

Structure of the propene · sulfur dioxide complex

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The rotational spectra of eight isotopomers of the propene · SO₂ complex have been observed with a Fourier transform microwave spectrometer. The rotational constants of the normal species are $A=4269.564$ MHz, $B=1577.2661$ MHz, and $C=1469.6335$ MHz. The structure of the complex was derived from least-squares fitting of the 24 moments of inertia. It has a stacked, near-parallel planes configuration. The distance between the centers of mass of the two monomers is 3.26(5) Å. The sulfur atom is approximately above the propene double bond. The C₂ axis of SO₂ nearly eclipses the carbon-carbon single bond with the oxygen atoms towards the methyl group. The dipole moment of the complex was determined by Stark effect measurements to be $\mu=1.34(3)$ D. The binding energy is estimated to be 2.9 kcal/mol from the pseudodiatomic model. Both electrostatic and *ab initio* calculations have been carried out to rationalize the structure and properties of the complex. The effect of methyl group substitution on the structures and properties of the ethylene · SO₂, propene · SO₂, and toluene · SO₂ complexes is discussed.

I. INTRODUCTION

Sulfur dioxide complexes form an important category of so-called weak charge transfer complexes. In particular, SO₂ · hydrocarbon complexes have been studied for over 40 yr.^{1,2} Recently, a group of SO₂ · hydrocarbon complexes has been studied by high resolution spectroscopy and detailed structures derived for ethylene · SO₂,³ acetylene · SO₂,⁴ benzene · SO₂,⁵ and toluene · SO₂.⁶ The complexes have a stacked configuration with the sulfur atom above the π -electron cloud of the hydrocarbon. In ethylene · SO₂ and acetylene · SO₂, the C₂ axis of SO₂ bisects the C-C bonds at 90°. The two monomer planes are nearly parallel deviating from this by 14° and 8°, respectively. In the benzene and toluene complexes, the SO₂ is more tipped with the SO₂ plane forming an angle of about 45° and 35°, respectively, with the hydrocarbon plane. One striking feature of toluene · SO₂ is its asymmetry; the C₂ axis of SO₂ and the C-CH₃ bond axis of toluene form an angle of about 47° with one S-O bond approximately aligned along the C-CH₃ bond suggesting an oxygen-methyl group interaction. In view of this methyl group effect, it seemed worthwhile to extend our investigations to the propene · SO₂ complex.

There has been no previous spectroscopic study on this complex. It is interesting that SO₂ and propene form a copolymer under certain conditions,⁷ which is sometimes referred to as poly(propene sulfone). Efforts have been made to understand the mechanism of formation, structure, and properties of the polymer. No evidence for this reaction was observed in our experiments.

This paper reports the observation and analysis of the spectra of propene · SO₂ and its isotopomers. Least-squares fitting of the moments of inertia gave a structure with a stacked configuration. The two molecular planes are very close to parallel and the torsional angle between propene

and SO₂ is such that the S atom lies above the double bond and the O atoms are above the methyl group. The structure appears to be the result of a sulfur interaction with the π bond and an oxygen interaction with the methyl group.

II. EXPERIMENTAL DETAILS

A. Samples

The propene · SO₂ complex was generated in a supersonic expansion of a gas mixture of roughly 1% propene and 1% SO₂ seeded in 98% of "first run" Ne-He carrier gas (~80% Ne, 20% He) at a total backing pressure of 1-2 atm. The spectrum was less intense when Ar was used as the carrier gas. The S¹⁸O₂ transitions were observed using enriched S¹⁸O₂ (99% ¹⁸O, Alfa Inorganics). The S¹⁸O¹⁶O sample was made by mixing equal amounts of S¹⁶O₂ and S¹⁸O₂ in a glass bulb. They exchange rapidly upon mixing to form a 2:1:1 mixture of S¹⁶O¹⁸O:S¹⁶O₂:S¹⁸O₂. The spectrum of the ³⁴S species was observed in its natural abundance of 4%. The enriched propene-2-*d*₁ species (98% D) was purchased from MSD Isotopes. The single-¹⁸O, propene-2-*d*₁ double substituted isotopic transitions were observed starting with a mixture of 0.5% S¹⁶O₂ and 0.5% S¹⁸O₂ plus 1% of propene-2-*d*₁ in the carrier gas.

B. Spectrometer

A Balle-Flygare type Fourier transform microwave spectrometer⁸ was used to observe the rotational spectrum of the complex. The spectrometer operates between 7-18 GHz and has a modified Bosch fuel injector for a pulsed supersonic nozzle source.⁹ Timing of the gas and microwave pulses was coordinated to minimize Doppler splittings of the transitions. With this system, linewidths were typically 25-30 kHz full width at half-maximum resulting from Doppler broadening. Center frequencies were usually

TABLE I. Observed rotational transitions of propene · SO₂ (MHz).

$J''_{K''_a K''_c}$	$J''_{K''_b K''_c}$	ν_{obs}	$\Delta\nu^a$ (kHz)	$J'_{K'_a K'_c}$	$J'_{K'_b K'_c}$	ν_{obs}	$\Delta\nu$ (kHz)
a type				b type			
3 ₁₃	2 ₁₂	8 976.854	0	5 ₂₄	5 ₁₅	9 056.834	2
3 ₀₃	2 ₀₂	9 127.719	0	6 ₂₅	6 ₁₆	9 389.134	-2
3 ₂₂	2 ₂₁	9 140.046	2	4 ₀₄	3 ₁₃	9 718.416	-1
3 ₂₁	2 ₂₀	9 152.630	0	7 ₂₆	7 ₁₇	9 779.352	-5
3 ₁₂	2 ₁₁	9 299.734	0	3 ₁₃	2 ₀₂	11 564.610	2
2 ₂₁	2 ₀₂	10 987.553	2	5 ₀₅	4 ₁₄	12 923.636	3
4 ₁₄	3 ₁₃	11 965.207	5	2 ₂₁	1 ₁₀	14 278.163	-3
4 ₀₄	3 ₀₃	12 155.304	-2	2 ₂₀	1 ₁₁	14 388.947	-3
4 ₁₃	3 ₁₂	12 395.482	0	4 ₁₄	3 ₀₃	14 402.095	5
5 ₀₅	4 ₀₄	15 170.422	4	c type			
5 ₂₄	4 ₂₃	15 225.454	8	5 ₂₄	5 ₁₄	7 443.623	8
5 ₃₃	4 ₃₂	15 241.935	-2	4 ₂₃	4 ₁₃	7 705.658	4
5 ₂₃	4 ₂₂	15 287.670	-4	3 ₂₂	3 ₁₂	7 917.197	0
5 ₁₄	4 ₁₃	15 487.480	-5	2 ₂₁	2 ₁₁	8 076.884	-2
b type				2 ₂₀	2 ₁₂	8 402.949	2
6 ₂₄	6 ₁₅	7 349.745	-6	3 ₂₁	3 ₁₃	8 578.725	2
5 ₂₃	5 ₁₄	7 552.926	-3	4 ₂₂	4 ₁₄	8 828.808	-3
4 ₂₂	4 ₁₃	7 752.738	-2	6 ₁₆	5 ₂₄	8 874.832	-3
3 ₂₁	3 ₁₂	7 932.932	0	2 ₁₁	1 ₀₁	9 001.197	-2
2 ₂₀	2 ₁₁	8 080.036	0	5 ₂₃	5 ₁₅	9 166.147	2
2 ₂₁	2 ₁₂	8 399.799	2	6 ₂₄	6 ₁₆	9 605.891	7
3 ₂₂	3 ₁₃	8 562.989	1	3 ₁₂	2 ₀₂	12 210.397	-1
2 ₁₂	1 ₀₁	8 678.288	0	2 ₂₀	1 ₁₀	14 281.313	-3
4 ₂₃	4 ₁₄	8 781.726	0	2 ₂₁	1 ₁₁	14 385.798	-2
				4 ₁₃	3 ₀₃	15 478.158	-3

^a $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in kHz, where ν_{calc} was obtained with the constants in Table II.

reproducible to within 2–3 kHz. For the normal isotopic species, some of the transitions were broader than the typical linewidth and some showed splitting due to internal rotation tunneling effects of the methyl group. The transitions for the propene-2-*d*₁ isotopic species were fairly broad due to additional quadrupole splitting from deuterium. A so-called axial nozzle was used to resolve some of the internal rotation and quadrupole splittings. The gas expansion axis and microwave propagation direction are parallel with an axial nozzle orientation and perpendicular with the regular arrangement. In the case of the axial nozzle, the Doppler splitting was much larger (50–90 kHz) and could be resolved easily while the Doppler broadening (i.e., line-

width) decreased to ~10 kHz. Hence, resolution improved with the axial nozzle and small splittings arising from internal rotation (15–25 kHz) and from nuclear quadrupole effects (10–20 kHz) could be resolved.

Stark effect measurements were used to determine the *J* quantum number of transitions during the initial assignment, and later on for determination of the dipole moment. The spectrometer is equipped with two parallel steel mesh plates 30 cm apart straddling the microwave cavity.¹⁰ Direct current voltages up to 9 kV were applied with opposite polarities to each plate. The electric field at each voltage was calibrated on a daily basis using the 2₀₁-1₁₁ transition of SO₂.¹¹

TABLE II. Spectroscopic constants for the isotopic species of the propene · SO₂ complex.^a

	C ₃ H ₆ · SO ₂	C ₃ H ₆ · S ¹⁸ O ₂	C ₃ H ₆ · S ¹⁸ O _A O	C ₃ H ₆ · SO ¹⁸ O _B	C ₃ H ₆ · ³⁴ SO ₂	2-DC ₃ H ₅ · SO ₂	2-DC ₃ H ₅ · S ¹⁸ O _A O	2-DC ₃ H ₅ · SO ¹⁸ O _B
<i>A</i> (MHz)	4269.564(2)	4044.281(1)	4158.959(2)	4155.105(1)	4260.693(6)	4191.373(4)	4085.668(10)	4080.290(10)
<i>B</i> (MHz)	1577.2661(3)	1535.4280(4)	1550.7816(5)	1560.0273(4)	1560.609(2)	1545.897(1)	1520.191(3)	1529.580(3)
<i>C</i> (MHz)	1469.6335(3)	1427.4560(5)	1452.0278(5)	1444.8016(4)	1455.389(2)	1448.094(1)	1429.713(2)	1423.466(2)
<i>D_J</i> (kHz)	3.173(6)	2.97(1)	3.16(1)	3.01(1)	3.17(3)	3.10(3)	3.09(6)	2.97(6)
<i>D_{JK}</i> (kHz)	14.06(2)	13.80(5)	13.85(4)	14.02(4)	13.6(5)	12.4(1)	11.6(8)	11.9(8)
<i>D_K</i> (kHz)	-16.4(3)	-16.0(3)	-17.0(3)	-16.5(2)	-17.6(13)	-14.4(9)	-15.6(14)	-16.2(15)
<i>d</i> ₁ (kHz)	0.182(2)	0.169(7)	0.239(8)	0.116(6)	0.18(4)	0.17(2)	0.13(6)	0.11(6)
<i>d</i> ₂ (kHz)	-0.2699(9)	-0.284(2)	-0.279(4)	-0.276(3)	-0.27(6)	-0.26(1)		
<i>n</i> ^b	47	29	28	28	14	27	14	14
$\Delta\nu_{\text{rms}}$ ^c (kHz)	3	2	2	2	4	6	6	7

^aThe uncertainties in parenthesis are the statistical values from the fitting program (1 σ). The labeling of the atoms in the isotopic species follows Fig. 1.

^bNumber of transitions in the fit.

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

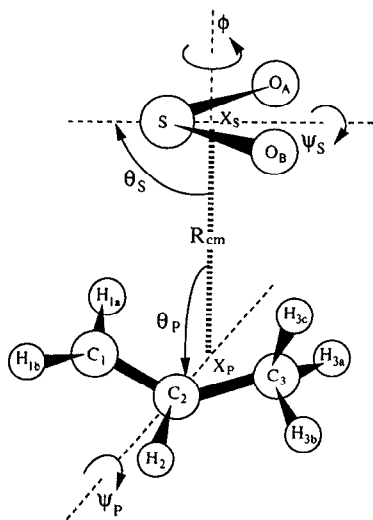


FIG. 1. Definition of the structural parameters employed in the structure fitting and atom labeling for the propene · SO₂ complex. X_S and X_P are the centers of mass of SO₂ and propene, respectively. R_{cm} is the distance between X_S and X_P . θ_S is the tilt angle of the C₂ axis of SO₂ with respect to R_{cm} and θ_P is formed between R_{cm} and X_P -C₂ of propylene. The twist of the SO₂ and propene planes with respect to R_{cm} are defined by the angles ψ_S ($\langle O_B$ -S- X_S - X_P) and ψ_P ($\langle C_1$ -C₂- X_P - X_S). The dihedral angle ϕ is the torsion between the two molecular planes. ($\langle S$ - X_S - X_P -C₂).

III. RESULTS AND ANALYSIS

A. Spectrum

Based on models similar to the structure of ethylene · SO₂, an initial search was made in the region 8.0–9.5 GHz, where many transitions were observed. With the aid of the Stark effect, a total of 14 *a*-type, 18 *b*-type, and 15 *c*-type transitions were assigned to the propene · SO₂ dimer. Some of the transitions were broader than usual; several exhibited two barely resolved components. This broadening and splitting is caused by the internal rotation of the methyl group which will be discussed later. Since the splitting was very small (15–25 kHz), we used a conventional Watson *S*-reduced Hamiltonian, *I'* representation¹² to fit the spectrum to the average frequency of the two components for those lines with split-

TABLE III. Structural parameters from least-squares fits of the moments of inertia.

	Structure I ^a	Structure II ^a
$\theta_S/\text{deg}(\langle X_P$ - X_S -S) ^b	93.1(7)	94.7(13)
$\theta_P/\text{deg}(\langle X_S$ - X_P -C ₂)	96.3(3)	96.6(7)
$\psi_S/\text{deg}(\langle O_B$ -S- X_S - X_P)	89.9(2)	88.5(4)
$\psi_P/\text{deg}(\langle C_1$ -C ₂ - X_P - X_S)	82.1(1)	82.3(3)
$\phi/\text{deg}(\langle S$ - X_S - X_P -C ₂)	-60.1(1)	120.0(1)
$R_{cm}/\text{Å}$	3.2648(2)	3.2649(4)
$\Delta I_{rms}/\text{amu Å}^2$ ^c	0.07	0.15

^aLeast-squares fit of 24 moments of inertia from the eight isotopic species. See text for a discussion of the two fits. Structure I is preferred by the authors.

^bStructural parameters defined in Fig. 1.

^c $\Delta I = I_x(\text{observed}) - I_x(\text{calculated})$ for a given isotopic species.

tings. The frequencies of the transitions are listed in Table I and the fitted rotational constants are listed in Table II.

The spectra of the isotopic species C₃H₆ · S¹⁸O₂, C₃H₆ · S¹⁸OO, C₃H₆ · SO¹⁸O, C₃H₆ · ³⁴SO₂, CH₃CDCH₂ · SO₂, CH₃CDCH₂ · S¹⁸OO, and CH₃CDCH₂ · SO¹⁸O have also been observed. Their transitions are available as supplementary data¹³ and the derived rotational constants are listed in Table II. The spectra of the latter two double substituted species were obtained to try to resolve a structural ambiguity remaining after assigning the other six isotopic species. This will be discussed in the next section.

B. Structure

The presence of three selection rules, two single ¹⁸O species, etc., indicate that propene · SO₂ has no symmetry planes. Based on this and on trial structures, the rotational constants are consistent with the stacked planes configuration.

In order to determine the exact structure of the complex, least-squares fits of the moments of inertia of all the isotopic species were carried out fixing the structures of each monomers to literature values.¹⁴ Six parameters are needed to define the structure of the propene · SO₂ dimer. As shown in Fig. 1, R_{cm} is the distance between X_S —the center of mass of SO₂, and X_P —the center of mass of propene. θ_S is the tilt angle of the C₂ axis of SO₂ with respect to R_{cm} , and θ_P defines the tilt of the propene X_P -C₂ axis with respect to R_{cm} . Dihedral angles ψ_S and ψ_P define the twist of the SO₂ and propene planes, respectively. Finally, the dihedral angle ϕ is the torsional angle between the two monomers, defined as O_B- X_S - X_P -C₂. The sign of the dihedral angles follows the definition in Ref. 15. These six structural parameters were varied in the least-squares fitting of the 24 moments of inertia. This resulted in two structures with reasonable fitting quality. These two structures are summarized in Table III. The only significant difference between these two structures involves the torsional angle ϕ . The torsional angles (absolute values) are the supplement of each other, indicating that the difference in these two structures is a rotation of the two monomers relative to each other by 180°.

The different torsional angles signify two very different configurations. This is shown in Fig. 2 where the projections in the *bc* inertial plane are illustrated. In order to

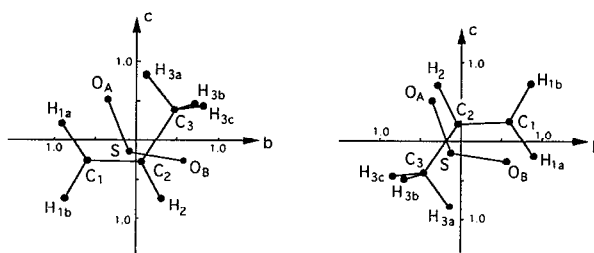


FIG. 2. The *bc* plane projections of structures I and II. Structure I is preferred.

TABLE IV. Principal axes coordinates (Å) of propene · SO₂ for structures I and II.

	<i>a</i>		<i>b</i>		<i>c</i>	
	I	II	I	II	I	II
O _A ^a	1.284	1.295	-0.688	-0.744	1.079	1.053
O _B	1.247	1.250	1.216	1.157	-0.494	-0.524
S	1.323	1.317	-0.194	-0.253	-0.264	-0.291
X _S ^b	1.294	1.295	0.035	-0.023	0.014	-0.013
X _P ^c	-1.969	-1.970	-0.053	0.035	-0.022	0.020
C ₁	-1.763	-1.778	-1.211	1.196	-0.522	0.519
C ₂	-2.020	-2.022	0.109	-0.126	-0.460	0.458
C ₃	-2.116	-2.102	0.884	-0.906	0.821	-0.822
H _{1a}	-1.610	-1.624	-1.790	1.774	0.374	-0.377
H _{1b}	-1.704	-1.730	-1.725	1.713	-1.471	1.468
H ₂	-2.162	-2.166	0.620	-0.636	-1.400	1.399
H _{3a}	-1.952	-1.937	0.239	-0.261	1.686	-1.687
H _{3b}	-3.098	-3.078	1.338	-1.369	0.941	-0.947
H _{3c}	-1.373	-1.351	1.677	-1.692	0.865	-0.859

^aSee Fig. 1 for atom label definitions.

^bCenter of mass of SO₂.

^cCenter of mass of propene.

choose a preferred structure in a case like this, a careful comparison of the coordinates of the substituted atoms determined from Kraitchman's equations¹⁶ vs the least-squares fitted values is usually instructive. The latter values are given in Table IV. It is interesting that the least-squares values of the coordinates for the two structures are very close to each other for all the atoms except that the *b* and *c* coordinates of propene have opposite signs. There are some noticeable differences in the *b* coordinates of the SO₂ atoms, otherwise the coordinates are quite indistinguishable. A check against the Kraitchman determined coordinates (Table V) indicates a preference for structure I, but the comparison is not very compelling. (This preference is likewise manifested in the better fit to the observed *I*'s for structure I, cf. ΔI_{rms} in Table III). What occurs in the structure fitting is that a rotation of propene relative to SO₂ by 180° leads to remarkably little change in the absolute values of the principal axis coordinates for the two configurations. Since propene has no symmetry, this might be considered fortuitous. In actuality, it has a "near C₂ axis" in an inertial sense since the CH₃ and terminal CH₂ group have similar masses. There is no apparent set of isotopically substituted species which is likely to resolve this ambiguity. At one stage we hoped that this was not the case and assigned the two doubly substituted S¹⁸O¹⁶O · CH₃CDCH₂ species with the expectation that a better match for the *b* coordinates of the SO₂ might result compared to the Kraitchman values. However, these data did not clearly resolve the ambiguity.

In the end, dipole moment data permitted a clear choice between the two structures. The vector sum of the dipole moments of SO₂ and propene compare very well with the experimentally determined value for structure I while for structure II the comparison is much poorer. This is discussed in the next section. Additional support for structure I is obtained from an electrostatic energy calculation which gave a minimum close to structure I and a maximum close to structure II on the energy vs torsional

angle curve. This will be discussed in the electrostatic calculation section. A side view projection of structure I is illustrated in Fig. 3.

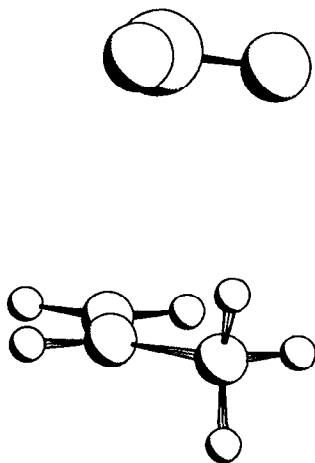
The uncertainties associated with structure I in Table III are the statistical values obtained from the least-squares fitting of the moments of inertia. The structure is the so-called *r*₀ structure and it is not easy to quantitatively estimate its deviation from the equilibrium structure *r*_e without correction of the moments for vibrational effects. Given the large amplitude nature of these internal motions in weakly bonded complexes, the vibrational effects could be sizeable. We recommend that *R*_{cm} and the angles should be within 0.05 Å and 5° of the equilibrium values.

C. Dipole moments

The Stark effect of nine *M* components from five different transitions was measured. The second order Stark coefficients are available as supplementary data.¹³ All the splittings have been checked carefully to ensure strictly second order behavior. Least-squares fit of the observed Stark coefficients to those calculated from the rotational

TABLE V. Comparison of the atomic coordinates from least-squares fit for structures I and II and Kraitchman substitution calculations.

		Structure I	Structure II	Kraitchman
O _A	<i>a</i>	1.284Å	1.295Å	1.276Å
	<i>b</i>	0.688	0.744	0.657
	<i>c</i>	1.079	1.053	1.092
O _B	<i>a</i>	1.247	1.250	1.244
	<i>b</i>	1.216	1.157	1.194
	<i>c</i>	0.494	0.524	0.507
S	<i>a</i>	1.323	1.317	1.291
	<i>b</i>	0.194	0.253	0.222
	<i>c</i>	0.264	0.291	0.280
H ₂	<i>a</i>	2.162	2.166	2.162
	<i>b</i>	0.620	0.636	0.624
	<i>c</i>	1.400	1.399	1.369

FIG. 3. Structure I in the ac plane.

constants gave $\mu_a=0.476(3)$ D, $\mu_b=0.697(38)$ D, $\mu_c=1.040(24)$ D, and a total dipole moment of $\mu_T=1.340(27)$ D.

These values can be compared with those calculated from the vector sum of the dipole moments of SO_2 and propene for the two structures discussed above. The dipole moment of SO_2 has been determined as 1.633 D^{11} from X_S to S (negative to positive). For propene the value of $\mu=0.364$ D was determined by Lide and Mann.¹⁷ They gave the orientation of the dipole moment as either 17° or 33° relative to the C–C single bond without specifying the positive and negative ends. We calculated the dipole moment for propene using the CADPAC *ab initio* program¹⁸ with a 6-31G** basis sets. The calculated value is in good agreement with the experimental value and closer to the 33° direction, which was also favored by Lide and Mann. The calculation indicated the sign of the dipole should be from C_1 to C_3 (negative to positive). With these results, we calculated the vector sums for structures I and II listed in Table VI. It is apparent that structure I has a much better agreement with the experimental values than structure II. This is convincing evidence to eliminate structure II. In essence the dipole moments of the monomers in structure I are aligned more nearly antiparallel which is energetically preferred. The differences between the values of structure I and the observed values arise in part from induction and vibrational averaging effects. It is normal behavior based on other SO_2 - π systems that the μ_a component in the complex usually increases by a large amount while the μ_b and/or μ_c components decrease by small amounts.

D. Electrostatic and *ab initio* calculation

In order to determine whether an electrostatic interaction model can rationalize the structure of the propene · SO_2 complex, a distributed multipole analysis along the lines of Buckingham and Fowler^{19,20} was explored. In this model, the charge distribution of each monomer is described by sets of point multipoles, which are located on the atoms and sometimes at bond midpoints. In this simple physical model, only the electrostatic inter-

TABLE VI. Comparison of observed dipole components with values predicted for structures I and II.

	I	II	obs.
$ \mu_a $	0.079D	0.054D	0.476(3)D
$ \mu_b $	0.735	1.340	0.697(38)
$ \mu_c $	1.064	1.448	1.040(24)
μ_T	1.296	1.974	1.340(27)

action between the monomers is considered. Buckingham and Fowler also incorporate a short range repulsion, described by an atom hard sphere term. The distributed multipole values for SO_2 were taken directly from Ref. 20. Those for propene were determined by an *ab initio* calculation using the CADPAC program¹⁸ with a 6-31G** basis set. These multipole moments (Table VII) were then used to calculate the electrostatic interaction energy between the two monomers. Starting with structure I in Table III and holding all the fitted parameters fixed except for the torsional angle ϕ , the energy versus ϕ curve in Fig. 4 was obtained. This gave a minimum (-2.5 kcal/mol) at 55° near the experimental value of 60° for structure I and a maximum (-0.8 kcal/mol) near structure II.

We have also calculated the electrostatic energy as a function of the tilt angle of SO_2 (θ_S) and of propylene (θ_P) with the other structural parameters fixed to those of structure I (neglecting repulsions). These two calculated curves are shown in Fig. 5. For both tilt angles, the calculated and observed minima values are within 10° – 15° of each other. The electrostatic model gave similar agreement for several other SO_2 systems, including ethylene · SO_2 ,³ acetylene · SO_2 ,⁴ benzene · SO_2 ,⁵ and toluene · SO_2 .⁶ This simplified distributed multipole model appears to capture much of the interaction anisotropy for SO_2 · π complexes.

GAUSSIAN 90 *ab initio* calculations²¹ were explored to estimate the minimum energy configuration of the propene · SO_2 complex. The calculations were at the HF/SCF level with either a 4-31G or a 6-31G basis set. The six structural parameters described earlier were varied to search for the most stable structure. The initial values for the six parameters were taken from structure I. The structures with either basis set were very similar while the 6-31G set gave a much larger stabilization energy. The optimized structure is in general agreement with the observed structure (Table VIII). This is similar to *ab initio*—experimental comparisons for SO_2 complexes with benzene,⁵ dimethylamine,²² trimethylamine,²² and dimethyl ether.²³ We conclude that the interaction forces which determine the asymmetric structure, presumably electrostatic, are represented adequately enough in a quantum mechanical calculation at this level to give a reasonable prediction of the general configuration. One aspect which remains unexplored is whether the *ab initio* calculation would quickly converge to this structure, or another minimum, if the initial structure was far from the experimental values.

A binding energy of 3.47 kcal/mol was obtained from the *ab initio* energies for propene · SO_2 , SO_2 and propene

TABLE VII. Atom coordinates and distributed multipole moments for SO₂ and propene (a.u.).^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>Q</i>	μ_x	μ_y	μ_z	θ_{xx}	θ_{xy}	θ_{yy}	θ_{zz}
S	0.000	0.6815	0.000	1.806	0.000	-1.628	0.000	1.328	0.000	-1.219	-0.109
O _A	2.338	-0.6815	0.000	-0.580	-0.031	-0.011	0.000	0.273	-0.384	-0.221	-0.052
A ^b	1.169	0.000	0.000	-0.323	-0.038	0.213	0.000	0.222	-0.417	0.372	-0.594
C ₁	2.4062	0.1161	0.0000	-0.0996	0.0500	0.0047	0.0000	0.0471	-0.0482	-0.0578	0.0107
C ₂	0.0000	0.8802	0.0000	-0.0088	-0.1773	-0.1390	0.0000	0.1190	0.2420	-0.0800	-0.0390
C ₃	-2.2327	-0.8692	0.0000	0.0066	0.1752	0.1375	0.0000	0.1405	0.3418	0.0399	-0.1804
H _{1a}	2.8659	-1.8937	0.0000	0.0241	0.0510	-0.2065	0.0000	0.0315	0.0253	-0.0758	0.0443
H _{1b}	3.9507	1.4531	0.0000	0.0264	0.1619	0.1417	0.0000	-0.0286	-0.0670	-0.0098	0.0384
H ₂	-0.4065	2.8995	0.0000	0.0230	-0.0390	0.2069	0.0000	0.0442	0.0254	-0.0809	0.0367
H _{3a}	-1.6372	-2.8312	0.0000	0.0092	0.0513	-0.1932	0.0000	0.0213	0.0280	-0.0631	0.0418
H _{3b} ^c	-3.4199	-0.5707	-1.6753	0.0095	-0.1138	0.0262	-0.1606	0.0002	0.0101	0.0375	-0.0377

^aThe distributed multipole moments for SO₂ were taken from Ref. 20. Those for propene were calculated using CADPAC program with a 6-31G** basis set. Dipole moment directions are from regions of negative to positive charge. Atom labels from Fig. 1. The multipole moment values for O_B and H_{3c} follow by symmetry from O_A and H_{3b}.

^bA is the midpoint of S-O bond.

^cThe θ_{xz} and θ_{yz} values are zero for all the atoms except for H_{3b} which are -0.0550 and 0.0108, respectively.

with the 6-31G basis set.²⁴ This is comparable to 2.92 kcal/mol from the distortion constant D_J using the pseudodiatomic (PD) model.²⁵ The binding energy for several other SO₂- π complexes from the PD model are 1.1 kcal/mol for C₂H₂ · SO₂,⁴ 1.4 kcal/mol for C₂H₄ · SO₂,³ 1.9 kcal/mol for benzene · SO₂,⁵ 2.4 kcal/mol for toluene · SO₂,⁶ and 3.02 kcal/mol for butadiene · SO₂.²⁶ We believe that the PD values for the ethylene, propene, benzene, and toluene complexes are too low based on the experimental value for benzene · SO₂ of 4.4 kcal/mol. Nevertheless, the PD (and *ab initio*) values for butadiene · SO₂ agree well with the experimental value of 3.24 kcal/mol.²⁷ In any case, the relative PD value for closely related systems are probably ordered correctly, suggesting that the binding energies for the propene and toluene complexes are about 0.5–1 kcal/mol higher than for the ethylene and benzene complexes. This may come from a methyl group-SO₂ interaction.

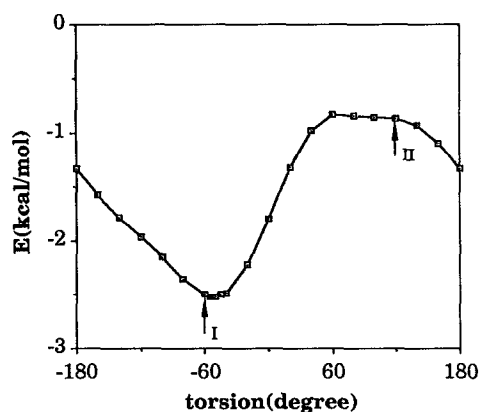


FIG. 4. The calculated electrostatic energy versus torsion angle (ϕ). The structure parameters (except ϕ) are fixed to that of structure I. The arrows indicate the spectroscopic fitted values for structures I and II, respectively. The calculation shows that structure I is close to the energy minimum and structure II close to maximum.

E. Internal rotation

Some of the transitions for propene · SO₂ have splittings of 10–25 kHz. We believe this splitting is caused by the internal rotation of the methyl group along its C₃ axis, which has a barrier of 692 cm⁻¹ in the propene monomer.¹⁷ Splittings for eight transitions of the propene · SO₂ normal species were fitted with a PAM internal rotation Hamiltonian.^{5,28} The quality of the fit ($\Delta\nu_{\text{rms}} = 5$ kHz) was good. The internal rotation barrier was determined from the fitting to be 690 cm⁻¹. Since the splittings are very small, the value for the barrier may not be very accurate. The uncertainty is perhaps $\pm 10\%$. Nevertheless, it is apparent that the barrier is not affected much upon complexation. This agrees with the electrostatic model for propene · SO₂ which gives a contribution to the barrier from complexation of only 61 cm⁻¹ (0.17 kcal/mol). This is the variation in the electrostatic energy as the methyl group is rotated. This can be compared to toluene · SO₂ where the methyl group internal rotation barrier increased by about 80 cm⁻¹ upon complexation.⁶ Finally, the orien-

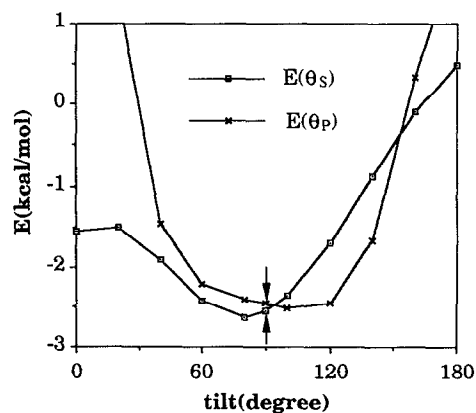


FIG. 5. The calculated electrostatic energy vs SO₂ and propene tilt angles (θ_S and θ_P , respectively). R_{cm} , ψ_S , ψ_P , ϕ , and θ_P (or θ_S) fixed at structure I values. The arrows indicate the spectroscopic fitted values.

TABLE VIII. Comparison between the experimentally determined structure and the optimized structure from GAUSSIAN 90 *ab initio* calculation.

	θ_S/deg	θ_B/deg	ψ_S/deg	ψ_B/deg	ϕ/deg	$R_{cm}/\text{\AA}$
Least-squares fit	93.1	96.3	89.9	82.1	-60.1	3.2648
GAUSSIAN 90/6-31G	90.7	96.8	83.9	81.0	-42.2	3.4264

tation of the methyl group in the complex was not determined. The moments of inertia are not sensitive to the methyl group torsional angle. An asymmetric $\text{CH}_2\text{D}-\text{CH}=\text{CH}_2$ species would have to be assigned in order to determine the methyl top orientation. Given the high barrier in free propene and the small effect on the barrier upon complexation, it seems unlikely that the orientation of the methyl group changes much from free propene.

IV. DISCUSSION

This study was undertaken to ascertain how methyl group substitution on ethylene would affect the interaction with SO_2 . As noted above, the SO_2 dipole moment (C_2 axis) has rotated by about 30° from crossed to the $\text{C}=\text{C}$ bond in C_2H_4 to align nearly antiparallel to the dipole moment direction in propene. This structural feature and the variation in electrostatic energy with torsional angle (Fig. 4) provide compelling evidence that an electrostatic interaction model can rationalize the gross configuration of the propene · SO_2 complex. It is attractive to describe the near parallel planes structure as a result of sulfur- π bond and oxygen-methyl group attractions. There are other structural features which suggest this: (a) the SO_2 is pulled over to the methyl substituted carbon, however the sulfur remains oriented largely over the $\text{C}=\text{C}$ bond (Fig. 2); (b) one oxygen (O_B) makes a close contact to the out-of-plane methyl hydrogen, $R(O_B-\text{H}_{3c})=3 \text{ \AA}$; (c) the twist angle of the propene (ψ_P) is 82° , i.e., the double bond is tilted slightly towards the sulfur end of the SO_2 moiety (Fig. 3).

The structural influence of a methyl group is also reflected in the toluene · SO_2 results.⁶ The toluene and SO_2 dipole moments similarly line up in a more nearly antiparallel configuration. An oxygen-methyl group interaction is suggested: the C_2 axis of SO_2 forms a torsional angle of 47° which aligns an S-O bond approximately parallel to the $\text{C}-\text{CH}_3$ bond axis. A distributed multipole electrostatic model could similarly rationalize the observed torsional angle. A notable difference in the toluene · SO_2 interaction from propene · SO_2 is the greater tilt of the SO_2 plane relative to toluene ($\sim 35^\circ$).

The larger SO_2 tilt angles in toluene · SO_2 and benzene · SO_2 (35° - 45°) compared to propene · SO_2 , and ethylene · SO_2 (8° - 14°) may be associated in part with polarization effects. In all these complexes the μ_a dipole component is approximately aligned along R_{cm} . It increases markedly compared to the vector sum expected from projection of the monomer values onto the a inertial axis of the complex. This presumably arises largely from polarization of the hydrocarbon π electrons by SO_2 .³ The increase in μ_a in ethylene · SO_2 and propylene · SO_2 is 0.3 D and 0.4 D,

respectively. In benzene · SO_2 and toluene · SO_2 , μ_a increases by 0.5 D and 0.6 D, respectively. The larger effects in the aromatic systems may be synergistically coupled to the greater tilting of the SO_2 plane in order to better polarize the π system. The small decreases in the μ_b and μ_c components are probably also explained by polarization effects from the SO_2 inducing smaller antiparallel components along these axes (see dipole moment section; the b and c axes lie approximately parallel to the carbon atom plane of the hydrocarbon).

One other structural effect associated with methyl group substitution is a decrease in R_{cm} from 3.50 \AA in the ethylene complex to 3.26 \AA in the propene complex. A similar shortening occurs in the benzene and toluene complexes: from 3.48 to 3.37 \AA . These shortenings are presumably a reflection of a greater stabilization upon methyl substitution. This increased stability was estimated to be approximately 0.5-1 kcal/mol based on values for the dissociation energy estimated from centrifugal distortion constants.

Finally, the ethylene · SO_2 complex displayed prominent tunneling effects arising from torsional tunneling of the ethylene about R_{cm} . This internal rotation barrier was estimated as $V_2=30 \text{ cm}^{-1}$. Due to its asymmetry, internal rotation tunneling in propene · SO_2 to an equivalent form would require a net relative rotation of 360° . No evidence is found for such motion in the spectrum. If the electrostatic calculation is a useful guide, the barrier is an order of magnitude larger than the ethylene complex. It is also noteworthy that the methyl group internal rotation barrier in propene ($V_3=692 \text{ cm}^{-1}$) is affected by less than $\pm 10\%$ upon complexation.

In summary, the structures and binding energies of the propene · SO_2 and toluene · SO_2 complexes indicate that the methyl group increases the stability of the complexes compared to the ethylene and benzene analogs. This was previously inferred from electronic spectroscopy data.^{2(a)} Apparently this can be rationalized by increased attractive electrostatic interactions. This may arise in part from the higher polarity of the substituted hydrocarbon and from favorable oxygen-methyl group interactions.

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- ¹I. Hanazaki, *J. Phys. Chem.* **76**, 1982 (1972); D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.* **55**, 1293 (1959).
- ²(a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.* **73**, 4169 (1951); (b) L. J. Andrews, *Chem. Rev.* **54**, 713 (1954).
- ³A. M. Andrews, A. Taleb-Bendiab, M. S. LaBarge, K. W. Hillig II, and R. L. Kuczkowski, *J. Chem. Phys.* **93**, 7030 (1990).
- ⁴A. M. Andrews, K. W. Hillig II, R. L. Kuczkowski, A. C. Legon, and N. W. Howard, *J. Chem. Phys.* **94**, 6947 (1991).
- ⁵A. Taleb-Bendiab, K. W. Hillig II, and R. L. Kuczkowski, *J. Chem. Phys.* **97**, 2996 (1992).
- ⁶A. Taleb-Bendiab, K. W. Hillig II, and R. L. Kuczkowski, *J. Chem. Phys.* **98**, 3627 (1993).
- ⁷C. S. Marvel and E. D. Weil, *J. Am. Chem. Soc.* **76**, 61 (1954).
- ⁸T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.* **52**, 33 (1981).
- ⁹K. W. Hillig II, J. Matos, A. Scioly, and R. L. Kuczkowski, *Chem. Phys. Lett.* **133**, 359 (1987).
- ¹⁰R. K. Bohn, K. W. Hillig II, and R. L. Kuczkowski, *J. Phys. Chem.* **93**, 3456 (1989).
- ¹¹D. Patel, D. Margolese, and T. R. Dyke, *J. Chem. Phys.* **70**, 2740 (1979).
- ¹²J. K. G. Watson, *J. Chem. Phys.* **46**, 1935 (1967).
- ¹³See AIP document No. PAPS JCPA-100-15-3 for 3 pages of isotopic transition frequencies and second order Stark coefficients. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 500 Sunnyside Boulevard, Woodbury, New York 11797-2999. The price is \$1.50 for each microfiche (60 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
- ¹⁴M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data* **8**, 619 (1979); D. R. Lide, Jr. and D. Christensen, *J. Chem. Phys.* **35**, 1374 (1961).
- ¹⁵E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- ¹⁶J. Kraitchman, *Am. J. Phys.* **21**, 17 (1953).
- ¹⁷D. R. Lide, Jr. and D. E. Mann, *J. Chem. Phys.* **27**, 868 (1957).
- ¹⁸R. D. Amos and J. E. Rice, *The Cambridge Analytic Derivatives Package. Issue 4.0* (Cambridge, England 1987).
- ¹⁹A. D. Buckingham and P. W. Fowler, *J. Chem. Phys.* **79**, 6426 (1983).
- ²⁰A. D. Buckingham and P. W. Fowler, *Can. J. Chem.* **63**, 2018 (1985).
- ²¹M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, *GAUSSIAN 90—Revision I* (Gaussian, Inc., Pittsburgh, PA, 1990).
- ²²J. J. Oh, K. W. Hillig II, and R. L. Kuczkowski, *J. Phys. Chem.* **95**, 7211 (1991).
- ²³J. J. Oh, K. W. Hillig II, and R. L. Kuczkowski, *Inorg. Chem.* **30**, 4583 (1991).
- ²⁴The energies (a.u.) obtained with a 6-31G basis set were: propene, -117.027 409; SO₂, -546.903 241; propene · SO₂, -663.936 181.
- ²⁵D. J. Millen, *Can. J. Chem.* **63**, 1477 (1985).
- ²⁶L.-W. Xu, A. Taleb-Bendiab, L. Nemes, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **115**, 5723 (1993).
- ²⁷J. R. Grover, E. A. Walters, J. K. Newman, and M. G. White, *J. Am. Chem. Soc.* **107**, 7329 (1985).
- ²⁸C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.* **31**, 841 (1959).