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Equilibrium Structure of Sulfuric Acid

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The equilibrium structure of the more stable conformer of H_2SO_4 , of C_2 symmetry, has been calculated ab initio using the CCSD(T) method and taking into account the core correlation correction. The accuracy of this structure has been checked by comparing it to that of similar molecules and by estimating the effects of basis set enlargement and of diffuse functions. Furthermore, the quadratic, cubic, and quartic force fields have been calculated at the MP2 level of theory using a basis set of triple- ζ quality. The spectroscopic constants derived from the force field are in satisfactory agreement with the experimental ones. The resulting band origins are compared to literature infrared values, including those for overtone and combination bands. Normal modes of vibration are pictured. Using this force field, semiexperimental equilibrium rotational constants are determined which allows us to check the accuracy of the ab initio structure and to refine it using a mixed regression method.

1. Introduction

Sulfuric acid, H_2SO_4 , is an important industrial chemical. It is one of the primary components of acid rain and plays a key role in the formation of tropospheric aerosols.¹ However, it is very difficult to experimentally investigate in the gas phase because it is not very volatile, tends to form hydrates in humid air, and is furthermore in equilibrium with SO_3 and H_2O . Nevertheless, the microwave spectra of H_2SO_4 and of three of its isotopologues (^{34}S , d_1 , and d_2) were measured by Kuczkowski et al.² They observed only one conformation and established that its symmetry is C_2 . This form is drawn in Figure 1 where atom numbering is also indicated. These authors also tried to determine an experimental structure but, as the number of independent structural parameters (eight) is too large, they had to assume a value for the $r(\text{OH})$ bond length. The crystal structure of pure H_2SO_4 was determined from X-ray data,³ and the position of the protons was precisely determined by neutron diffraction.⁴ However, the crystal structure is not directly comparable to the gas-phase structure, particularly because of the existence of strong intermolecular hydrogen bonds in the crystal.

Vibrational spectra of the gas phase have also been reported.^{5–8} There are also matrix isolation data.^{9–11} The ab initio structure of H_2SO_4 has been repeatedly calculated. Particularly, Givan et al.⁹ calculated the structure and a harmonic force field using the second-order Møller–Plesset perturbation theory (MP2)¹² with the 6-311++G(2d,2p) basis set. Later, Al Natsheh et al.¹³ carried out density functional theory (DFT) calculations with the PW91 functional of Perdew and Wang¹⁴ and TZP basis set, and compared their results with those of earlier studies. Havey et al.¹⁵ used the 6-311++G(2d,2p) basis set with another DFT

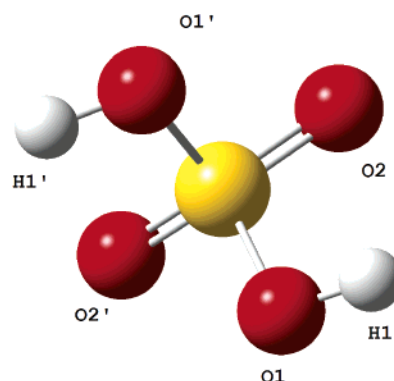


Figure 1. The more stable conformer of H_2SO_4 (C_2 symmetry).

method, the B3LYP one which consists of the Becke's three-parameter hybrid exchange functional¹⁶ and the Lee–Yang–Parr correlation functional.¹⁷ Hintze et al.⁸ performed ab initio calculations using three different methods to predict the structure and the infrared spectrum: Hartree–Fock (HF) self-consistent field, B3LYP, and quadratic configuration interaction including singles and doubles (QCISD) theory with the 6-311++G(2d,2p) basis set. Finally, Miller et al.¹⁸ computed the vibrational frequencies from ab initio MP2/TZP potential points using the correlation corrected vibrational self-consistent field (CC-VSCF) method. However, the level of these calculations did not allow them to obtain an accurate equilibrium structure. Finally, it is worth noting that the structural, spectroscopic, and thermochemical properties of H_2SO_4 have been recently reviewed.¹⁹

The principal aim of the present paper is to accurately determine the equilibrium structure of H_2SO_4 . Two different techniques are employed: ab initio geometry optimization and semiexperimental structure determination. The paper is organized as follows. Section 2 describes the techniques used for the determination of equilibrium structures. Section 3 focuses on the determination of the most stable conformer of H_2SO_4 . Section 4 is devoted to the ab initio structure, and section 5

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details the semiexperimental structure and also highlights the vibrational spectroscopic constants.

2. Methods of ab Initio Structure Determination

Most correlated-level ab initio computations of this study have been carried out at two levels of electronic structure theory, second-order Møller–Plesset perturbation theory (MP2)¹² and the coupled-cluster (CC) method with single and double excitations (CCSD)²⁰ augmented by a perturbational estimate of the effects of the connected triple excitations [CCSD(T)].²¹

Dunning's correlation-consistent polarized n -tuple ζ basis sets cc-pVnZ²² with $n \in \{D, T, Q\}$ were employed extensively. For sulfur, they were replaced by the cc-pV($n+d$)Z basis sets where an extra hard d function was added to take into account innershell polarization effects in the case of second-row atoms.²³ Throughout this paper these basis sets are abbreviated as V($n+d$)Z. Versions of VnZ sets augmented with diffuse functions (aug-cc-pV($n+d$)Z, AV($n+d$)Z in short)²⁴ were also employed. To improve computed equilibrium structural parameters through the inclusion of core correlation effects,²⁵ the correlation-consistent polarized weighted core-valence n -tuple ζ (wCVnZ)^{26,27} were used. We also used mixed basis sets composed of, for example, VTZ on all non-hydrogen atoms and VDZ on H, denoted as V(T,D)Z.

The CCSD(T) computations were performed with the MOLPRO^{28–30} electronic structure program package, while the lower-level B3LYP and MP2 computations utilized the Gaussian 03 (G03) program.³¹ Most calculations were performed on the HP-XC 4000 cluster of the ULB/VUB computing center.

The frozen-core approximation (hereafter denoted as fc), that is, keeping the 1s orbitals of the first-row atoms and the 1s, 2s, and 2p orbitals of S doubly occupied, was used extensively to perform correlated-level calculations. Some geometry optimizations were also carried out by correlating all electrons (hereafter denoted as ae).

The anharmonic force field has been evaluated using G03. The harmonic part has been obtained using analytic second derivatives of the energy, and the corresponding cubic and quartic force fields have been determined in a normal-coordinate representation via numerical differentiation of the analytically evaluated quadratic force constants, as implemented in G03. This procedure was repeated for each isotopologue.

3. Stable Conformers of H₂SO₄

There is some controversy concerning the number of stable conformations of H₂SO₄. Kuczkowski et al.² could assign the spectrum of only one conformer but they could not rule out the presence of other forms. Givan et al.⁹ calculated the potential surface at the MP2/6-311++G(2d,2p) level of theory and found only one stable conformation. This result was confirmed by a recent B3LYP/VTZ calculation in which a relaxed potential scan was performed.¹⁹ However, Al Natsheh et al.¹³ found two stable forms at the PW91/TZP level of calculation. Their result was confirmed by Havey et al.¹⁵ who obtained a potential-energy surface using the MP2/6-31+G** method. They also confirmed the existence of two minimum energy geometries of symmetry C_2 and C_s , the C_s form being 6.1 kJ/mol above the C_2 one. They also found some evidence of the existence of the second conformer in the infrared spectrum, one band observed at 3620.2 cm^{−1} being in good agreement with the calculated value of the symmetric stretch of the C_s form. This conclusion was further confirmed by Hintze et al.⁵ who reanalyzed the infrared spectra of H₂SO₄, HDSO₄, and D₂SO₄ under higher spectral resolution.

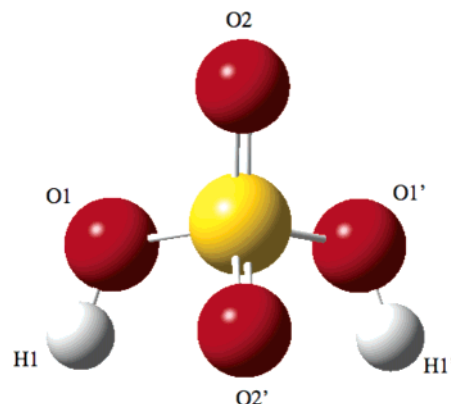


Figure 2. The second conformer of H₂SO₄ (C_s symmetry).

TABLE 1: SO Bond Lengths (Å) in Some Sulfur Derivatives

	SO	SO ₂	SO ₃	SO ₂ F ₂	HOSH
r_e	1.4811 ^a	1.4308 ^b	1.4173 ^c	1.4013 ^d	1.6616(1) ^e
CCSD(T)(fc)/ V(T+d)Z	1.4931	1.4469	1.4261	1.4076	1.6720
offset ^f	−0.0120	−0.0161	−0.0088	−0.0063	−0.0104
MP2 core	−0.0034	−0.0036	−0.0035	−0.0034	−0.0034
correction					
CCSD(T) core	−0.0029	−0.0028	−0.0028		−0.0035
correction					

^a Reference 55. ^b Reference 56. ^c Reference 36. ^d Reference 37. ^e Reference 38. ^f Offset = $r_e - r[\text{CCSD(T)(fc)/V(T+d)Z}]$.

Calculations at the B3LYP/6-311+G(2d,2p) and MP2/V(T+d)Z levels of theory confirm the existence of two stable conformers, the C_2 form being more stable by 5.5 kJ/mol at the MP2/V(T+d)Z level and by 5.3 kJ/mol at the MP2/V(Q+d)Z level. Adding diffuse functions (MP2/AV(Q+d)Z level), the difference decreases to 3.28 kJ/mol. It was checked that this conformer has no imaginary vibrational frequency, that is, it is a true minimum. Note that the top of the barrier between the two conformers lies 14.8 kJ/mol above the C_2 conformer at the MP2/VTZ level of theory. It is interesting to note that the C_s conformer has a larger dipole moment and could therefore be observable by microwave spectroscopy even though it is not the more stable one. For the C_s conformer, the results at the MP2/AV(Q+d)Z level of theory are (in D) $\mu_b = 3.59$ and $\mu_c = 1.38$, to be compared with $\mu_c = \mu_t = 3.09$ D for the C_2 conformer (the experimental value is 2.73 D²). This second form is drawn in Figure 2 and is characterized by dihedral angles $\tau(\text{H}_1\text{—O}_1\text{—S—O}_1') = -\tau(\text{H}_1'\text{—O}_1'\text{—S—O}_1) = 97.6$ degrees, while both angles are equal to -84.3 degrees in the C_2 conformer and to 2.0 and -113.4 degrees, respectively, at the top of the barrier. The geometries of the C_s conformer and of the maximum of the barrier are given in Table S1 of the Supporting Information.

4. Ab Initio Structure of H₂SO₄

4.1. Offset Method. The structure of the C_2 form (the more stable one) was first calculated at the CCSD(T)(fc)/V(T+d)Z level of theory. The T_1 diagnostic value,³² used to estimate the suitability of the single-reference CCSD(T) method for properly describing electron correlation effects, is 0.0147. It is significantly smaller than the usual cutoff value, 0.020, indicating dominant single-reference character. This suggests that non-dynamical electron correlation is small and that the CCSD(T) results are likely to be reliable. However, at this level of calculation, the convergence of the basis set is not yet achieved. Furthermore, the innershell correlation effects are neglected. The

TABLE 2: Ab Initio Structure of H₂SO₄ (Distances in Å and Angles in deg)

method internal coordinate ^a	CCSD(T)			MP2							<i>r_c</i> (1)	<i>r_c</i> (2)	<i>r_c</i> (3)	best
	V(D+d)Z	V(T+d)Z	wCVTZ	V(T+d)Z	V(Q+d)Z	AV(Q+d)Z	wCVQZ	wCVQZ	wCVTZ					
							(fc)	(ae)						
1 <i>r</i> (S–O ₁)	1.6119	1.5854	1.5775	1.5861	1.5813	1.5819	1.5801	1.576	1.5777	1.5750	1.5765	1.5758	1.5758	
2 ∠O ₁ –S–O ₁ '	101.44	102.05	102.112	102.019	102.173	102.198	102.181	102.196	102.103	102.20	102.217	102.206	102.206	
3 <i>r</i> (O–H)	0.9665	0.9662	0.9693	0.968	0.9666	0.9673	0.9666	0.9658	0.9755	0.9636	0.9640	0.9596	0.9640	
4 ∠HOS	106.75	107.87	108.270	107.710	108.240	108.375	108.298	108.403	108.133	108.40	108.509	108.541	108.509	
5 τ(HO ₁ SO ₁)	–83.20	–84.28	–83.573	–83.743	–84.282	–84.206	–84.164	–84.304	–82.625	–84.82	–84.958	–85.251	–84.958	
6 <i>r</i> (S=O ₂)	1.4301	1.4191	1.4129	1.4201	1.4173	1.4184	1.4153	1.4121	1.4139	1.4103	1.4131	1.4111	1.4111	
7 ∠O ₁ –S=O ₂ '	105.34	105.66	105.664	105.518	105.529	105.494	105.522	105.553	105.476	105.67	105.705	105.741	105.741	
8 τ(O ₂ –S– O ₁ –O ₁)	–112.95	–113.44	–113.549	–113.488	–113.592	–113.648	–113.604	–113.614	–113.641	–113.54	–113.555	–113.522	–113.522	
9 ∠O ₂ –S=O ₂ '	125.411	124.249	124.073	124.34	124.163	124.117	124.153	124.100	124.153	124.077	124.012	124.021	124.021	
10 τ(O ₂ –mO ₂ – mO ₁ –O ₁) ^b	87.853	87.986	87.936	87.817	87.801	87.740	87.789	87.815	87.703	87.971	87.997	88.049	88.048	

^a The coordinates 1 through 8 form a complete set of independent internal coordinates defining the structure of the C₂-symmetric H₂SO₄; an alternative, more easily visualizable set is defined by coordinates 1 through 6 plus 9 and 10. The former set corresponds to the output of the quantum-chemical calculations. ^b mO₁ = mid(O₁,O₁'), mO₂ = mid(O₂,O₂).

TABLE 3: Effects of the Basis Size on the Structural Parameters (Distances in Å and Angles in deg)

molecule	parameter	A–N(T) ^a	A–N(Q) ^b	5–Q ^c
SO	<i>r</i> (SO)	0.0016	0.0003	–0.0020
SO ₂		0.0037	0.0013	–0.0017
SO ₃		0.0030	0.0009	–0.0015
HOSH		0.0033	0.0011	–0.0017
HNSO		0.0042	0.0012	–0.0014
HOSH	<i>r</i> (OH)	0.0019	0.0009	0.0002
BF ₂ OH		0.0013	0.0007	0.0000
BH ₂ OH		0.0011	0.0006	–0.0001
BHFOH		0.0012	0.0006	–0.0001
trans-HONO		0.0026	0.0003	0.0003
trans-HCOOH		0.0014	0.0007	0.0000
cis-HCOOH		0.0018	0.0008	0.0001
BF ₂ OH	∠BOH	0.35	0.08	0.12
HOSH	∠HOS	0.70	0.24	0.22
HNSO	∠NSO	–0.39	–0.16	–0.05
BH ₂ OH	∠BOH	0.21	0.09	0.10
trans-HCOOH	∠HOC	0.44	0.17	0.14
cis-HCOOH	∠HOC	0.53	0.19	0.15
trans-HONO	∠HON	0.44	0.01	0.18
SO ₂	∠OSO	–0.28	–0.10	–0.03
HOSH	τ(HOSH)	0.47	0.20	0.13

^a AV(T+d)Z – V(T+d)Z. ^b AV(Q+d)Z – V(Q+d)Z. ^c V(5+d)Z – V(Q+d)Z.

remaining errors are generally mainly systematic and correction factors, or “offsets”, may be estimated by comparing with results on molecules whose structure is accurately known and whose bonding is similar. For this reason, we also calculated the structures of SO₃ and HOSH at the CCSD(T)(fc)/V(T+d)Z level of theory. These results are listed in Table 1. As far as the S=O bond length is concerned, the bonding in H₂SO₄ and SO₃ are similar. The equilibrium structure of SO₃ was already determined theoretically,³³ the value being *r_e*(SO) = 1.41764 Å. Furthermore, the experimental equilibrium structure was determined independently for three isotopologues: 1.417340(1) Å for ³²S¹⁶O₃,³⁴ 1.417347(7) Å for ³⁴S¹⁶O₃,³⁵ and 1.417339(3) Å for ³⁴S¹⁸O₃.³⁶ The agreement between these different values is excellent. The CCSD(T)(fc)/V(T+d)Z S=O bond length in SO₃ being 1.4261 Å, one can estimate the related offset to Δ*r* = –0.0088 Å. It is also possible to determine an offset from SO₂F₂, from the equilibrium value, *r_e*(S=O) = 1.401(3) Å³⁷ and the CCSD(T)(fc)/V(T+d)Z value 1.4076 Å, to –0.0066 Å. This latter correction is less precise than but fully compatible with the former one.

In HOSH, sulfur is divalent, whereas it is hexavalent in H₂SO₄. Although this is not ideal for the prediction of an

TABLE 4: Experimental and Computed Quartic Centrifugal Distortion Constants for H₂SO₄ (in kHz)

	exptl ^a	calcd ^b	exptl – calcd
τ _{aaaa}	–8.98(64)	–8.98	0.00
τ _{bbbb}	–6.78(47)	–6.59	–0.19
τ _{cccc}	–12.8(79)	–6.68	–6.12
τ ₁	–8.33(75)	–6.68	–0.70

^a Reference 2. ^b From the ab initio force field calculated at the MP2/6-311G(2d,p), see text.

accurate offset for the S–O bond length, HOSH is the only molecule available for comparison, because it was not possible to find another molecule with a single S–O bond whose structure is accurately known. The equilibrium structure of HOSH was calculated at the CCSD(T)(ae)/CVQZ level of theory by Baum et al.³⁸ These authors also determined an accurate semiexperimental structure from the rotational constants of four isotopologues. The equilibrium value is *r_e*(SO) = 1.6616(1) Å and the CCSD(T)(fc)/V(T+d)Z value is 1.6720 Å giving an offset of –0.0010 Å.

The same procedure can be applied to the OH bond, this time using equilibrium structures recently determined.³⁹ The resulting offset for the OH bond is –0.0026 Å with a standard deviation of 0.0008 Å.

The CCSD(T)(fc)/V(T+d)Z structure corrected with these offsets is given in Table 2 where it is called *r_c*(1).

4.2. Second Method. Another way to improve the CCSD(T)(fc)/V(T+d)Z structure is to calculate the structural effects of further basis-set improvement at a lower level of theory. For this goal, the MP2 method is known to give satisfactory results.^{40–42} To estimate the core and core-valence correlation effects, the wCVQZ basis set was employed with the MP2 method. The MP2/wCVQZ core correction is indeed accurate for bond lengths involving first-row atoms⁴² but slightly overestimates the correction when a second-row atom is involved in the bond.⁴³ However, this overestimation is rather small in the particular case of the SO bond. Calculations on SO₂, SO₃, and HOSH indicate that the error is smaller than 0.0010 Å, see Table 1 (it is negligible for the single S–O bond and amounts to 0.0008 Å for the S=O bond). The structure labeled *r_c*(2) in Table 2 is calculated with the following formula:

$$r_c(2) = \text{CCSD(T)(fc)/V(T+d)Z} + \frac{\text{MP2(fc)/V(Q+d)Z} - \text{MP2(fc)/V(T+d)Z} + \text{MP2(ae)/wCVQZ} - \text{MP2(fc)/wCVQZ}}{1}$$

TABLE 5: Calculated Harmonic Wavenumbers ω_i and Anharmonic Vibrational Band Centers ν_i for H₂SO₄ (in cm⁻¹)[#]

sym	mode	type	gas	matrix Ar ^e	matrix O ₂ ^f	matrix Ne ^g	liquid ^a	cryst ^a	present ω_i	present ν_i	obsd – calcd
A	1	OH sym s.	3609.2 ^a	3563	3591.6		2970	2970	3788.22	3610.0	0.8
	2	S=O ₂ sym s.	1222.2 ^b	1216.1	1218.6	1222.0		1240	1229.3	1211.5	11.0
	3	SOH sym b.	1138 ^c	1135.9		1134.2	1137	1170	1175.4	1142.5	4.5
	4	S(OH) ₂ sym s.	834.1 ^a	831.4	842.3	835.2	910	907	815.0	796.4	37.7
	5	S=O ₂ b.	550.5 ^a	548.1	549.4/545.8		563	548/573	541.1	535.6	14.9
	6	O–S=O b.	400 ^d	421.7			422	412	440.6	404.5	4.5
	7	O–S=O twist	380/390 ^d	378.5			392	386	373.1	353.6	26.4/36.4
	8	OH sym torsion		224			332		257.6	232.7	
B	9	OH asym s.	3609.6 ^b	3566.7	3591.6	3603.3	2450	2450	3783.0	3605.2	4.4
	10	S=O ₂ asym s.	1465.2 ^b	1452.4	1452.0	1461.2	1368	1365	1487.2	1462.1	3.1
	11	SOH asym b.	1157.1 ^a	1156.9		1156.4	1195	1170	1189.0	1161.2	4.1
	12	S(OH) ₂ asym s.	891.4 ^a	881.7	884.6	887.3	973	967	871.4	850.1	41.3
	13	O–S=O rock	568 ^c	558.0	578/560			623	543.9	536.9	31.1
	14	S=O ₂ wagging		506			422		491.4	483.8	
	15	OH asym torsion	265 ^d	287.7			675	650	333.3	290.9	25.7
Other Bands											
	mode		gas						present ν_i		obsd – calcd
	3 ²		2278 ^b						2275		3
	2 + 10		2676.8 ^b						2665		12
	9 – 15		3328.5 ^b						3314		15
	9 – 8		3393.9 ^b						3372		22
	8 + 9		3825.1 ^b						3838		13
	9 + 15		3890.3 ^b						3896		6
	3 + 9		4736 ^b						4737		1
	1 + 11		4760.8 ^b						4761		0
	9 ²		7060.7 ^b						7092		31
	9 ² + 3/11 ^h		8163 ^a								
	9 ³ ^h		10350.3 ^a								

[#] Normal mode types (s.= stretching; b. = bending) are in agreement with Figure 3. Combination and overtone band assignments are based on optimal energy match with predictions from the present calculations. All experimental values correspond to band origins (ν_i). ^a Reference 8; information on band contours and relative intensities are provided. ^b Reference 5. ^c Reference 6; information on band contours is provided. ^d Reference 7. ^e Reference 9; relative intensities are provided. ^f Reference 10; relative intensities are provided. ^g Reference 11. ^h Preference was given to combination/overtone involving mode 9 rather than mode 1 because mode 9 is predicted to be the predominant contribution in lower energy bands. No calculated value is provided because it is difficult to reliably access the role of the Darling–Dennison anharmonic resonance for such high excitation ranges. Relevant information is also available in the following: Giguère, P. A.; Savoie, R. *Can. J. Chem.* **1960**, *38*, 2467. Walrafen, G. E.; Dodd, D. M. *Trans. Faraday Soc.* **1961**, *57*, 1286. Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1962**, *40*, 644. Stopperka, K.; Kilz, F. Z. *Anorg. Allg. Chem.* **1969**, *370*, 49; *Anorg. Allg. Chem.* **1969**, *59*. Majkowski, R. F.; Blint, R. J.; Hill, J. C. *Appl. Opt.* **1978**, *17*, 975. Eng, R. S.; Petagana, G.; Nill, K. W. *Appl. Opt.* **1978**, *11*, 1723. Shingaya, Y.; Ito, M. *Chem. Phys. Lett.* **1996**, *256*, 438–444 (but not included in the table). Numbers from a private communication (by Feierabend, K. J.; Havey, D. K.; Hintze, P. E.; and Vaida, V.) are cited by Miller, Y.; Cahaban, G. M.; Gerber, R. B. *J. Phys. Chem. A* **2005**, *109*, 6566–6574.

The agreement between $r_e(2)$ and $r_e(1)$ is pleasing, the only significant difference being for the S=O bond, for which $r_e(1) = 1.4103$ and $r_e(2) = 1.4131$ Å. This is somewhat surprising because, from the preceding discussion of the core correction, we would expect $r_e(2) < r_e(1)$. This probably indicates that the offset derived from SO₃ is too large. This discrepancy does not arise from the neglect of the diffuse functions. Indeed, although their effect is likely to be important, diffuse functions (at the CCSD(T)/AV(T+d)Z level) increase the S=O bond length by 0.0030 Å for SO₃, their neglect similarly affects the results in H₂SO₄ and thus cancels out in the present calculations.

4.3. Third Method. A third way to determine the ab initio equilibrium structure is to first calculate it at the CCSD(T)(ae)/wCVTZ level. To save computer time, the 1s electrons of sulfur were kept frozen because they lie too deep to interact appreciably with the valence shell. Furthermore, the small VDZ basis set was used for the H atoms. Then, the correction due to basis set enlargement was calculated at the MP2 level. The structure, called $r_e(3)$, is calculated using the following formula:

$$r_e(3) = \text{CCSD(T)(ae)/wCV(T,D)Z} + \text{MP2(ae)/wCVQZ} - \text{MP2(ae)wCV(T,D)Z} \quad (2)$$

This structure is expected to be accurate except perhaps for the

OH bond length which is known to be more accurately determined by the previous two methods. This third structure is in very good agreement with the previous ones, except, as expected, for the OH bond. It is interesting to note that for the S=O bond, one has $r_e(1) < r_e(3) < r_e(2)$. The differences are rather small (< 0.003 Å) and, in the absence of decisive criteria, we selected the intermediate value, $r_e(3)$, as the best estimate.

4.4. Accuracy of the Equilibrium Structure. There are mainly two factors which may affect the equilibrium structure: the missing contribution of the diffuse functions and the fact that the basis set is not yet fully converged at the quadruple- ζ level. As already pointed out, the effect of diffuse functions are indeed not negligible at the triple- ζ level as can be seen in Tables 2 and 3. However, it is well established that their effect rapidly decreases as the size of the basis set increases, see for instance Table 3. This is again confirmed for H₂SO₄ in Table 2, even for the dihedral angles for which their effect is smaller than 0.1° at the AV(Q+d)Z level. Table 3 also addresses the convergence problem. The results indeed confirm that the basis set is not fully converged at the quadruple- ζ level. But it is interesting to note that the effect of basis set improvement (VQZ \rightarrow V5Z) is small for the bond lengths, and furthermore in the opposite direction to (and of the same order of magnitude as)

the effect $VQZ \rightarrow AVQZ$. Although the $V5Z$ basis set is too large to be used for H_2SO_4 , it may therefore be safely concluded that the structure obtained at the quadruple- ζ level is accurate for the bond lengths, the accuracy being about 0.002 \AA . As far as bond angles are concerned, the situation is less favorable because now both corrections have the same sign. However, inspection of Table 3 shows that the accuracy remains good, of the order of $0.2\text{--}0.3^\circ$. The case of dihedral angles is different because much less energy is required to distort them than bond angles. As an example, the distortion of a $\angle(CCC)$ bond angle by 10° requires 10.3 kJ/mol , compared to 0.9 kJ/mol for the torsional distortion of the $CCCC$ chain by 10° .⁴⁴ In consequence, the dihedral angle is determined with an accuracy which is about 1 order of magnitude lower than that of the bond angles. One should finally note that, for the dihedral angles of H_2SO_4 , the contributions of the diffuse functions and of the core correlation are small. This situation is different from other case studies such as H_2O_2 , for which the core correlation increases the torsional angle by 2.4° .⁴⁵

5. Semiexperimental Structure

In this section, the theoretical rotation–vibration interaction constants (α -constants) deduced from an ab initio anharmonic force field are combined with the known experimental ground-state rotational constants to yield the semiexperimental equilibrium–rotational constants. These latter constants are input in a least-squares fit program to calculate the equilibrium structure.

5.1. Anharmonic Force Field. We checked that the MP2/6-311G(2d,p) level of theory was good enough to predict a reliable force field. Particularly, this was confirmed by a calculation made with the significantly larger basis set 6-311+G(2df,2p) for the parent isotopologue. The experimental and calculated quartic centrifugal distortion constants are reported in Table 4. Although the experimental values are not precise, the agreement is satisfactory. Table 5 lists the computed harmonic wavenumbers ω_i and vibrational band centers ν_i for all normal modes of vibrations. These are pictured in Figure 3, which illustrates and globally confirms the vibrational assignments previously made in the literature^{5,8} for the different modes (see Table 5). It is worth noting, however, that significant mechanical coupling occurs in some of the normal coordinates. In particular, let us point out the admixture of (a)symmetric SOH bending with (a)symmetric $S=O_2$ stretching in (ν_{10}) ν_2 , and the mixing of symmetric $S=O_2$ bending with OH symmetric torsion and $O-S=O$ twist in ν_6 and ν_7 , respectively. The full set of anharmonic constants x_{ij} was also computed. The values are given in Table 6. The comparison of the computed band centers with the experimental gas-phase values from the literature is again satisfactory. We selected the most recent experimental values to appear in Table 5. Additional information on band contours and/or relative intensities can be found in refs 6 and 8. We included in Table 5, for completeness, the values of the fundamental bands as reported in the literature from other phases and environments. All published overtone and combination band centers are also listed in Table 5. The reported assignments were selected from comparison with predicted band-center energies calculated using the present constants. These assignments, thus only based on energy match, confirm and sometimes refine those proposed in the literature. The very good agreement for all fundamental, combination, and overtone bands supports the quality of the present force field. It is interesting to point out that the present predictions show better agreement with the experimental values than the calculated CC-VSCF band centers of Miller et al.¹⁸ Finally, it has to be noted

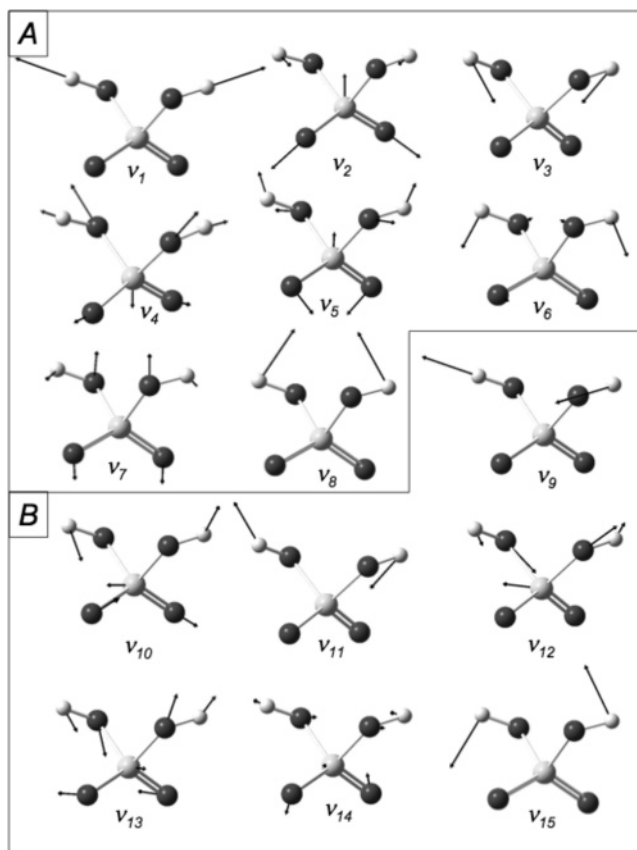


Figure 3. Normal modes of the C_2 conformer of sulfuric acid, calculated at the MP2/6-311G(2d,p) level. Atomic displacements are scaled by a factor of 1.5 for all modes.

that the largest deviations are observed for ν_4 , ν_7 , ν_{12} , and ν_{13} . The use of the force field calculated at the MP2/6-311+G(2df,2p) only slightly reduces the deviations. The calculated values from this second force field are (in cm^{-1}) $\nu_4 = 813.1$, $\nu_7 = 373.3$, $\nu_{12} = 862.2$, and $\nu_{13} = 559.9$. The slight improvement (13 to 23 cm^{-1}) is mainly due to a better harmonic force field.

5.2. Semiexperimental Equilibrium Structure. The ground state, semiexperimental equilibrium, and ab initio equilibrium–rotational constants are given in Table 7. It is obvious that the ab initio rotational constants are much closer to the semiexperimental than to the ground-state values. This is again an indication of the quality of the force field and of its compatibility with the ab initio structure. The agreement is optimal for the B rotational constants where the largest deviation is only 0.57 MHz . It is, however, less satisfactory for the C constants which show differences up to 9 MHz , that is, 0.18% of the rotational constant only, but 50% of $(C_e - C_0)$. To check if this disagreement could be attributed to the neglect of the magnetic correction,⁴⁶ we calculated this correction at the B3LYP/AVTZ level of theory using gauge-including atomic orbitals (GIAOs),⁴⁷ in the absence of experimental values for the rotational g tensor. The B3LYP/AVDZ results given in parentheses indicate that convergence is achieved, providing reasonable confidence into the calculated results. These are $g_{aa} = -0.051$ (-0.051); $g_{bb} = -0.0045$ (-0.043) and $g_{cc} = -0.045$ (-0.044). This amounts to an increase of the rotational constants of 0.12 MHz , which is negligible. The disagreement for the C constants is therefore due either to a defect of the force field or to the inaccuracy of the ab initio structure. This point will be discussed below.

It is not possible to input the semiexperimental equilibrium–rotational constants just determined in a least-squares fit program to calculate a meaningful equilibrium structure because the

TABLE 6: Anharmonicity Constants x_{ij} (cm⁻¹) of H₂SO₄ Calculated at the MP2/6-311G(2d,p) Level of Theory

i, j	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	-40.89														
2	-163.46	-40.81													
3	-2.04	-2.05	-3.67												
4	-1.15	-1.13	-8.44	-2.78											
5	-10.12	-10.18	-3.34	-1.87	-4.17										
6	-10.77	-10.80	-4.59	-1.31	-17.83	-4.85									
7	-0.98	-0.97	0.09	-1.62	-2.79	-8.74	-2.61								
8	-0.91	-0.90	-0.93	-1.06	0.68	-1.52	-8.45	-2.20							
9	-0.42	-0.41	-2.67	-1.60	0.40	0.57	-2.13	-2.11	-0.15						
10	-0.38	-0.34	-2.49	-1.64	0.94	1.81	-2.23	-1.53	-0.12	-0.17					
11	-1.11	-1.10	-1.27	-1.21	0.17	0.95	-2.49	-2.88	0.09	-0.35	-0.01				
12	-0.13	0.00	-1.90	-1.17	-0.71	2.07	-1.25	-1.79	-0.80	-1.41	-1.48	-3.33			
13	0.14	0.24	-1.16	-1.75	0.21	0.24	-1.43	-1.21	0.38	-0.34	-0.94	-6.82	-1.60		
14	-1.42	-1.48	-3.56	0.42	5.22	-2.55	2.87	-4.56	-2.77	-1.64	-1.77	-19.84	-5.52	-8.20	
15	-0.06	0.10	-1.15	-0.88	0.28	6.22	-2.15	-1.15	-1.79	-0.76	-1.64	-23.73	-14.76	-15.47	1.81

TABLE 7: Ground State (0), Semiexperimental Equilibrium (se) and ab Initio Equilibrium (e)-Rotational Constants (MHz) for Sulfuric Acid

	H ₂ SO ₄	H ₂ ³⁴ SO ₄	HDSO ₄	D ₂ SO ₄
A_0	5160.61	5159.04	5122.31	5042.42
B_0	5024.53	5023.04	4831.92	4651.80
C_0	4881.02	4881.20	4725.75	4613.25
$A_e - A_0$	25.91	25.63	22.75	20.09
$B_e - B_0$	54.54	54.29	48.87	43.79
$C_e - C_0$	11.77	11.60	15.63	18.81
A_{se}^a	5186.66	5184.82	5145.20	5062.65
B_{se}^a	5079.19	5077.46	4880.90	4695.70
C_{se}^a	4892.91	4892.92	4741.49	4632.17
A_e	5184.70	5182.87	5142.52	5058.19
B_e	5078.86	5077.11	4880.33	4695.26
C_e	4883.75	4883.75	4735.05	4629.08
$A_{se} - A_e$	1.96	1.95	2.68	4.46
$B_{se} - B_e$	0.33	0.34	0.57	0.43
$C_{se} - C_e$	9.16	9.16	6.44	3.09
$A_{se} - A_{calcd}^b$	0.09	0.01	-0.01	-0.11
$B_{se} - B_{calcd}^b$	0.07	0.03	-0.28	0.19
$C_{se} - C_{calcd}^b$	0.02	0.02	0.33	-0.36

^a Magnetic correction taken into account, see text. ^b Residual of the least-squares fit, values calculated using parameters of last column of Table 8.

number of isotopologues (i.e., the number of data) is too small. This problem is made worse by the fact that the sulfur atom is close to the center of mass (about 0.13 Å). Hence, the rotational constants of H₂³⁴SO₄ practically do not bring any new information. Furthermore, H₂SO₄ is a heavy molecule with large moments of inertia. Thus, the effect of an isotopic substitution on these moments of inertia is small and impedes the determination of an accurate structure.⁴⁸ To overcome these difficulties, we used in the least-squares fit the ab initio parameters (Table 2, “best”) as predicate observations⁴⁹ in addition to the semiexperimental equilibrium rotational constants. This “mixed regression” technique has two advantages:⁵⁰ (i) using data of different origins improves the conditioning and makes the errors more random, and (ii) it allows the compatibility of the data to be checked.

A weighting procedure was used, based on accuracies which were assumed as follows: 0.002 Å for the bond lengths, 0.2° for the ∠OSO bond angles, 0.5° for the ∠HSO bond angle, 0.5° for the torsional angles except $\tau(\text{H}_1\text{O}_1\text{S}-\text{O}_1)$ for which 1° was chosen. The accuracy of the semiexperimental equilibrium-rotational constants was assumed to be 0.4 MHz. The resulting structure is given in Table 8 where it is compared with the ab initio structure and the previous empirical structure of Kuczkowski et al.² The largest, still acceptable, residual is found for the C rotational constant of D₂SO₄: -0.36 MHz (see Table 7). A fit where all C rotational constants are underweighted

TABLE 8: Structures of H₂SO₄ (Distances in Å and Angles in deg)

internal coordinates	ab initio ^a	semi-experimental ^b	empirical ^c
$r(\text{S}-\text{O})$	1.5758	1.5751(10)	1.574(10)
$\angle(\text{O}_1-\text{S}-\text{O}_{1'})$	102.206	102.27(9)	101.3(10)
$r(\text{O}-\text{H})$	0.9640	0.9645(13)	0.970(10)
$\angle(\text{H}-\text{O}-\text{S})$	108.509	108.58(9)	108.5(15)
$\tau(\text{H}_1-\text{O}_1-\text{S}-\text{O}_{1'})$	-84.958	-86.66(12)	-89.1(10)
$r(\text{S}=\text{O})$	1.4111	1.4099(9)	1.422(10)
$\angle(\text{O}_1-\text{S}=\text{O}_{2'})$	105.741	105.722(23)	106.4(5)
$\tau(\text{O}_2=\text{S}-\text{O}_1-\text{O}_{1'})$	-113.522	-113.844(73)	-113.7(10)
$\angle(\text{O}_2=\text{S}=\text{O}_{2'})$	124.020	123.54(13)	123.3(10)
$\tau(\text{O}_{2'}-\text{mO}_2-\text{mO}_1-\text{O}_{1'})^d$	88.049	87.84(2)	88.4(1)

^a This work, see last column of Table 2. ^b This work, mixed regression, see text. ^c r_0 , r_s structure; ref 2. ^d $\text{mO}_1 = \text{mid}(\text{O}_1, \text{O}_{1'})$, $\text{mO}_2 = \text{mid}(\text{O}_2, \text{O}_{2'})$.

TABLE 9: Cartesian Principal Axis Coordinates (PAS) of H₂SO₄ (corresponding to Columns “ab Initio” of Table 8 and “best” of Table 2^a)

atoms	a [Å]	b [Å]	c [Å]
S	0.00000	0.00000	-0.13245
O ₁	1.04546	-0.64111	0.85701
O _{1'}	-1.04546	0.64111	0.85701
H ₁	1.68150	0.03700	1.11169
H _{1'}	-1.68150	-0.03700	1.11169
O ₂	0.61483	1.08377	-0.79468
O _{2'}	-0.61483	-1.08377	-0.79468

^a This table uniquely defines the position of that partner in each of the three pairs of symmetry-equivalent atoms to which a prime has been affixed. Disregarding a common sign change of components a and c of all atoms, this table can be directly compared with Table 7 of ref 2.

(10 MHz accuracy instead of 0.4 MHz) shows that all C constants have similar residuals: 1.7–1.9 MHz. Furthermore, the underweighting of the C rotational constants is almost of no significance for the derived parameters. Finally, as a further check, the iteratively reweighted least-square method was applied with Huber weighting.⁵¹ It confirms that our choice of the weights is roughly correct.

Table 9 presents the principal axis (PAS) coordinates of the ab initio structure of Table 8. The result of a calculation of these Cartesian coordinates from a complete set of independent internal coordinates (e.g., the first eight internal coordinates of Table 2 or Table 8) is not unique: a common sign change of any two of the three PAS coordinate components a , b , or c of all atoms does not change the structure. However, affixing the prime to one partner of a pair of symmetry-equivalent atoms is unambiguous and is more clearly seen in the Cartesian coordinate system.

TABLE 10: Structural Parameters and Stretching Force Constants of Selected Sulfuryl Compounds (Bond Lengths in Å, Bond Angles in deg, Force Constants in aJ Å⁻²)

molecule	$r(\text{S}=\text{O})$	$\angle\text{OSO}$	ref for r	$f(\text{S}=\text{O})$	ref for f
SO ₂ F ₂	1.401(3)	124.91(20)	37	11.22	57
H ₂ SO ₄	1.409(1)	124.02(10)	this work	10.93	9
FSO ₂ Cl	1.409(1)	124.04(4)	58	10.85	58
SO ₂ Cl ₂	1.418(3)	123.5(2)	59	10.53	57
CH ₃ SO ₂ F	1.417(3)	121.8(2)	54	10.51	57
CH ₃ SO ₂ Cl	1.424(3)	120.8(8)	60	10.19	57
(CH ₃) ₂ SO ₂	1.436(3)	119.7(11)	61	9.61	57

6. Discussion

With the exception of the dihedral angle $\tau(\text{H}_1\text{O}_1\text{SO}_1^-)$, there is a very good agreement between the semiexperimental and ab initio structures. For $\tau(\text{H}_1\text{O}_1\text{SO}_1^-)$, the difference is 1.4°. As explained above, it might be because it is more difficult to calculate accurate ab initio dihedral angles. However, the limited accuracy of the cubic force field may also affect the result. This is particularly true for H₂SO₄ for which the structure is sensitive to small variations of the rotational constants. However, the MP2/6-311+G(2df,2p) force field does not give a significantly different semiexperimental structure. The comparison with the empirical structure of Kuczkowski et al.² is also interesting. Taking into account its limited accuracy, the agreement is rather good, the only noticeable discrepancy being the dihedral angle $\tau(\text{H}_1\text{O}_1\text{SO}_1^-)$ which is too large (in absolute value). It is likely that the determination of the rotational constants of the ¹⁸O isotopologues would improve both the semiexperimental and empirical structures. Actually, the $1_{10} \leftarrow 0_{00}$ ground state rotational transition, whose value is approximately $A_0 + B_0$, has been measured for both ¹⁸O isotopologues.⁵² The experimental values are 9929.341 MHz for the S-¹⁸OH form and 9940.519 MHz for the S=¹⁸O form. The corresponding values, calculated with the semiexperimental structure and the force field, are 9927.6 and 9939.8 MHz. The agreement is satisfactory. However, to improve the fit, it would be necessary to use the value of the C rotational constant, which has not been determined.

It is also worth emphasizing that the present results confirm that the two OSO planes are nonperpendicular, the deviation being about 2°. The $r(\text{S}=\text{O})$ bond lengths, S=O stretching force constants, and $\angle\text{O}=\text{S}=\text{O}$ bond angles fit well in the series of related sulfuryl compounds and are in good agreement with the empirical correlation established by Brunvoll and Hargittai.⁵³ see Table 10. It is interesting to note that the structure of the SO₂ moiety is almost identical to that of FSO₂Cl.⁵⁴ The S—O bond length in H₂SO₄ at 1.576 Å, is much shorter than in HSOH where the value is 1.662 Å but the $\angle\text{HOS}$ angles are similar for both molecules (108.6° and 107.2°, respectively).³⁸

The present results also bring information on the relative stability of the conformers. They show that one of the reasons why the C_2 conformer is more stable is the probable occurrence of internal hydrogen bonds between the hydrogens and the sp² oxygen atoms. Indeed, the sum of the van der Waals radii $r(\text{H}) + r(\text{O}) = 2.72$ Å is larger than the distance between the H and O atoms which is calculated to be only 2.42 Å. Moreover, the $r_e(\text{OH})$ bond length, 0.964 Å, is slightly longer than the median value of $r_e(\text{OH})$ bond lengths (0.962 Å for 36 molecules).³⁹ This conclusion is consistent with the fact that the original experimental study of H₂SO₄ showed no evidence of internal rotation.²

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Supporting Information Available: Structure (internal coordinates and Cartesian coordinates) of the C_s conformer of H₂SO₄ calculated at the MP2/V(Q+d)Z level of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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