(1)	87.0(2)	96.7
φ (°)	103(4)	102.5(7)	104.1(9)	143.7
ΔI_{rms}^c (amu Å ²)	0.7281	0.1144	0.1599	...

^a“Literature value” and “Adjusted value” refer to whether the literature or adjusted values for the SO₂ monomer structural parameters were used in the fitting process. Refer to the text for a full discussion.

^bValues calculated from the structure obtained using the ORIENT model (see text).

^c ΔI_{rms} is the standard deviation when fitting the 21 moments of inertia.

ture values for the SO₂ monomer structure [$r(S-O) = 1.4308$ Å and an OSO angle of 119.3°,⁸ a P_{bb} value for the monomer of 48.77 amu Å² may be calculated compared to the ground state spectroscopic value⁹ of 49.05 amu Å². It is readily apparent that these values for P_{bb} of the monomer and P_{cc} for the complex (47.78 amu Å²) are significantly different. This arises from large amplitude vibrational effects that lead to a contamination of the effective moments of inertia.

The normal species and data from an additional six isotopic species (³⁴SO₂-CS₂, SO₂-C³²S³⁴S, SO₂-C³⁴S³²S, SO₂-¹³CS₂, S¹⁸O₂-CS₂ and ³⁴SO₂-¹³CS₂) allowed a least squares fitting of the moments of inertia to structural parameters. The University of Michigan implementation of the STRFTQ program of Schwendeman¹⁰ was employed in the fitting of the inertial data. Three parameters are required to describe the structure of this dimer: a center of mass separation (R_{CM}), an angle θ (the S₆-C₅··M₄ angle in Fig. 1 and the angle φ (the C₅··M₄··S₁ angle). Figure 1 illustrates the

atom numbering scheme and the three fitted parameters. The parameters obtained from using the literature values for the SO₂ given above and the CS₂ monomer structure [$r(C-S) = 1.552$ Å⁸] are given in the first column of Table IV; the ΔI_{rms} value of 0.728 amu Å² which results from this fit is relatively high. The rather poor quality of this fit arises from the difference in the values of P_{cc} for the complex calculated from the monomer structure of SO₂ and those derived from the experimental data. Small adjustments to the structure of the SO₂ are often found to be necessary¹¹⁻¹³ in order to bring the observed and calculated P_{cc} (or equivalent) values into better agreement as a means of compensating for vibrational effects arising from large amplitude motions in the complex which affect the observed moments of inertia. In this case, the S-O bond length was decreased by 0.003 Å and the OSO angle decreased by 1.5° in order to better reproduce the experimentally observed P_{cc} value. With this adjusted structure there was a marked improvement in the quality of the inertial fit as is illustrated in the second and third columns of Table IV. It should be noted that the uncertainties in Table IV are statistical uncertainties (1 σ) resulting from the fitting process. The structure suggested by the parameters in Table IV may therefore be considered an effective ground state structure and we expect the equilibrium values to fall within approximately 0.05 Å for the R_{CM} distance and 5° or so for the angles θ and φ .

During the course of the fitting with the adjusted SO₂ structure, it became apparent that two structures closely fit

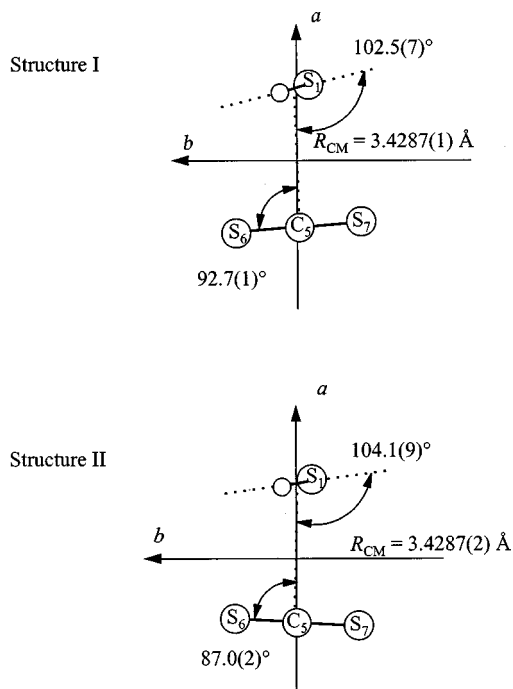


FIG. 2. The two possible fitted structures for the SO₂-CS₂ complex: (a) structure I, $\Delta I_{rms} = 0.1144$ amu Å² and (b) structure II, $\Delta I_{rms} = 0.1599$ amu Å².

TABLE V. Principal axis coordinates for the two possible fitted structures (I and II) of SO₂-CS₂.^a All coordinates are given in Angstroms.

Atom	a		b		c	
	I	II	I	II	I	II
S ₁	1.9531	1.9416	-0.2880	-0.4057	0.0000	0.0000
O ₂	1.7668	1.7796	0.4256	0.3138	1.2226	1.2226
O ₃	1.7668	1.7796	0.4256	0.3138	-1.2226	-1.2226
M ₄ ^b	1.8599	1.8606	0.0689	-0.0458	0.0000	0.0000
C ₅	-1.5665	-1.5670	-0.0580	0.0386	0.0000	0.0000
S ₆	-1.6976	-1.4467	1.4884	1.5859	0.0000	0.0000
S ₇	-1.4353	-1.6874	-1.6045	-1.5087	0.0000	0.0000

^aStructures I and II refer to the two possible structures that result from the fitting of the inertial data. Structure I has $\Delta I_{rms} = 0.1144$ amu Å² and structure II has $\Delta I_{rms} = 0.1599$ amu Å². See the text for a more detailed discussion and Fig. 2.

^bM₄ is the center of mass of the SO₂.

TABLE VI. Absolute values of the Kraitchman substitution coordinates in Å for SO₂-CS₂ obtained from the single and double substitution isotopic data.

Atom	a	b	c
S ₁	1.9184	0.2848	0.0390
O _{2,3}	1.7291	0.3826	1.2818
C ₅	1.5632	0.0000	0.0000
S ₆	1.6850	1.4930	0.0000
S ₇	1.4208	1.6090	0.0000

the experimental data. The two structures, I and II (shown in Fig. 2) had values of $\Delta I_{\text{rms}} = 0.114$ and $0.160 \text{ amu } \text{Å}^2$, respectively, and differ only in the relative tilt of the CS₂ molecule (corresponding to the atom S₇ tilted either towards or away from the S₁ atom of the SO₂, respectively, using R_{CM} as a reference axis—see Fig. 2). The structural parameters that result for structures I and II from the least-squares fitting of the 21 moments of inertia are given in Table IV. It can be seen that structure I gives a slightly better fit when using the adjusted values of the SO₂ monomer structure, based on the value of ΔI_{rms} and on the slightly lower uncertainties in the derived parameters. Structures I and II are clearly almost equivalent, with R_{CM} and φ agreeing to within experimental uncertainty. The angle θ , however, does differ quite significantly between the two structures. In structure I this corresponds to the C₂ axis of the SO₂ and the CS₂ axis deviating 9.8(8)^o from parallel, while in structure II the deviation is 17.7(1.1)^o. This may also be viewed as a sliding of the SO₂ moiety along an axis parallel to the CS₂ molecular axis with a resultant switching of the centers of mass of both species across the a axis. Also included in Table IV for comparison purposes are the parameters that result from the use of a semi-empirical model, ORIENT, which will be discussed in Sec. IV.

As was also the case with the SO₂-OCS complex,² the dipole moment components that are derived from a simple projection of the SO₂ monomer moment onto the principal axis system of the fitted structures are noticeably different from the components obtained from the experimental measurement of the dipole. In structure I, μ_a and μ_b components of 0.41 and 1.58 D result, while for structure II we obtain values of 0.36 and 1.59 D, respectively. Both structures overestimate the a -component of the dipole and the b -component by approximately 0.4 D. Vibrational averaging effects and induced dipole moments within the monomers that reduce

TABLE VII. Comparison of the predicted rotational constants of the ³⁴SO₂-¹³CS₂ isotopic species for structures I and II with the experimental constants.

Rotational constant (MHz)	Experimental	Predicted ^a	
		Structure I	Structure II
A	2411.390	2411.114	2409.384
B	1082.255	1081.904	1082.087
C	869.875	869.703	869.596

^aRotational constants predicted from the structure I or II that result from fitting the moment of inertia data.

the dipole components are likely explanations for this discrepancy. As a check that induction effects will reduce the projected values, a simple point polarizability model was used. The experimental values of the polarizabilities¹⁴ for CS₂ ($\alpha_{zz} = 15.090 \text{ Å}^3$, $\alpha_{xx} = \alpha_{yy} = 5.090 \text{ Å}^3$) and SO₂ ($\alpha_{xx} = 3.007 \text{ Å}^3$, $\alpha_{yy} = 5.317 \text{ Å}^3$, $\alpha_{zz} = 3.511 \text{ Å}^3$) were placed at the center of mass of each monomer. An *ab initio* calculation using GAUSSIAN 98¹⁵ for each monomer provided the electric field at the center of mass of the other monomer in the complex. Calculations were carried out at the SCF level using the AUG-cc-pVTZ basis set from the Gaussian library. This gave induced moments of $\mu_a = 0.36 \text{ D}$ and $\mu_b = 0.74 \text{ D}$ with the expected signs. Applying these induced dipole corrections to the projected dipole moment components from structure I reduces μ_a to 0.05 D, close to the value in the complex but overcorrects μ_b by about 0.4 D.

Table V contains the principal axis coordinates of the complex for both of the fitted structures and Table VI contains the coordinates that were obtained from the single and double isotopic substitution Kraitchman calculations.¹⁶ Table VI shows that the coordinates for the carbon and sulfur atoms of CS₂ are very close to those of either model I or II although there is a slight preference for structure I. For the SO₂ coordinates there is a definite preference for structure I, particularly apparent in the b coordinates of the sulfur and oxygen atoms. This better agreement for structure I is, however, still not conclusive.

In order to attempt to resolve this ambiguity there are several approaches that may yield evidence to differentiate in favor of one structure. Occasionally, small changes in the dipole moment components on isotopic substitution may be used. The small rotations of the principal axes that are encountered upon isotopic substitution may occasionally be sufficient¹⁷ to choose between possible structures. In the present case, the μ_b component is calculated to change very little upon isotopic substitution although the changes in the μ_a component are computed to be somewhat larger. However, given the small magnitude of the μ_a component and the uncertainty in the measurement of that dipole, the changes are likely to be too insignificant to definitively support one structure.

Another possible approach is to use a semi-empirical model to deduce which structure is correct. In this particular case, the agreement between the calculated and experimental structures was just not good enough to enable us to use this method (see below). Careful *ab initio* calculations which could differentiate between I and II are beyond the scope of this study.

Finally, there is the possibility that a doubly substituted isotopomer may yield rotational constants that distinguish between the structures. For this purpose, the ³⁴SO₂-¹³CS₂ isotopomer was chosen. Table VII compares the experimental rotational constants for the ³⁴SO₂-¹³CS₂ species with the predicted constants for structures I and II. From the table it is clear that structure I gives much better agreement for the A rotational constant. B and C are much less clear cut with II giving slightly better agreement for B while I is better for the C rotational constant. Although there seems to be a definite preference for structure I, we cannot completely rule out

TABLE VIII. Distributed multipole moments (DMM's) for CS₂. The components are given in spherical tensor notation and all quantities are in atomic units.

Atom	z^a	Q_{00}	Q_{10}	Q_{20}	Q_{30}	Q_{40}
C	0.0000	0.826 16	0.000 11	-0.442 01	0.000 05	0.829 38
S	-2.9340	0.458 20	0.646 81	1.950 15	0.487 18	0.158 39
S	2.9340	0.458 20	-0.646 81	1.950 15	-0.487 18	0.158 39
BC1 ^b	-1.4670	-0.871 23	-0.131 84	0.802 82	0.521 07	0.748 95
BC2 ^b	1.4670	-0.871 23	0.131 84	0.802 82	-0.521 07	0.748 95

^a z -coordinate of the atoms (in atomic units).^bBC1 and BC2 refer to the midpoints of the C-S bonds.

structure II. Nevertheless, since the two structures are very similar, the major feature of the interaction, namely nearly parallel units, is common to both models.

IV. DISCUSSION

A semi-empirical model was employed in the initial modeling of this complex in order to explore possible structures and make predictions of spectra to aid us in our assignments. The ORIENT model of Anthony Stone was used¹⁸ with *ab initio* distributed multipole moments (DMM's) for the SO₂ and CS₂ molecules. These DMM's were calculated at the SCF level using the CADPAC suite of programs¹⁹ with a TZ2P basis set taken from the CADPAC library. Multipoles up to and including hexadecapole moments were calculated on sites located at each atomic center, with additional sites placed at the bond midpoints; the DMM's employed in the calculations are listed in Tables VIII and IX. Dispersion and repulsion interactions are included in the intermolecular interaction potential by means of combined dispersion-repulsion atom-atom parameters of the familiar exp-6 form. The combined dispersion-repulsion portion of the interaction energy for an interaction between two molecules *A* and *B* may be expressed as a sum over all of the individual sites:²⁰

TABLE IX. Distributed multipole moments (DMM's) for the SO₂ monomer. The coordinates of the SO₂ are as follows: x (S)=0.00 000, y (S)=0.00 000; x (O)=±2.33 328, y (O)=-1.36 619 and x (BC)=±1.16 962, y (BC)=-0.68 324 (all distances and multipoles are in atomic units).

Component	Atoms				
	S	O	O	BC1	BC2
Q ₀₀	1.908 11	-0.081 98	-0.081 98	-0.872 08	-0.872 08
Q _{11c}	0.000 00	-0.428 45	0.428 45	-0.199 28	0.199 28
Q _{11s}	-1.783 74	0.417 97	0.417 97	0.167 83	0.167 83
Q ₂₀	-0.202 67	-0.250 03	-0.250 03	-0.664 04	-0.664 04
Q _{22c}	1.321 195	0.356 91	0.356 91	-0.243 56	-0.243 56
Q _{22s}	0.000 00	-0.857 11	0.857 11	-0.698 49	0.698 49
Q _{31c}	0.000 00	0.438 57	-0.438 57	-0.374 98	0.374 98
Q _{31s}	0.194 47	-0.329 47	-0.329 47	0.127 72	0.127 72
Q _{33c}	0.000 00	0.302 26	-0.302 26	-0.004 23	0.004 23
Q _{33s}	0.432 77	0.607 14	0.607 14	-0.465 19	-0.465 19
Q ₄₀	0.271 40	0.26853	0.268 53	0.089 71	0.089 71
Q _{42c}	-0.197 08	-0.089 80	-0.089 80	0.093 19	0.093 19
Q _{42s}	0.000 00	0.385 57	-0.385 57	0.455 09	-0.455 09
Q _{44c}	-0.422 92	-0.467 65	-0.467 65	-0.631 53	-0.631 53
Q _{44s}	0.000 00	-0.209 26	0.209 26	-0.122 04	0.122 04

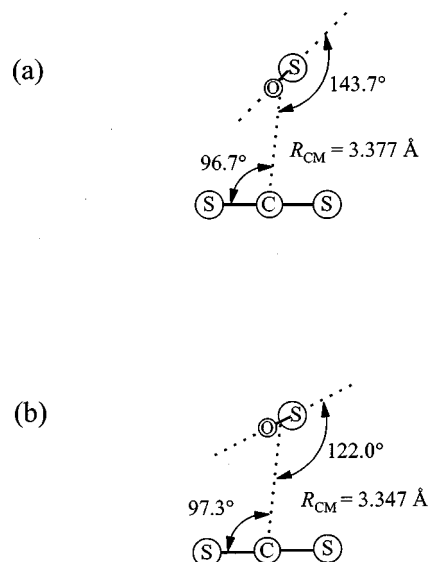


FIG. 3. Structures resulting from the use of the ORIENT model using the default parameters, with (a) no polarization and (b) polarization included.

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

K is an energy unit and is taken to be $0.001 E_h$ (hartree) in the present work. R_{ij} is the distance between the sites i and j on the molecules *A* and *B*, respectively. α_{ij} describes the hardness of the exponential repulsion, ρ_{ij} is a sum of effective radii of the sites i and j , and C_6^{ij} is an empirical site-site dispersion term. Values for α_{ij} , ρ_{ij} and C_6^{ij} were taken from the tabulated values of Mirsky²¹ in Table 11.2 of Ref. 18. Values for atom-atom pairs not available in Ref. 18 were generated by means of the following approximate combining rules: harmonic mean for α (i.e., $1/\alpha_{ij} \approx 1/\alpha_i + 1/\alpha_j$), geometric mean for C_6 and arithmetic mean for ρ .

The ORIENT model was used starting with numerous possible structures for the SO₂-CS₂ complex. The global minimum structure that emerged from the calculations (-699.4 cm^{-1}) is pictured in Fig. 3(a) and is, at first glance, a reasonable approximation to the experimental structure, especially in the close prediction of the R_{CM} distance (3.377 \AA vs. the experimental distance of 3.429 \AA). However, the last column of Table IV reveals that even though the model closely reproduces the R_{CM} separation, the tilt of the SO₂ monomer with respect to the CS₂ molecule (the angle φ in Fig. 3) is markedly different from experiment (by around 40°).

Neglect of errors in the distributed multipole moments are likely responsible for some of the discrepancy between the ORIENT values and the experimental values. The values of the dipole moment recovered from the *ab initio* DMM calculation for the SO₂ monomer overestimates the total dipole moment of SO₂ ($\mu = 1.63 \text{ D}^6$) by some 25%. The neglect of induction effects also contribute to the structural discrepancy. It is possible to include induction interactions at the simplest level in the ORIENT intermolecular potential by the introduction of a point molecular polarizability placed at the center of mass of each monomer. The tilt of the SO₂ is considerably different in the structure resulting from this calculation [Fig.

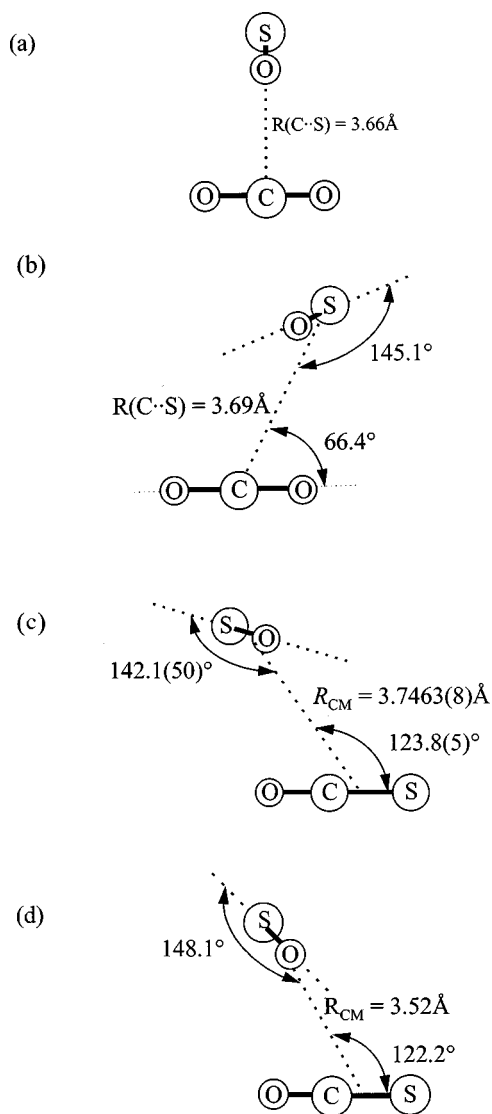


FIG. 4. Experimental and predicted structures for the $\text{SO}_2\text{-OCS}$ and $\text{SO}_2\text{-CO}_2$ complexes. (a) and (b) show the experimental and predicted structures for the $\text{SO}_2\text{-CO}_2$ complex and (c) and (d) show the experimental and predicted structure for $\text{SO}_2\text{-OCS}$. Note that (b) and (d) used DMM's with additional multipole sites located at bond midpoints and that the value of the preexponential factor K was changed to improve the agreement in the prediction of the intermolecular separation.

3(b)] compared to the calculation in which induction was ignored [Fig. 3(a)], with the angle φ decreasing by approximately 20° to a value of 122° . Although this is a crude model, it does serve to illustrate that there are indeed appreciable polarization effects that significantly affect the calcu-

TABLE X. Relative contributions to the intermolecular interaction energy in the ORIENT model for the $\text{SO}_2\text{-OCS}$, $\text{SO}_2\text{-CS}_2$ and $\text{SO}_2\text{-CO}_2$ complexes. All energies are in hartrees (E_h).

Complex	Electrostatic	Repulsion	Dispersion	Total ^a
$\text{SO}_2\text{-CS}_2$	-0.000 432	0.002 658	-0.005 412	-0.003 187
$\text{SO}_2\text{-CO}_2$	-0.002 838	0.002 478	-0.003 496	-0.003 856
$\text{SO}_2\text{-OCS}$	-0.001 850	0.002 057	-0.003 409	-0.003 201

^aAll energies exclude polarization contributions.

lated structure. Our initial efforts at introducing distributed polarizabilities into the model did not lead to significant improvement.

V. SUMMARY

It is interesting that the $\text{SO}_2\text{-CS}_2$ complex possesses a structure which is not readily extrapolated from a simple dipole-quadrupole interaction between the monomers or by a straightforward argument by analogy from $\text{SO}_2\text{-CO}_2$ or $\text{SO}_2\text{-OCS}$. In $\text{SO}_2\text{-CO}_2$, the experimental structure had C_{2v} symmetry with the SO_2 crossed relative to the CO_2 axis [Fig. 4(a)]. In $\text{SO}_2\text{-OCS}$, the SO_2 is shifted considerably from directly over the carbon atom compared to either $\text{SO}_2\text{-CO}_2$ or $\text{SO}_2\text{-CS}_2$. This translation places the sulfur atom of the SO_2 much more directly over the oxygen end of the OCS molecule [Fig. 4(c)].

The ORIENT modeling program reproduced R_{CM} and came within 6° of the tilt angles in $\text{SO}_2\text{-OCS}$ [Fig. 4(d)].² As noted above, the tilt angles are much less well reproduced for $\text{SO}_2\text{-CS}_2$ and similarly for $\text{SO}_2\text{-CO}_2$ [Fig. 4(b)]. For the latter, the C_{2v} structure was found as a transition state on the interaction potential energy surface,¹ some 35 cm^{-1} higher in energy than the less symmetric C_s structure in Fig. 4(b). We also have observed that the relative contributions from the electrostatic and dispersion terms in the ORIENT model vary significantly for the three SO_2 complexes (Table X).

This mixed behavior in the modeling results is in contrast to the recent studies of the trimers $\text{CO}_2\text{-CO}_2\text{-OCS}$,^{22,23} OCS-OCS-CO_2 ,²⁴ and $\text{CO}_2\text{-CO}_2\text{-N}_2\text{O}$,²⁵ where the simple ORIENT model used here (sans polarization) was remarkably successful in predicting rotational constants and assignment of the spectrum. Thus, this simple model can be very helpful to a spectroscopist in suggesting the general structural features and symmetry, and in some cases it even closely predicts the rotational constants. Additional comparisons between experiment and such models may be helpful to map out further the reliability patterns and perhaps suggest further improvements. While many essential features of the intermolecular forces are captured by the model, the simplicity of the terms included and the neglect of others such as polarization, and anisotropy in the dispersion and repulsion terms suggests that such complications are probably ultimately needed.²⁰ The quality of the distributed multipole moments from the *ab initio* calculation should also be systematically explored. In summary, the bent triatomic SO_2 is a good test case for exploring such modeling questions as it has proven to be frequently recalcitrant in both simple dimers like $\text{SO}_2\text{-CS}_2$ and more complex ones.²⁶

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