

AN AB INITIO STUDY OF THE STRUCTURE AND TORSIONAL MODES OF THE H₂SO₄ MOLECULE

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ABSTRACT

Ab initio calculations at the STO-3G and 4-31G levels have been carried out for the H₂SO₄ molecule as a function of the pair of twist angles of the H-O bonds about the respective O-S bonds. Values for the remaining bond angles and lengths were taken from the recent microwave structural determination by Kuczkowski et al. The results indicate a minimum energy for a structure with a (sc, sc) conformation and C₂ symmetry, where sc denotes synclinal, or *gauche*. This structure corresponds to that observed. At a higher energy of 11.5 kJ mol⁻¹ (4-31G) there is a structure with a (+sc, -sc) conformation and C_s symmetry. The torsional modes corresponding to the *a* and *b* irreducible representations of the C₂ point group are estimated to have frequencies of 280 and 265 cm⁻¹, respectively.

INTRODUCTION

The detailed structure of the gaseous H₂SO₄ molecule has recently been determined [1] from the microwave spectra of four isotopic species. The structure is characterized by C₂ symmetry, with the conformation of the OH groups being (+sc, +sc), where "sc" denotes synclinal (*gauche*). This observed conformation differs from the C_{2v} (ap, ap) conformation, where "ap" denotes antiperiplanar (*trans*), predicted [2] from CNDO/2 calculations. We report here the results of an ab initio study of the molecule at the single-determinant STO-3G and 4-31G levels using the program Gaussian-70 [3]. The principal result is the location of a minimum energy structure with a (+sc, +sc) conformation and C₂ symmetry, in agreement with experiment.

The observed structure [1] is characterized by the distances (in Å) S-O₁ = 1.574 ± 0.01, S-O₂ = 1.422 ± 0.01, O₁-H₁ = 0.97 ± 0.01, by the bond angles (in degrees) O₁-S-O₁' = 101.3 ± 1, O₂-S-O₂' = 123.3 ± 1, H₁-O₁-S = 108.5 ± 1.5, and by an H₁-O₁-S-O₁' dihedral angle of -90.9 ± 1°. This dihedral angle corresponds to a value of 89.1° for both ϕ and ϕ' in Fig. 1. In addition, the angle P₁P₂ between the O₁SO₁' and O₂SO₂' planes is 88.4 ± 0.1°, with this small deviation from 90° bringing the atoms O₂ and O₂' closer to O₁' and O₁, respectively.

In our ab initio studies we have assumed the values of the three bond lengths and three bond angles given above, and have explored the variation

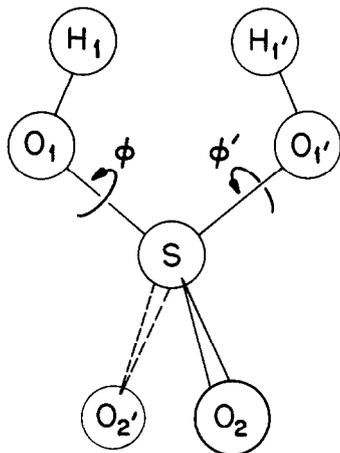


Fig. 1. Atomic designations for the H_2SO_4 molecule. The variables considered in this study are the twist angles ϕ and ϕ' , shown here for the energy maximum at $\phi = \phi' = 180^\circ$, corresponding to the (p, p) structure, where "p" denotes periplanar, or *cis*.

of the total energy with respect to the pair of twist angles ϕ and ϕ' . For most of our studies the angle P_1P_2 has been set equal to 90° , since only a small difference in energy has been found between the observed structure with the angle $\text{P}_1\text{P}_2 = 88.4^\circ$ and one identical except with the angle $\text{P}_1\text{P}_2 = 90^\circ$ (0.2 kJ mol^{-1} favoring the latter).

POTENTIAL ENERGY SURFACE

Using a grid of points corresponding to 30° increments of ϕ and ϕ' , we first generated the STO-3G potential energy surface shown in Fig. 2. The mutually perpendicular dashed lines represent mirror planes of symmetry for the surface, so that the grid of 169 points is constructed from 43 calculated points. The global minimum on this surface has C_2 symmetry and a (+sc, +sc) conformation with $\phi = \phi' = 81.4^\circ$, somewhat smaller than the observed value of $\phi = 89.1^\circ$. There is also a local minimum with C_s symmetry and a (+sc, -sc) conformation with $\phi = -\phi' = 76.0^\circ$ and an energy of 5.7 kJ mol^{-1} relative to the C_2 minimum. In locating these we made use of four additional calculations with 5° increments in the twist angles with the constraints $\phi = \phi'$ for C_2 symmetry and $\phi = -\phi'$ for C_s symmetry. The saddle point between these minima has a (\pm sc, ap) conformation with approximate twist angles $\phi = 90^\circ$, $\phi' = 0^\circ$ and an energy of 14.0 kJ mol^{-1} . The (\pm sc, p) saddle point, where "p" denotes periplanar, or *cis*, near $\phi = 60^\circ$, $\phi' = 180^\circ$ is at a higher energy, namely 17.4 kJ mol^{-1} . Both the (ap, ap) and (p, p) C_{2v} structures are local maxima, with energies of 30.1 and 70.6 kJ mol^{-1} , respectively. These results are summarized in Table 1. In contrast to the CNDO/2 results [2], the (ap, ap) structure is clearly excluded as the equilibrium geometry. We also note that whereas least motion racemization lead through the

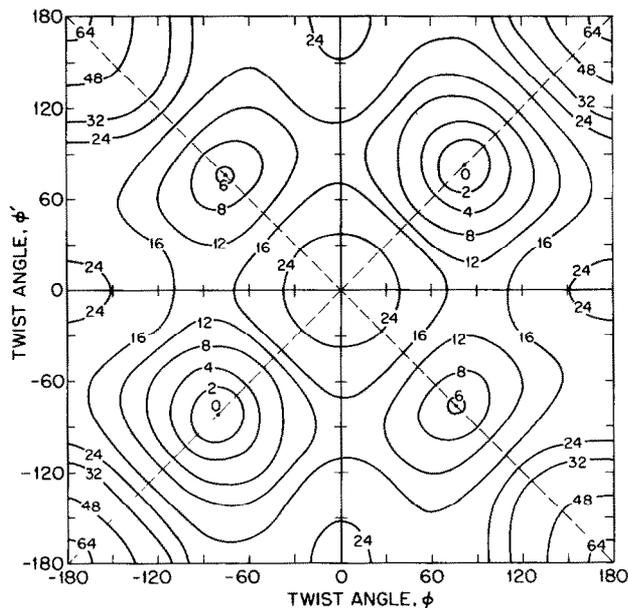


Fig. 2. Total energy vs. ϕ and ϕ' for H_2SO_4 at the STO-3G level. The numbers on the contours denote values of the energy in kJ mol^{-1} relative to the energy of the (+sc, +sc) conformation with $\phi = \phi' = 81.3^\circ$. The lowest energy computed point is at $\phi = \phi' = 81.4^\circ$, where the STO-3G total energy is -689.23602 au.

high energy C_{2v} maxima, the lowest energy racemization pathway corresponds to "circular" motion (Fig. 2) through the C_s local minima and two (\pm sc, ap) saddle points previously described.

In order to support the above conclusions, calculations at eleven selected points in ϕ, ϕ' space were done using the larger 4-31G basis set, with the key results summarized in Table 2. The structure with C_2 symmetry has a minimum energy for $\phi = \phi' = 85.1^\circ$, somewhat closer to the observed value of 89.1° than is the STO-3G value of 81.3° . The structure with C_s symmetry

TABLE 1

STO-3G Energies for H_2SO_4

Symmetry	Extremum	ϕ ($^\circ$)	ϕ' ($^\circ$)	ΔE (kJ mol^{-1}) ^a
C_2	Min	81.3	81.3	0.0
C_s	Min	75.9	-75.9	5.7
C_1	Saddle	0.0	87.5	14.0
C_1	Saddle	180.0	60.0	17.4
C_{2v}	Max	0.0	0.0	30.1
C_{2v}	Max	180.0	180.0	70.6
C_s	Max	0.0	180.0	26.2

^aRelative to the energy at the extrapolated C_2 minimum, namely -689.23602 au, the same value as that computed for $\phi = \phi' = 81.4^\circ$.

TABLE 2

4-31G Energies for H₂SO₄

Symmetry	ϕ (°)	ϕ' (°)	ΔE (kJ mol ⁻¹) ^a
<i>C</i> ₂	85.1 ^b	85.1	0.0
<i>C</i> _s	70.0 ^b	-70.0	11.5
<i>C</i> ₁	0.0	87.5	10.1
<i>C</i> _{2v}	0.0	0.0	23.8
<i>C</i> _{2v}	180.0	180.0	101.0

^aRelative to the computed energy at the extrapolated *C*₂ minimum, namely -696.90154 au for $\phi = \phi' = 85.1^\circ$.

^bValues found by minimization of energy with respect to ϕ .

is found to have a minimum energy for $\phi = -\phi' = 70.0^\circ$, somewhat smaller than the STO-3G value of 75.9° . The energy at the *C*_s minimum is 11.5 kJ mol⁻¹ higher than that at the *C*₂ minimum, an energy difference twice as great as that found in the STO-3G calculations, but nonetheless below that of either the structures with *C*_{2v} symmetry (Table 2). However, we have not directly demonstrated that the two *C*_{2v} structures are local maxima in ϕ, ϕ' space at the 4-31G level. Similarly, while the *C*_s structure is clearly a local minimum at the STO-3G level (Fig. 2), the 4-31G energy of 11.5 kJ mol⁻¹ is slightly above the 10.1 kJ mol⁻¹ value (Table 2) for a *C*₁ structure with $\phi = 0.0^\circ, \phi' = 87.5^\circ$, which is the approximate location of a saddle point at the STO-3G level. Thus the 4-31G results suggest that while the *C*_s structure has a minimum ($\phi = -\phi' = 70.0^\circ$) with respect to its totally symmetric (*a'*) displacement mode in ϕ, ϕ' space, it is either a shallow minimum or possibly a maximum with respect to its antisymmetric (*a''*) displacement mode.

TORSIONAL VIBRATIONS

There are two torsional modes of vibration for the H₂SO₄ molecule with *C*₂ symmetry, these corresponding to *a* and *b* irreducible representations. From the 4-31G level energies computed at the extrapolated minimum ($\phi = \phi' = 85.1^\circ$) and for structures slightly displaced along each symmetry coordinate, we obtain molecular force constants of 6.90×10^{-3} and 6.25×10^{-3} kJ mol⁻¹ deg⁻² for the *a* and *b* modes, respectively (these are second derivatives of the total electronic energy, including nuclear-nuclear repulsion). Using a projected O-H of 0.92 Å, these values become $4.45 \times 10^{+3}$ and $4.02 \times 10^{+3}$ erg cm⁻², respectively, which, when combined with a reduced mass taken as 1 amu, yield harmonic frequencies of 280 and 265 cm⁻¹ for the *a* and *b* modes, respectively. These modes may be described as radial and tangential displacements with respect to the *C*₂ symmetry minima (Fig. 2).

Since the surface in Fig. 2 is periodic in 2π for both ϕ and ϕ' , we consider the closure of this surface to form a torus, which is the appropriate representation given this periodicity. The closure may be visualized by joining the top and bottom horizontal edges to form a cylinder, after which the right- and left-hand circular ends are joined, completing the torus. The torsional motions and racemization of H_2SO_4 may then be viewed as motions of a mass point on the surface of the torus with a position-dependent potential energy. A similar portrayal [4] has been given for the ring deformations of cycloheptane.

DISCUSSION

The results of this study resemble those found for other $\text{AB}_2(\text{OR})_2$ or $\text{A}(\text{OR})_2$ systems, such as $\text{CH}_2(\text{OH})_2$ [5, 6], $\text{O}(\text{OH})_2$ [5], and $[\text{PO}_2(\text{OCH}_3)_2]$

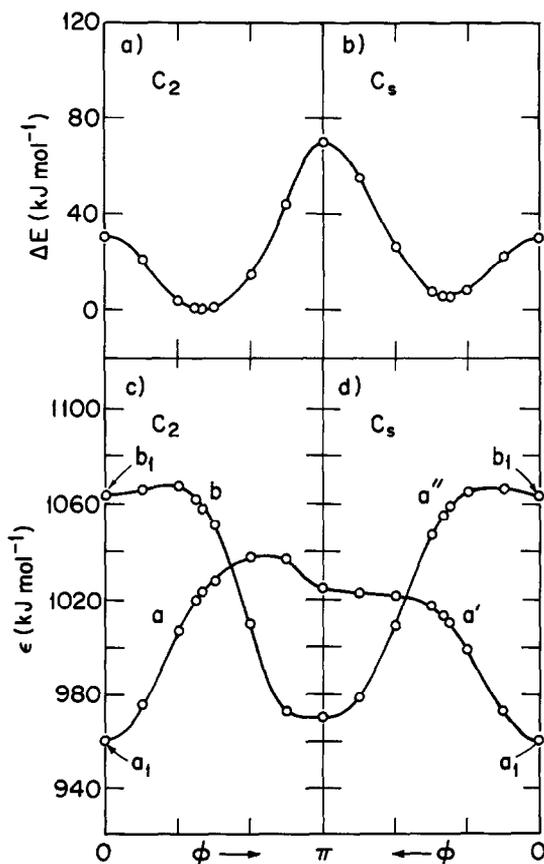


Fig. 3. Total energy vs. ϕ for the C_2 -symmetry isomer (a) and the C_s -symmetry isomer (b) at the STO-3G level, together with energies of the a and b LUMO's for the C_s -symmetry isomer (c) and energies of the a' and a'' LUMO's for the C_s -symmetry isomer (d). All energies are in kJ mol⁻¹.

TABLE 3

Energies of valence shell molecular orbitals for H₂SO₄

Number	Symmetry ^a	- ϵ (eV) ^b	Number	Symmetry ^a	- ϵ (eV) ^b
1	<i>a</i>	38.32	9	<i>a</i>	16.44
2	<i>b</i>	34.45	10	<i>b</i>	15.02
3	<i>a</i>	33.79	11	<i>a</i>	14.95
4	<i>b</i>	33.55	12	<i>b</i>	13.80
5	<i>a</i>	22.51	13	<i>a</i>	12.79
6	<i>b</i>	20.10	14	<i>b</i>	12.63
7	<i>a</i>	18.03	15	<i>a</i>	12.41
8	<i>b</i>	17.62	16	<i>b</i>	12.09 ^c

^aRepresentation of the group C₂.^bValues from 4-31G computation at C₂ minimum with $\phi = \phi' = 85.1^\circ$.^cHOMO; the *a* and *b* virtual LUMO energies are +3.37 and +4.15 eV, respectively.

[7], in that a structure of C₂ rather than C_{2v} symmetry corresponds to the equilibrium geometry. The instability of the C_{2v} forms of H₂SO₄ is emphasized in Fig. 3(a), which shows the variation of the total energy *E* (STO-3G level) with respect to ϕ for C₂ structures ($\phi = \phi'$). The symmetry C_{2v} obtains for $\phi = 0$ (ap, ap) and for $\phi = \pi$ (p, p). Correspondingly in Fig. 3(c) are shown the energies ϵ of the lowest virtual (empty) orbitals of *a* and *b* symmetries, these orbitals both being largely OH antibonding in character. A decrease in *E* is clearly associated with increases in ϵ , reflecting the collective increased stabilization of occupied orbitals of the same symmetries. Similar results obtain for the variation of *E* with respect to ϕ for C_s structures ($\phi = -\phi'$), Fig. 3(b), with the energies of the *a'* and *a''* virtual orbitals being shown in Fig. 3(d). The C₂, C_s and C_{2v} (ap, ap) structures may all be thought of as being derived from eclipsed SO₂(CH₃)₂ with OH replacing CH₃. The computed energy ordering of these structures then reflects the destabilizing effects of interactions between lone pairs on different oxygen atoms.

In Table 3 we present the energies of the valence shell molecular orbitals at the 4-31G level for the C₂ symmetry equilibrium geometry ($\phi = \phi' = 85.1^\circ$). The first four of these levels are predominantly O(2s) in character, while the *b* HOMO (no. 16) and the *a* level below it (no. 15) are predominantly O(2p) lone pairs on the O atoms without attached H atoms. Interestingly, the Mulliken charge distribution indicates little difference between the two types of O atoms, the computed charges being -0.81 and -0.80 for the O's with and without attached H atoms, respectively, while the S and H charges are +2.25 and +0.49, respectively.

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