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The Microwave Spectrum, Structure, and Dipole Moment of the Butadiene–Sulfur Dioxide Complex

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Abstract: The microwave spectrum of the butadiene·SO_2 complex has been observed with a Fourier transform microwave spectrometer. The rotational constants were determined as A = 2793.8856(3) MHz, B = 1325.4117(2) MHz, and C = 1123.0275(2) MHz. In addition to the normal species, the spectra of eight other isotopic species were assigned. The structure was determined from the moments of inertia of all the isotopic species in a least-squares fitting procedure. The centers of mass of the two monomers are separated by 3.32(5) Å with SO_2 sitting above the center of the butadiene plane. The two molecular planes are close to parallel with the C_2 axis of SO_2 rotated 44(5)° relative to the C–C single bond of butadiene. The dipole moment was determined to be μ_{total} = 1.475(15) D. Electrostatic and *ab initio* calculations have also been carried out to better understand the structure and binding of this complex.

Introduction

The study of weakly bound complexes provides information on intermolecular interactions, which play an important role in chemical and physical processes. It is expected that the investigation of a group of related complexes will be helpful in determining patterns and trends leading to a better understanding of intermolecular forces. Quite a few SO_2-containing complexes have now been studied.[1] A major category is the complexes of SO_2 with π-systems, such as ethylene,[2] acetylene,[3] and benzene.[4] The patterns observed for their structures are as follows. All of them have a stacked near parallel plane configuration. The sulfur end of SO_2 is usually closer to the π-electron cloud with the tilt of the SO_2 plane relative to the R_{cm} deviating from perpendicular by 10–45°. The distances between the centers of mass of the two moieties (R_{cm}) vary from 3.37 Å for toluene·SO_2[5] to 3.73 Å for cyclopropane·SO_2.[6] In several systems, like ethylene·SO_2 and benzene·SO_2, the spectra displayed internal rotation effects.

Butadiene·SO_2 is an attractive candidate to extend the study of SO_2–π complexes. We were principally interested in determining where SO_2 would reside, i.e., above one of the double bonds, like in ethylene, or more nearly above the center of butadiene.

There has been one previous spectroscopic study of butadiene·SO_2 by Grover *et al.*[7] using photoionization techniques. The dissociation energy of the complex was determined as 3.24 ± 0.48 kcal/mol, which is similar to the other SO_2–π systems mentioned above. The structure could not be determined experimentally, but the minimum energy configuration calculated with the program CHARMM suggested that the SO_2 plane is perpendicular to the butadiene plane with one oxygen pointing toward butadiene and the other oriented away. This contrast with the other SO_2–π complexes provided further motivation to investigate this complex.

In this paper, we report the analysis of the rotational spectra of butadiene·SO_2 and eight isotopic species. The rotational constants indicate a stacked structure with the two molecular planes close to parallel. The center of mass distance between the two moieties is determined to be 3.32 Å, which is on the short side compared to other SO_2–π systems. The calculated binding energy from the distortion constant D_J also indicates that butadiene·SO_2 is a reasonably strong complex.

Experimental Section

The spectrum was observed using a Fourier transform microwave spectrometer operated between 7 and 18 GHz.[8,9] The weakly bound complexes were generated by a pulsed supersonic expansion through a modified Bosch fuel injector. Timing of the gas and microwave pulses was coordinated to minimize Doppler splittings of the transitions. Line widths were typically 25–30 kHz full width at half-maximum. Center frequencies were usually reproducible to within 2–3 kHz.

A gas mixture of roughly 1% butadiene and 1% SO_2 buffered in 98% Ne gas at a total pressure of 1–2 atm was employed. Ne was used instead of Ar since the spectrum was more intense with the former. The butadiene·SO_2 complex is sometimes called an internally reactive small cluster since butadiene and SO_2 can react with each other and form 3-sulfolene. In addition, butadiene itself can polymerize easily. Therefore, our butadiene–SO_2 mixtures were stabilized by adding a few crystals of 4-*tert*-butylchatechol or hydroquinone to the gas bulb. They have low volatility and add no complications to the spectrum. $S^{18}O_2$ transitions were observed using enriched $S^{18}O_2$ (99% ^{18}O, Alfa Inorganics) without dilution. An $S^{18}O^{16}O$ sample was made by mixing equal amounts of $S^{16}O_2$ and $S^{18}O_2$ in a glass bulb. They exchange rapidly upon mixing to form a 2:1:1 mixture of $S^{16}O^{18}O$:$S^{16}O_2$:$S^{18}O_2$. A spectrum of the ^{34}S species was observed in its natural abundance (4%). 1-^{13}C-substituted butadiene was obtained from MSD Isotopes. It was mixed with the normal species of butadiene in a 1:4 ratio in order not to consume this expensive isotope too fast. A single ^{13}C, double ^{18}O substituted species was observed with $S^{18}O_2$ and the 1:4 mixture of ^{13}C/normal species of butadiene.

The dipole moment of the complex was determined by Stark effect measurements. The spectrometer was equipped with two parallel steel mesh plates 30 cm apart straddling the microwave cavity.[10] DC voltages

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Table I. Observed Rotational Transitions of Butadiene·SO_2 (MHz)

$J'_{K_pK_o}$	$J''_{K_pK_o}$	ν_{obs}	$\Delta\nu^a$
3_{03}	2_{02}	7268.224	−1
4_{04}	3_{03}	9608.140	2
4_{14}	3_{13}	9352.638	0
4_{13}	3_{12}	10154.964	0
5_{05}	4_{04}	11895.880	−3
5_{14}	4_{13}	12648.473	−1
2_{20}	1_{11}	9726.369	−2
2_{21}	1_{10}	9504.483	−1
3_{31}	3_{22}	7860.128	1
3_{30}	3_{21}	7764.955	−2
3_{13}	2_{02}	8315.270	−1
3_{21}	2_{12}	12453.458	0
3_{22}	2_{11}	11749.980	2
4_{32}	4_{23}	7910.203	1
4_{31}	4_{22}	7637.103	1
4_{14}	3_{03}	10399.685	1
4_{04}	3_{13}	8561.092	0
4_{23}	3_{12}	13891.667	0
5_{33}	5_{24}	8007.979	0
5_{32}	5_{23}	7414.523	2
5_{15}	4_{04}	12452.760	−1
5_{05}	4_{14}	11104.340	2
6_{34}	6_{25}	8171.254	2
6_{16}	5_{05}	14512.202	0
7_{35}	7_{26}	8416.573	−1
7_{43}	7_{34}	10701.189	−1
2_{21}	1_{11}	9706.862	−3
2_{20}	1_{10}	9523.989	0
3_{12}	2_{02}	9528.305	4
3_{22}	2_{12}	12357.108	1
4_{13}	3_{03}	12415.037	−3
5_{14}	4_{22}	8630.448	1

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

up to 7 kV were applied with opposite polarities to each plate. The electric field at each voltage was calibrated on a daily basis using the 2_{01}–1_{11} transition of SO_2.[11]

Results and Analysis

I. Spectrum. The butadiene·SO_2 spectrum exhibited all three selection rules with *b*-type transitions strongest. The assignment was not straightforward at the beginning since the *a*-type R-branch patterns were spread out ($\kappa = -0.75775$) and interspersed among other, stronger transitions. Stark effect measurements were very helpful for the initial assignment. Altogether, 6 *a*-type, 20 *b*-type, and 6 *c*-type transitions were observed and fitted with a Watson S-reduced Hamiltonian (I^r representation).[12] Observed transition frequencies and differences between the observed and calculated frequencies are listed in Table I. No tunneling splittings were observed in this spectrum. The spectra of eight different isotopic species of butadiene·SO_2 have also been observed. They are double ^{18}O, two single ^{18}O, ^{34}S, two single ^{13}C, and two single ^{13}C, double ^{18}O substituted species. Observed frequencies are listed in Table II. Derived spectroscopic constants are summarized in Table III.

Several of the species in Tables II and III have a small number of transitions. Fitting them to several distortion constants serves the purpose of confirming that the assignments are correct since the distortion constants agree reasonably well with the better determined systems. If the transitions are fit to only *A*, *B*, and *C* while holding distortion constants fixed to the normal species values, changes in the constants have a negligible effect on the derived structural parameters.

II. Structure. Some qualitative structural inferences were apparent upon assignment of the spectrum. The fact that all three selection rules were observed indicates that butadiene·SO_2 has no geometrical symmetry elements. The rotational constants were consistent with SO_2 sitting above the center of the butadiene plane rather than over a carbon–carbon double bond. The weak intensities of the *a*-type transitions compared to the strong intensities of the *b*-type transitions indicate only a small tilt of the SO_2 plane from parallel to the butadiene plane.

Assuming that the structures of the two monomers remain unchanged,[13,14] six parameters are needed to define the structure of the complex. They are illustrated in Figure 1. R_{cm} is the distance between the centers of mass of butadiene and SO_2, Θ_S is the tilt angle of the C_2 axis of SO_2 with respect to R_{cm}, and Θ_B is the tilt angle of the C–C single bond of butadiene with respect to R_{cm}. Ψ_S defines the twist angle of the SO_2 plane around its C_2 axis, and similarly Ψ_B defines the twist angle of the butadiene plane around its C–C single bond. Φ is the torsion angle between the C_2 axis of SO_2 and the C–C single bond of butadiene.

The moments of inertia of the nine isotopic species were fit using a least-squares procedure to determine the six parameters. There was one complication involved in the structure fitting. Two different spectra were observed for the single ^{18}O and the single ^{13}C substituted species, respectively. This implies that the two oxygen (carbon) positions are unequivalent in the complex. From Table III, one can see that the two sets of rotational constants for each ^{18}O (^{13}C) species are different but, on the other hand, close enough to cause a problem in the structure assignment. When determining a structure, one starts with an initial structure model and assigns each set of rotational constants to an isotopic substitution at a specific position. When two sets of rotational constants are very close to each other, there are alternative ways to assign them. Therefore, using the constants of the normal, double ^{18}O, two single ^{18}O, ^{34}S, and two single ^{13}C isotopic species, four different structures of a similar fitting quality were obtained. In an effort to distinguish among them, we investigated the spectra of a double-substituted species, viz. the 1-$^{13}C^{12}C_3H_6{\cdot}S^{18}O_2$ species. This also resulted in two different spectra. When these two sets of rotational constants were included in the fitting, eight different structures resulted. This time, however, six of them were of poor fitting quality and could be eliminated. This left two very similar but different structures. The structural parameters resulting from these two fits are listed in Table IV. Both fits have similar, small values of ΔI_{rms} of 0.12 and 0.17 amu Å^2, where $\Delta I = I_{exp} - I_{calc}$, so that neither one can be readily eliminated. The ΔI_{rms} of the six rejected structures ranged from 0.41 to 0.70 amu Å^2 and gave poor Kraitchman coordinate checks (see below).

These two structures are quite similar to each other. For both structures, the two tilt angles (Θ_S,Θ_B) and the two twist angles (Ψ_S,Ψ_B) are close to 90°, which implies that the two molecular planes are close to parallel. The torsion angle is around 45°, i.e., the C_2 axis of SO_2 is rotated 45° from eclipsed to the C–C single bond of butadiene. The major differences are in the tilt and twist angles of butadiene and the torsional angle of SO_2 relative to butadiene. However, these differences are no more than 9°. Structure II is illustrated in Figures 2 and 3.

Sometimes, one can distinguish between two structural models obtained from least-squares fits by comparing the atomic coordinates with those from a Kraitchman single-substitution calculation.[15] Such a comparison is shown in Table V for the five isotopically substituted atoms. There is a trend for the SO_2 *b* coordinates to match better for structure II than for structure I. We think the differences are large enough to suggest structure II as the preferred model. However, large amplitude motion contamination of the moments does not make this completely unambiguous. One may notice that for both fits, the *c* coordinates

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Table II. Observed Transitions for Isotopic Species of Butadiene·SO_2(MHz)[a]

		$C_4H_6{\cdot}S^{18}O_2$		$C_4H_6{\cdot}S^{18}O_BO$		$C_4H_6{\cdot}SO^{18}O_A$		$C_4H_6{\cdot}^{34}SO_2$	
$J'_{K_pK_o}$	$J''_{K_pK_o}$	ν_{obs}	$\Delta\nu^b$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
4_{04}	3_{03}			9485.015	1	9477.983	−2	9505.415	0
4_{14}	3_{13}							9251.613	0
2_{20}	1_{11}	9376.559	−2	9553.278	−1	9551.045	−4	9701.497	−4
2_{21}	1_{10}	9179.867	1	9348.826	0	9337.347	0	9484.797	0
3_{31}	3_{22}			7707.997	0	7690.869	0	7915.859	−3
3_{13}	2_{02}	8105.934	0	8219.985	0	8198.496	−2	8255.509	2
4_{32}	4_{23}	7571.766	0	7751.890	1	7738.462	0	7963.586	4
4_{14}	3_{03}	10157.772	0	10292.806	0	10260.539	3		
4_{04}	3_{13}	8328.273	0	8433.678	0	8447.183	1	8438.399	−3
5_{33}	5_{24}			7837.864	0			8056.914	4
5_{15}	4_{04}					12291.498	−1		
5_{05}	4_{14}			10946.032	0	10955.596	0	10958.425	0
5_{14}	4_{23}							8714.339	1
6_{34}	6_{25}							8213.024	−4
2_{21}	1_{11}	9360.362	2	9536.221	1	9532.511	4	9682.933	1
2_{20}	1_{10}	9196.066	−1					9503.365	0
3_{12}	2_{02}	9187.915	0					9443.144	2

		$1\text{-}^{13}CC_3H_6{\cdot}SO_2$		$4\text{-}^{13}CC_3H_6{\cdot}SO_2$		$1\text{-}^{13}CC_3H_6{\cdot}S^{18}O_2$		$4\text{-}^{13}CC_3H_6{\cdot}S^{18}O_2$	
$J'_{K_pK_o}$	$J''_{K_pK_o}$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
2_{20}	1_{11}	9576.024	−2	9558.796	−4	9235.079	−1	9220.382	−1
2_{21}	1_{10}	9349.464	0	9328.775	−1	9033.764	1	9016.165	−1
3_{31}	3_{22}	7707.513	0	7651.426	0	7389.426	−1	7340.711	0
3_{13}	2_{02}	8182.413	0	8185.043	0	7977.803	0	7980.700	0
4_{32}	4_{23}					7433.637	2	7386.307	0
4_{14}	3_{03}	10231.368	0	10237.302	0	9994.658	0		
4_{04}	3_{13}	8465.577	0	8505.091	0	8235.286	0	8270.796	0
5_{33}	5_{24}					7520.083	−1	7475.376	0
2_{21}	1_{11}	9555.425	2	9537.493	5	9217.900	0	9202.651	1
2_{20}	1_{10}							9033.899	1

[a] The labeling of the atoms in the isotopic species follows Figure 1 and results in structure II discussed in the text. Structure I results when the 1-^{13}C and 4-^{13}C species are interchanged. [b] $\Delta\nu = \nu_{obs} - \nu_{calc}$ in kHz, where ν_{calc} was calculated with the constants in Table III.

Table III. Spectroscopic Constants for Isotopic Species of the Butadiene·SO_2 Complex[a]

	$C_4H_6{\cdot}SO_2$	$C_4H_6{\cdot}S^{18}O_2$	$C_4H_6{\cdot}S^{18}O_BO$	$C_4H_6{\cdot}S^{18}O_A$	$C_4H_6{\cdot}^{34}SO_2$	$1\text{-}^{13}CC_3H_6{\cdot}SO_2$	$4\text{-}^{13}CC_3H_6{\cdot}SO_2$	$1\text{-}^{13}CC_3H_6{\cdot}S^{18}O_2$	$4\text{-}^{13}CC_3H_6{\cdot}S^{18}O_2$
A (MHz)	2793.8856(3)[b]	2693.584(2)	2745.5620(5)	2742.769(1)	2791.250(1)	2747.906(7)	2740.252(14)	2650.457(2)	2643.886(9)
B (MHz)	1325.4117(2)	1279.793(4)	1299.7313(8)	1304.417(2)	1309.393(1)	1311.867(4)	1316.895(8)	1266.717(4)	1271.156(14)
C (MHz)	1123.0275(2)	1099.297(2)	1112.3355(4)	1109.254(1)	1111.254(1)	1105.908(2)	1108.182(4)	1082.578(2)	1084.669(14)
D_J (kHz)	2.155(4)	2.08(11)	2.16(2)	2.20(4)	2.14(2)	1.68(8)	1.64(15)	2.02(10)	2.39(50)
D_{JK} (kHz)	20.75(1)	17.93(12)	19.52(2)	21.05(12)	20.63(3)	17.1(11)	17.9(22)	18.02(7)	17.90(16)
D_K (kHz)	−21.47(4)	−18.36(38)	−20.15(6)	−21.22(22)	−20.98(16)	−17.73(43)	−18.93(87)	−18.20(27)	−20.4(18)
d_1 (kHz)	−0.327(2)	−0.28(6)	−0.33(2)	−0.36(3)	−0.351(9)			−0.27(5)	−0.21(8)
d_2 (kHz)	−0.074(1)								−0.11(4)
n^c	32	9	11	11	15	7	7	9	9
$\Delta\nu_{rms}{}^d$ (kHz)	2	1	1	2	2	1	2	1	1

[a] See footnote a in Table II. [b] The uncertainties are statistical values from the fitting program (1σ). [c] Number of transitions in the fit. [d] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

of the carbon atoms do not compare very well with that from the Kraitchman calculation. The Kraitchman *c* coordinates of the two end carbon atoms are zero (imaginary), suggesting that the atoms lie very close to the *ab* plane. The least-squares fits give *c* coordinates of around 0.35 Å, which is larger than expected from the Kraitchman calculation. These discrepancies probably arise from the influence of large amplitude van der Waals vibrational modes on the rotational constants. They can be reconciled by small changes in P_{cc} values of the normal and ^{13}C species. The uncertainties associated with the structural parameters in Table IV are the statistical values resulting from the least-squares fitting procedure. The structure itself is the so-called r_o or effective structure. An estimate of how close it is to the equilibrium structure r_e is not possible without knowledge of the elusive vibrational potential function. Considering the large amplitude motions which affect the I's, we estimate that R_{cm} and the angles for preferred structure II are within 0.05 Å and 5°, respectively, of their equilibrium values.

III. Dipole Moment. To determine the dipole moment of this complex, second-order Stark shifts were measured. The second-order Stark coefficients were obtained from plots of $\Delta\nu$ vs E^2 and are listed in Table VII. The line splittings were examined carefully to ensure that they varied strictly with the square of the electric field. A least-squares fit of these observed coefficients gave dipole components of $\mu_a = 0.3416(4)$ D, $\mu_b = 1.316(4)$ D, $\mu_c = 0.572(2)$ D, and a total dipole moment of $\mu_T = 1.475(4)$ D. Uncertainties are the statistical values from least-squares fitting of the Stark coefficient. Experience indicates that the actual uncertainties in the dipole components may be as large as 1%,[16] resulting in an overall dipole moment of 1.475(15) D. It is interesting to note that the total dipole moment of the complex is smaller than the SO_2 monomer ($\mu_{SO_2} = 1.633$ D). Projections of the SO_2 dipole moment on the principal axes are $\mu_a = 0.188$ D, $\mu_b = 1.500$ D, and $\mu_c = 0.618$ D for structure I and $\mu_a = 0.246$ D, $\mu_b = 1.511$ D, and $\mu_c = 0.568$ D for structure II. The general agreement is good for both structures and does not allow one to distinguish between them on this basis. The decrease in μ_T from the SO_2 value is believed to arise from the induced dipole moments between SO_2 and butadiene. Similar to the cases of ethylene·SO_2[2] and acetylene·SO_2,[3] the μ_b or μ_c components decrease by small

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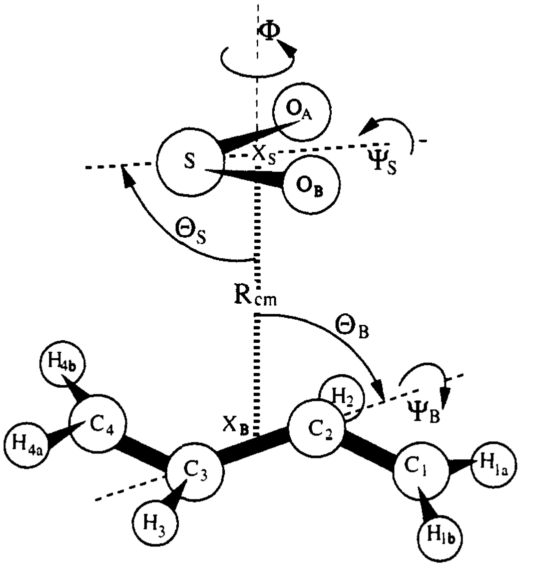

Figure 1. Definition of structural parameters for the dimer and atom labels. X_S and X_B are the centers of mass of SO_2 and butadiene, respectively, and R_{cm} is the center-of-mass distance between them. Θ_S is the tilt angle between the C_2 axis of SO_2 and R_{cm} and Θ_B is formed by the C–C single bond of butadiene and R_{cm}. The wagging of the SO_2 plane about its C_2 axis and the twist of the butadiene plane about its single bond are defined by the dihedral angles Ψ_S ($\angle X_B$–X_S–S–O_B) and Ψ_B ($\angle C_1$–C_2–X_B–X_S). The dihedral angle Φ ($\angle$S–X_S–X_B–C_3) defines the torsion between the C_2 axis of SO_2 and the C–C single bond of butadiene. Signs of the dihedral angles are defined in ref 27.

Table IV. Structure Parameters from Least-Squares Fits of Moments of Inertia and from a GAUSSIAN90 Calculation (6-31G Basis Sets, HF Level)

	struct I[a]	struct II[a]	*ab initio*
Θ_S/deg($\angle X_B$–X_S–S)[b]	98.6(11)	96.5(7)	96.97
Θ_B/deg($\angle X_S$–X_B–C_2)	77.1(5)	81.1(6)	95.19
Ψ_S/deg($\angle X_B$–X_S–S–O_B)	91.1(6)	90.6(4)	92.85
Ψ_B/deg($\angle C_1$–C_2–X_B–X_S)	101.3(14)	109.8(5)	104.86
Φ/deg($\angle$S–X_S–X_B–C_3)	–47.4(5)	–44.2(3)	–19.60
R_{cm}/Å	3.3195(3)	3.3192(2)	3.4321
ΔI_{rms}/amu Å^2 [c]	0.17	0.12	

[a] Least-squares fit of 27 moments of inertia from nine isotopic species. See text for a discussion of the two fits and footnote a in Tables II and III leading to structures I and II. Structure II is preferred by the authors. [b] Structural parameters defined in Figure 1. A value of Θ_S greater than 90° implies that the sulfur end is tipped away from butadiene. A value of Θ_B less than 90° implies that angle C_2–X_B–R_{cm} is acute, where X_B (center of mass) sits halfway between C_2 and C_3. A value of Ψ_S larger than 90° implies that O_A is tipped toward C_4H_6 and O_B is away. A value of Ψ_B greater than 90° implies that C_4 is tipped toward SO_2 and C_1 is tipped away. The torsional angle Φ is viewed along R_{cm} from SO_2 to C_4H_6. It is 0° when the C_2 axis of SO_2 and the C_2–C_3 bond axis are eclipsed and S is over C_3. The negative sign implies that C_3–X_B is rotated counter-clockwise from S–X_S. [c] $\Delta I = I_x$(observed) – I_x(calculated) for a given isotopic species.

amounts. A simple explanation is that the component of the SO_2 dipole lying parallel to the plane of the hydrocarbon induces an opposing dipole in this plane which results in smaller μ_b and/or μ_c components overall. On the other hand, the μ_a component in the complex increases because the component induced in the hydrocarbon along the *a* axis adds to the component along this axis from SO_2. The increase in μ_a is much larger in those systems where sulfur dioxide lies over a π-bond. Some of the decrease in a dipole component may also arise from vibrational averaging effects.[16]

Discussion

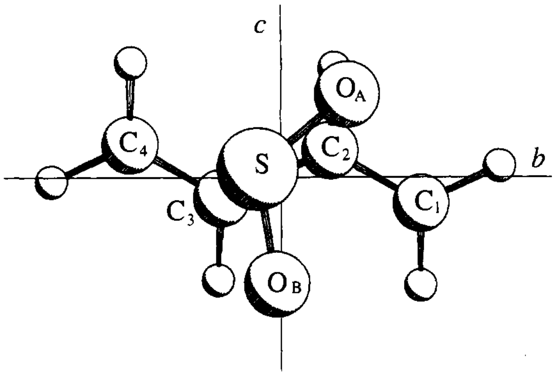

Figure 2. Projection of butadiene·SO_2 in a *bc* inertial plane (structure II).

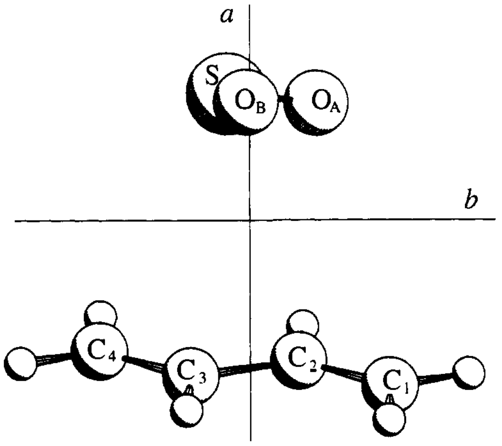

Figure 3. Projection of butadiene·SO_2 in an *ab* inertial plane (structure II).

Table V. Comparison of Atomic Coordinates from Least-Squares Fits and Kraitchman Substitution Calculations

		struct I (Å)	struct II (Å)	Kraitchman (Å)
O_A	$\|a\|$	1.480	1.458	1.448
	$\|b\|$	0.741	0.818	0.844
	$\|c\|$	0.996	1.004	1.014
O_B	$\|a\|$	1.475	1.471	1.473
	$\|b\|$	0.200	0.049	0.000[a]
	$\|c\|$	1.287	1.309	1.284
S	$\|a\|$	1.560	1.574	1.534
	$\|b\|$	0.393	0.284	0.265
	$\|c\|$	0.128	0.099	0.137
C_1[b]	$\|a\|$	1.611	1.586	1.562
	$\|b\|$	1.872	1.859	1.901
	$\|c\|$	0.359	0.387	0.000[a]
C_4[b]	$\|a\|$	1.984	2.010	1.973
	$\|b\|$	1.726	1.739	1.761
	$\|c\|$	0.381	0.323	0.000[a]

[a] Set to zero; actual calculated coordinates were imaginary. [b] Note that in structure II, C_1 becomes C_4 and C_4 becomes C_1. See Table VI.

It is apparent from the examples discussed in the Introduction that the structure of the butadiene·SO_2 complex is not readily extrapolated from the previously studied SO_2·π complexes where the sulfur end of SO_2 lies over a π-orbital and strongly polarizes it. In this case, SO_2 prefers to lie over the C–C single bond and the SO_2 and hydrocarbon planes are very nearly coplanar. The structure also deviates markedly from that predicted by the CHARMM program.[7] This calculation placed SO_2 over the center of butadiene; however, the planes of SO_2 and butadiene were nearly perpendicular. The CHARMM program is widely used in biochemical modeling and includes Lennard–Jones and electrostatic terms.

We explored whether a distributed multipole electrostatic model and *ab initio* calculations would be more successful at matching the experimental geometry. These models have a good,

Table VI. Principal Axes Coordinates (Å) of Butadiene·SO_2 for Structures I and II

	a		*b*		*c*	
	I	II	I	II	I	II
O_A[a]	1.480	1.458	0.741	0.818	0.996	1.004
O_B	1.475	1.471	–0.200	–0.049	–1.287	–1.309
S	1.560	1.574	–0.393	–0.284	0.128	0.099
X_S[b]	1.519	1.519	–0.061	0.050	–0.009	–0.027
X_B[c]	–1.798	–1.798	0.073	–0.060	0.011	0.032
C_1	–1.611	–2.010	1.872	1.739	–0.359	–0.323
C_2	–1.606	–1.702	0.714	0.608	0.310	0.320
C_3	–1.989	–1.894	–0.569	–0.728	–0.288	–0.256
C_4	–1.984	–1.586	–1.726	–1.859	0.381	0.387
H_{1a}	–1.321	–1.854	2.803	2.711	0.116	0.134
H_{1b}	–1.905	–2.427	1.924	1.729	–1.404	–1.326
H_2	–1.305	–1.285	0.700	0.656	1.357	1.324
H_3	–2.290	–2.310	–0.554	–0.776	–1.335	–1.261
H_{4a}	–2.274	–1.741	–2.658	–2.831	–0.095	–0.071
H_{4b}	–1.690	–1.168	–1.779	–1.849	1.426	1.390

[a] See Figure 1 for atom label definitions. [b] Center of mass of SO_2. [c] Center of mass of butadiene.

Table VII. Stark Coefficients ($\Delta\nu/E^2$)[a] and Dipole Moment of the Butadiene·SO_2 Complex

$J'_{K_pK_o} - J''_{K_pK_o}$	$\lvert M \rvert$	obs	obs – calc[c]
3_{13}–2_{02}	1	28.69	0.43
	2	109.60	0.26
4_{04}–3_{13}	1	–9.39	–0.01
	2	–32.18	–0.01
	3	–70.06	0.10
2_{20}–1_{11}	0	–16.47	–0.14
	1	209.00	0.72
2_{21}–1_{10}	0	7.25	0.12
	1	–257.60	0.72

$\mu_a = 0.3416(4)^c$ D; $\mu_b = 1.316(4)$ D; $\mu_c = 0.572(2)$ D; $\mu_T = 1.475(4)$ D;

[a] Second-order Stark effect in MHz/(kV/cm)^2. [b] Stark coefficients calculated using rotational constants listed in Table III. [c] The uncertainties are statistical values from the least-squares fit of the nine Stark coefficients (1σ).

although not perfect, record of predicting the correct configuration for many SO_2 complexes.[1–5]

Electrostatic energy calculations using the distributed multipole model of Buckingham and Fowler[17,18] were carried out. The multipole moments of SO_2 were taken directly from the literature,[18] and those of butadiene were calculated using the CADPAC program[19] with a 6-31G** basis set. These values are listed in Table VIII. Calculated electrostatic energies are –1.01 kcal/mol for structure I and –1.18 kcal/mol for structure II. They are not very different, which is reasonable considering that both structures are actually quite similar. We also calculated the electrostatic energy for the CHARMM structure mentioned in the Introduction. It turned out to be –0.12 kcal/mol, i.e., much less stable. For a structure identical to ethylene·SO_2 with SO_2 over a carbon–carbon double bond, the stabilization energy was –1.20 kcal/mol when the sulfur end was over the H_2,H_{1a} side of the C_1–C_2 double bond. When sulfur was over the H_{1b},C_3 side, the stabilization was –1.78 kcal/mol.[20]

To examine the structural parameters in more detail, we calculated the electrostatic energy as a function of torsional angle Φ with all the other parameters fixed at that of either structure I or structure II. The result is plotted in Figure 4. Both curves have a minimum around –20°, which is within 20–30° of the observed value and is considered reasonable agreement give the crudeness of the model and the complex interaction process. On the other hand, similar calculations for the tilt angles of SO_2 and butadiene (Θ_S and Θ_B, respectively) did not predict minima close to the observed values, unlike the very good agreement obtained in cases such as ethylene·SO_2, acetylene·SO_2, and benzene·SO_2.

In summary, although a global energy surface was not explored, it appears from the relative ordering of selected geometries and from some of the structural features and conformational trends that the electrostatic model captures a good deal of the anisotropic forces in intermolecular interactions. On the other hand, it is disappointing that this simple model seems to prefer SO_2 over a carbon–carbon double bond in contrast to the experimental result. It is not clear whether this prediction of another isomer is reliable. There remain weaker, unassigned lines in the spectra, but whether they arise from another dimer or other species was not systematically explored.

GAUSSIAN90 *ab initio* calculations[21] at the Hartree–Fock level were also employed to obtain an optimized structure of the butadiene·SO_2 complex. The six structure parameters defined earlier were varied to search for the minimum energy configuration. The input structure corresponded to structure II in Table IV. STO-3G basis sets were initially used, but the calculation did not converge. A 4-31G basis set calculation converged at a structure resembling the experimental structure quite well. A 6-31G basis set calculation gave similar results. The structural parameters from the latter *ab initio* calculation are listed in Table IV. The reasonable agreement with experiment, even though the basis set is quite small and correlation is not included, suggests that various errors are canceling or are structurally insensitive in the calculation. It is interesting that this agreement is similar to results on other SO_2 complexes with hydrocarbons,[1–5] amines, and, to some extent, ethers.[22] This suggests that such *ab initio* calculations may be useful in the prediction of general conformations of such complexes. It appears that the electrostatic interaction and its anisotropy are expressed sufficiently well in the calculation at this level. While the electrostatic and *ab initio* models reflect a good deal of the structural features, they do not lead to a simple qualitative interpretation for why SO_2 prefers to lie over the center of butadiene as opposed to lying over a carbon–carbon double bond. Does conjugation affect properties of the π-bond so markedly that the analogy to ethylene falters? Does SO_2 prefer the center site where interactions with more atomic centers can occur, as perhaps suggested by Figure 2? These are questions which might be appropriate to test and explore in future work.

The binding energy was also estimated from an *ab initio* calculation with the 4-31G basis set. The energies of butadiene and SO_2 were subtracted from the calculated minimum energy of the complex to give a binding energy of 2.98 kcal/mol.[23] The value estimated from the centrifugal distortion constant D_J using the pseudodiatomic model predicted a similar value of 3.02 kcal/

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(17) Buckingham, A. D.; Fowler, P. W. *J. Chem. Phys.* **1983**, *79*, 6426.

(18) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.

(19) Amos, R. D.; Rice, J. E. *The Cambridge Analytic Derivatives Package, Issue 4.0*; Cambridge, 1987.

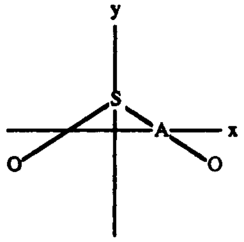
(20) It was pointed out by a referee that these calculations (and the ones described in the next paragraph) only consider the electrostatic interaction term and do not include other attractive terms such as dispersion or polarization or a repulsive term. This, of course, makes the utility of the calculations of questionable value and unlikely to reasonably reflect actual stabilization energies or geometries, except in so far as the anisotropy in the electrostatic interaction term will dominate structural trends. The Buckingham and Fowler paper[18] shows that this seems to be the case for many simpler systems. Our previous work on SO_2 complexes with ethylene, benzene, and acetylene suggested that we should also explore its success with butadiene·SO_2. If the model can be shown to work well for systems as complex as this, it may have some utility as a simple model to rationalize and predict structural trends.

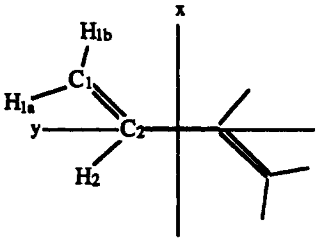
(21) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN90-Revision I; Gaussian, Inc.: Pittsburgh, PA, 1990.

(22) Oh, J. J.; Hillig, K. W., II; Kuczkowski, R. L. *Inorg. Chem.* **1991**, *30*, 4583.

(23) The energies (au) obtained with a 4-31G basis set after six iterations were butadiene, –154.698499362; SO_2, –546.346751508; butadiene·SO_2, –701.050000938.

Table VIII. Atom Coordinates and Distributed Multipole Moments for SO_2 and Butadiene (au)[a]





	x	y	z	μ_x	μ_y	θ_{xx}	θ_{yx}	θ_{yy}	θ_{zz}
S	0.0000	0.6815	0.8060	0.0000	−1.6280	1.3280	0.0000	−1.2190	−0.1090
O	2.3380	−0.6815	−0.5800	−0.0310	−0.0110	0.2730	−0.3840	−0.2210	−0.0520
A[a]	1.1690	0.0000	−0.3230	−0.0380	0.2130	0.2220	−0.4170	0.3720	−0.5940
C_1	2.1070	2.7817	−0.0947	0.0235	0.0232	0.0234	0.0770	−0.0576	0.0341
C_2	0.0000	1.3870	0.0032	0.0226	−0.1744	−0.2118	0.0302	0.2025	0.0093
H_{1a}	2.0352	4.8301	0.0332	−0.0079	0.2155	0.0486	0.0044	−0.0875	0.0389
H_{1b}	3.9703	1.9162	0.0282	0.1969	−0.0846	−0.0612	0.0440	0.0166	0.0447
H_2	−1.8349	2.3187	0.0301	−0.1867	0.1032	−0.0562	0.0484	0.0129	0.0433

[a] The SO_2 data were taken from ref 18. A is the middle point of the S–O bond. The butadiene data were calculated using the CADPAC program with a 6-31G** basis set. The following distributed multipoles are zero; μ_z, θ_{xz} and θ_{yz}. For equivalent atom sites, the values of the distributed multipole follow by symmetry. Dipole moment directions are from regions of negative to positive charge.

mol.[24] These agree well with the experimentally determined dissociation energy (3.24 kcal/mol).[7] Considering the crudeness of the pseudodiatomic model and the approximations made in the *ab initio* calculation, we consider this agreement to be accidental. There are not yet enough cross checks between such models and experimental values to know if such a pattern will hold more generally. It is also worth noting that the stabilization energy computed with the electrostatic model is low by a factor of about 3. A similar underestimate by a factor of 2 was also observed in benzene·SO_2,[4] although the value predicted for ethylene·SO_2 appears to be in better agreement with the true value.

As pointed out by a referee, it is interesting that no tunneling motions have been detected. Given the structure, the most likely motion resulting in equivalent forms would be the torsional motion about an axis joining SO_2 and C_4H_6, as observed in ethylene·SO_2[2] and benzene·SO_2.[4] In these systems, torsional barriers were estimated as 30 and 0.3 cm^{-1}, respectively. In acetylene·SO_2, a lower limit to the barrier was placed at 150 cm^{-1} and tunneling was quenched.[25] Assuming that Figure 4 can be used as a rough gauge for the torsional barrier, we would expect a value greater than 150 cm^{-1} and tunneling to be quenched.[26] However, an electrostatic model prediction of the barrier in ethylene·SO_2 was about 160 cm^{-1}, considerably different from the value estimated from the spectrum.

Summary

This study has dealt with a weakly-bound dimer probably as large and asymmetric as can be effectively managed by current high-resolution spectroscopic techniques. It illustrates some of the difficulties and challenges: for example, numerous isotopic species are necessary to obtain unambiguous structural data, and even then, a unique structure was not found. Theoretical approaches such as CHARMM, electrostatic calculations, or *ab initio* methods are equally strained to produce reliable quantitative results, although qualitative structural predictions are often satisfactory. In the present case, the CHARMM algorithm fared quite poorly. Equally noteworthy is the observation of a structure not easily extrapolated from ethylene·SO_2. Hence, qualitative extrapolations or predictions of low-level *ab initio* or electrostatic models regarding the detailed structure for a new weakly bound dimer as complex as butadiene·SO_2 should be used cautiously. More sophisticated theoretical models may eventually be necessary to provide insight to such systems.

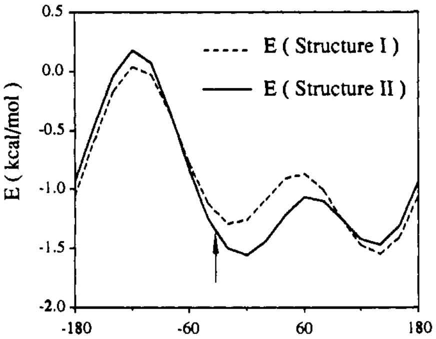


Figure 4. Distributed multipole electrostatic interaction energy as torsional angle Φ is varied with other parameters fixed at values for structure I or structure II (Table IV). The arrow indicates the experimental value for Φ, which has similar values for both structures.

Acknowledgment. This work was supported by a grant from the Experimental Physical Chemistry Division of the National Science Foundation. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. We are grateful for an allotment of computing time at the San Diego Supercomputing Center and a travel grant from the Horace Rackham Graduate School Program to Promote International Partnerships. L.N. acknowledges the assistance of the Research Laboratory for Inorganic Chemistry for a leave of absence while at Michigan.

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[24] Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477.

[25] It is interesting that D_{JK} and D_K which contain angle-dependent vibrational information are each a factor of 2 smaller than those in acetylene·SO_2 but an order of magnitude smaller than those in ethylene·SO_2.

[26] This is the difference between the minimum and the lower of the two barriers for structure II in Figure 4. The two minima in Figure 4 are not equivalent due to the tilt and twist angles (Θ,Ψ) for SO_2 and C_4H_6 which were held fixed in this calculation. Presumably, these angles might readjust to give equivalent structures at 180° intervals during an actual tunneling process.

[27] Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.