Sulfur Compounds, 211[‡]

Gas-Phase Acidities of Nine Sulfur Oxoacids of Composition [H_2,S,O_n] (n = 1–4)

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The gas-phase acidities of the most stable conformations of nine sulfur oxo acids were determined by ab initio MO calculations at the CBS-Q, G2(MP2), and G2 levels of theory. The most accurate G2 results are as follows ($\Delta G°_{298}$ of the deprotonation reaction in kJ mol^{-1}): H–S–O–*H* 1468, *H*–S–O–H 1449, $(HO)_2S$ 1426, *H*–S(=O)OH 1406, $H_2S{=}O$ 1394, H–S(=O)O*H* 1361, $(HO)_2S{=}O$ 1324, $H_2S({=}O)_2$ 1321, $H_2O{\rightarrow}S$ 1294, *H*–$S({=}O)_2OH$ 1287, H–$S({=}O)_2O$*H* 1279, $(HO)_2S({=}O)_2$ 1268. These values are in excellent agreement with the few experimental data that can be considered reliable. For molecules of analogous structure, the acidity increases with increasing oxidation number of the sulfur atom. While sulfenic acid, HSO*H*, is as weak an acid as HOCl, sulfurous acid, $(HO)_2SO$, is as strong a proton donor as nitric acid, HNO_3, and sulfonic acid, *H*$S(O)_2OH$, is even stronger than hydrogen iodide, HI, surpassed only by sulfuric acid, H_2SO_4. These results are of relevance to phenomena such as acid rain and aerosol formation in the earth's atmosphere.

Introduction

Sulfur forms a large number of oxo acids, $H_xS_yO_z$, because: (a) the oxidation number(s) of the S atom(s) can vary between –1 and +6 and (b) sulfur–sulfur bonds may occur if $y > 1$.[1–3] Most of these compounds are too unstable to be isolated in pure form. Consequently, the physical and chemical properties of these nevertheless important species are not well-known, and this also holds for their acidities. Only a few experimental and theoretical data are available for the acidities in water and/or in the gas phase.

The most simple ("mononuclear") oxo acids of sulfur are of composition H_2SO_n with n ranging from 1 to 4. However, even in these cases, several isomeric forms are sometimes possible. For example, the oxidation of hydrogen sulfide, H_2S (sulfane), by oxygen atoms (produced by photolysis of ozone) in an argon matrix yields the sulfane oxide $H_2S{=}O$ as well as the isomeric sulfenic acid H–S–O–H ("oxadisulfane").[4] The latter molecule was shown by ab initio MO calculations to be more stable than the former.[5] The energy barriers for the isomerisations $H_2S{=}O \rightarrow$ HSOH and HSOH $\rightarrow H_2S{=}O$ were calculated at the HF/6-31G(d) level of theory as 225 and 361 kJ mol^{-1}, respectively.[5f] The acidities of HSOH and $H_2S{=}O$, defined as the standard enthalpy change for the deprotonation reactions, were calculated at the MP4/6-311++G(d,p)//MP2(fu)/6-311++G(d,p) level of theory.[5d] At 298 K the following results were obtained (kJ mol^{-1}): 1536 for HSO*H*, 1492 for *H*SOH and 1430 for $H_2S{=}O$. The same authors determined the SH acidity of *H*SOH by mass spectrometry as 1481 ± 15 kJ mol^{-1} in very good agreement with the theoretical value.

The energy hypersurface of [H_2,S,O_2] shows stationary points for at least six structures: two conformers of the chain-like sulfur dihydroxide HOSOH, sulfinic acid HS(=O)OH, sulfane dioxide $H_2S({=}O)_2$, the chain-like peroxide HSOOH, the branched superoxide $H_2S{\rightarrow}O{=}O$ and the cyclic thiadioxirane $H_2S–O^a–O^b(S–O^b)$.[6a][6b] At the MP4/6-31G(d)//MP2(fu)/6-31G(d) level of theory, the two first-mentioned isomers are considerably more stable than all the others and the chain of C_2 symmetry is the global minimum of what is usually termed as "sulfoxylic acid". The only reliable experimental information on [H_2,S,O_2] is the mass spectrometric observation of the molecule HOSOH, which had been generated by dissociative ionisation of dimethyl sulfate, followed by neutralisation and reionisation.[7] An earlier report on the matrix isolation of sulfinic acid as a photolysis product of an HI–SO_2 mixture in solid argon[8] has been disputed because the reported infrared spectrum of the product mixture does not match the spectra calculated for various [H_2,S,O_2] isomers.[6a] The gas-phase acidities of these isomers were studied at the MP4/6-31G(d)//MP2/3-21G$^{(*)}$ + ZPVE level[6c] and the following $\Delta H°_{298}$ values were obtained: 1444 kJ mol^{-1} for HS(O)O*H* and 1467 kJ mol^{-1} for *H*S(O)OH. Several authors reported the absolute energies both for the acids and the corresponding anions;[6a][6h] this allows the enthalpy change for the deprotonation reaction to be calculated. From the more recent and more reliable data obtained at the MP4/6-31G(d)//MP2(fu)/6-31G(d) level,[6a] the following $\Delta H°_{298}$ values for the deprotonation may be calculated (in kJ mol^{-1}): HOSOH (C_2) 1530, HOSOH (C_s) 1519, *H*S(=O)OH 1477, HS(=O)O*H* 1450, and $H_2S({=}O)_2$ 1377.

On the energy hypersurface of [H_2,S,O_3], the well-known molecules of sulfurous acid $(HO)_2S{=}O$ and sulfonic acid

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H–S(=O)$_2$OH were identified as structures of minimal energy but, in addition, a 1:1 adduct of H_2O with SO_2 exists which has also been characterised by infrared and microwave spectroscopy.[9] This adduct will not be discussed further. Here we are mainly interested in the acidities of the two mentioned acids of composition H_2SO_3. Several ab initio MO calculations have shown that gaseous sulfurous acid is more stable than sulfonic acid.[6h][10] At the G2 level of theory, including ZPE correction, the energy difference at 0 K is 41 kJ mol^{-1}.[10c] However, both acids are unstable with respect to the decomposition products H_2O and SO_2. The reaction enthalpies for this decomposition at 298 K are –18 kJ mol^{-1} for (HO)$_2$SO and –53 kJ mol^{-1} for HS(O)$_2$OH at the G2 level[10c] but –45 kJ mol^{-1} were calculated for HS(O)$_2$OH (at 270 K) at the QCISD(T)/6-311++G(d,p)//MP2/6-31G(d) level.[10d] Sulfurous acid was nevertheless observed in the vapour phase by neutralisation–reionisation mass spectrometry.[11] The molecule was generated by ionisation-induced decomposition of diethyl sulfite which loses two molecules of ethene to give (HO)$_2$SO. The fragmentation pattern on collisional activation demonstrated the connectivity of sulfurous acid.

Sulfonic acid has never been observed but its anion H–SO_3^- is well-known from salts such as $CsHSO_3$ and from aqueous solutions. The rational nomenclature for this anion containing an S–H bond is sulfonate ion but it is often termed as hydrogen sulfite or as bisulfite ion, especially in the industrial literature. The name hydrogen sulfite ion should be restricted to the isomer with the connectivity HO–SO_2^-. While solid $CsHSO_3$, according to an X-ray diffraction analysis, contains the sulfonate ion,[12] aqueous solutions of the sodium salt exhibit ^{17}O-NMR signals which can be attributed to both tautomers.[13] From the peak areas, the equilibrium quotient $c(\mathrm{HO–SO_2^-})/c(\mathrm{H–SO_3^-})$ was found to be 4.9 ± 0.1 at 298 K in solutions of ion strength 1.0 M. These results were later confirmed by a Raman spectroscopic investigation of aqueous $NaHSO_3$ solutions.[14] Ab initio MO calculations on the two ions of composition $[H,S,O_3]^-$ have been carried out.[6h][15] At the G2 level, the sulfonate ion of C_{3v} symmetry is more stable, by 16 kJ mol^{-1}, than the hydrogen sulfite ion, which surprisingly is of C_1 symmetry.[10c] However, if lower levels of theory are applied, the order of stabilities may be reversed, especially if the symmetry of the hydrogen sulfite ion is restricted to C_s, as has been done in some earlier publications on this subject. Attempts to model the impact of solvation on the stability of the two anions indicated that they are still of very similar energy if dissolved in water.[15c]

The gas-phase acidities of sulfurous and sulfonic acids were studied by various authors.[6h,10b,10c] At the G2 level the deprotonation enthalpies $\Delta H°_{298}$ were calculated as follows (in kJ mol^{-1}): (HO)$_2$SO 1358, *H*S(O)$_2$OH 1323, HS(O)$_2$O*H* 1308.[10c]

Sulfuric acid, H_2SO_4, is the only sulfur oxo acid whose vapour-phase structure was determined experimentally. According to a microwave spectroscopic investigation,[16] the molecule is of C_2 symmetry which was confirmed by a number of ab initio MO calculations.[17] Several conformational (torsional) isomers were theoretically identified at higher energies. In addition, the adduct $SO_3 \cdot H_2O$ was observed by infrared spectroscopy (in matrix isolation experiments),[18] and its gas-phase structure was determined both by microwave spectroscopy[19] and by ab initio MO calculations.[17b,17c] The gas-phase acidity of sulfuric acid was derived from an investigation of the proton transfer in certain ion–molecule reactions as $\Delta G°_{368}$ = 1265 kJ mol^{-1} ($\Delta H°_{368}$ = 1295 kJ mol^{-1}).[20] This value is in excellent agreement with the results of an ab initio MO calculation: At the MP2/6-311++G(d,p)//HF/6-31+G(d) level of theory the deprotonation enthalpy ($\Delta H°$) of H_2SO_4 at 0 K was obtained as 1300 kJ mol^{-1}.[17e]

To obtain accurate gas-phase acidities for the most important of the above-mentioned species *at identical levels of theory*, we calculated the energies of nine acids HA and their corresponding anions A^- at the G2 level of theory, which had formerly been shown to provide reliable acidity data for sulfur compounds, and agree with the best experimental values within ca. 8 kJ mol^{-1}.[21] In addition, the CBS-Q and G2(MP2) methods were applied to all species, since these more economical levels of theory will be used exclusively in two upcoming publications on several larger sulfur oxo acid molecules such as thiosulfuric acid, polythionic acids and polysulfuric acids. In this way a comparison of data for different acids will be possible, as well as a discussion of trends in acidities as a function of molecular structure. Since the gas-phase acidity has been defined in the literature as either $\Delta G°_{298}$ or $\Delta H°_{298}$ of the deprotonation reaction, we also calculated both values for the systems investigated.

Calculations

Ab initio molecular orbital calculations were performed at the CBS-Q,[22] G2(MP2),[23] and G2[24] levels of theory with the GAUSSIAN program system.[25] The G2 method essentially implies an energy calculation at the QCISD(T)/6-311+G(3df,2p) level using geometries optimised at the MP2(full)/6-31G(d) level. Harmonic vibrational wavenumbers were obtained at the HF/6-31G(d) level and were scaled by a factor of 0.8929. All the vibrational eigenvalues of all the molecules investigated were positive. The G2(MP2) method is a modified version of G2 but uses the second-order Møller–Plesset perturbation theory (MP2) for the basis set extension correction rather than the fourth order (MP4). The G2(MP2) method is almost as accurate as the G2 method, but at a substantially reduced computational expense. The excellent performance of these methods and also of CBS-Q in predicting gas-phase acidities of small molecules is well established.[26]

In some cases {$[H_2,S,O_3]$ and $[H_2,S,O_4]$} geometries were calculated with MP2 in combination with the 6-311++G(3df,2p) basis sets. The thermal corrections (no scaling) were obtained using even this level for $[H_2,S,O_3]$ and less expensive MP2/6-311G++(d,p) calculations for $[H_2,S,O_4]$. Then the energies were improved by QCISD(T)/

6-311++G(3df,2p) single point calculations. In addition to the procedures described above, the MP4/6-311++G(d,p) level of theory was applied to the smallest system [H_2,S,O] to optimise the structures.

For details of the quantum chemical methods, see ref.[27] All calculations were carried out on a Cray J90 or on a Linux workstation. To allow for the thermal corrections to the Gibbs free energy of the proton, a value of –0.010654 hartree (–28 kJ mol^{-1}) was used.

Compounds of Composition [H_2,S,O]

To obtain reliable geometries of the three acids H–S–O–H, $H_2S{=}O$, and $H_2O{\rightarrow}S$, as well as of their anions H–O–S$^-$ and H–S–O$^-$, these structures were optimised at the MP4/6-311++G(d,p) level; the results are shown in Table 1. The absolute enthalpies and Gibbs free enthalpies of the species mentioned were calculated by the CBS-Q method based on MP2/6-31G(d′) geometries as well as by the G2(MP2) and G2 methods based on MP2/6-31G(d) geometries. Vibrational wavenumbers and thermal energies were obtained at the HF/6-31G(d′) [CBS-Q] and HF/6-31G(d) [G2(MP2) and G2] levels, respectively. The results are presented in Table 2, and the relative stabilities are shown in Table 3. The stabilities of the acids decrease in the order HSOH > H_2SO > H_2OS. In the case of the anions, HOS$^-$ is more stable than HSO$^-$.

Table 1. Geometries of the acids HSOH, H_2SO, and H_2OS and of their anions HOS$^-$ and HSO$^-$, optimised at the MP4/6-311++G(d,p) level (internuclear distances in pm, bond angles and torsion angles in degrees)

Species	Symmetry	*d*(SH)	*d*(SO)	*d*(HO)	α(OSH)	α(SOH)	τ(HOSH)
HSOH	C_1	134.3	170.1	96.4	97.4	106.7	94.0
H_2SO	C_s	137.9	151.1	–	109.3	–	–
H_2OS	C_s	–	196.6	96.6	–	107.9	–
HOS$^-$	C_s	–	182.4	96.1	–	101.2	–
HSO$^-$	C_s	137.7	162.1	–	105.9	–	–

Table 2. Enthalpies and Gibbs free energies (negative a. u.) of the acids HSOH, H_2SO, and H_2OS and of their anions at 298 K

	Species	CBS-Q	G2(MP2)	G2
$H°$	HSOH	474.044601	474.027258	474.035959
	H_2SO	474.018747	474.001229	474.008258
	H_2OS	473.983262	473.966092	473.976418
	HOS$^-$	473.483768	473.463909	473.474246
	HSO$^-$	473.475996	473.457653	473.466741
$G°$	HSOH	474.072204	474.054902	474.063603
	H_2SO	474.045904	474.028399	474.035427
	H_2OS	474.011289	473.994117	474.004443
	HOS$^-$	473.510585	473.490747	473.501084
	HSO$^-$	473.502920	473.484578	473.493666

All geometrical parameters listed in Table 1 have reasonable values. The most stable isomer HSOH is an intermediate between disulfane, HSSH, and hydrogen peroxide, HOOH, and in fact the torsional angle of HSOH ($\tau = 94°$) has a value intermediate between those which have been determined for HSSH (90°)[28] and HOOH (112°).[29] The S–O bond length of 170 pm agrees reasonably well with the experimental value in gaseous CH_3–O–S–S–O–CH_3 (165.3 pm),[30] whose S–O bonds may be considered to be standard single bonds. As expected, the SO bond in the sulfoxide $H_2S{=}O$ (151.1 pm) is much shorter, but, surprisingly, in the "water sulfide" H_2OS (196.6 pm) it is much longer. The latter may therefore be considered to be a donor–acceptor complex of a water molecule and a sulfur atom, symbolised by $H_2O{\rightarrow}S$. Remarkably, the OH bond lengths of $H_2O{\rightarrow}S$ (96.6 pm) and HSOH (96.4 pm) are practically identical, while the SH bond lengths of HSOH (134.3 pm) and $H_2S{=}O$ (137.9 pm) differ substantially. Otherwise, the pyramidal structures of H_2SO and H_2OS are similar, as can be seen from the similar bond angles HSO (109.3°) versus HOS (107.9°). The angles HSH (86.6°) and HOH (105.8°) are similar to those in H_2S (92.1°) and H_2O (104.5°).

Table 3. Relative enthalpies and Gibbs free energies (kJ mol^{-1}) of the acids HSOH, H_2SO, and H_2OS and of their anions HOS$^-$ and HSO$^-$

Species	CBS-Q		G2(MP2)		G2	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
HSOH	0	0	0	0	0	0
H_2SO	68	69	68	70	73	74
H_2OS	161	160	161	160	156	155
HOS$^-$	0	0	0	0	0	0
HSO$^-$	20.4	20.1	16.4	16.2	19.7	19.4

The two isomeric anions differ remarkably in their SO bond strength as indicated by the differing S–O bond lengths of 182.4 pm for the more stable isomer HOS$^-$ and 162.1 pm for HSO$^-$. The latter value suggests that the SO bond has some double-bond character.

Table 4. Gas-phase acidities (kJ mol^{-1}) of HSOH, H_2SO, and H_2OS at 298 K

Species	CBS-Q		G2(MP2)		G2	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
HSO*H*	1499	1467	1502	1469	1501	1468
*H*SOH	1479	1447	1485	1453	1481	1449
H_2SO	1431	1398	1433	1400	1428	1394
H_2OS	1318	1287	1325	1294	1325	1294

The acidities of the three compounds of composition [H_2,S,O] are given in Table 4, both as the reaction enthalpies and the Gibbs free reaction enthalpies of the deprotonation at 298 K. The acidities increase in the order HSO*H* < *H*SOH < H_2SO < H_2OS. The value of $\Delta H°_{298} = 1481$ kJ mol^{-1}, obtained for *H*SOH at the G2 level, perfectly agrees with the only available experimental value (see Introduction). The fact that *H*SOH is a stronger acid than HSO*H* is due to the stronger OH bond of the latter, but also due to the higher stability of the anion HOS$^-$ which is formed on deprotonation of *H*SOH. On the other hand, H_2OS is a much stronger acid than H_2SO since the rather weak SO bond of H_2OS is turned into the rather strong SO bond in HOS$^-$. In contrast, the strong SO bond of H_2SO

changes on deprotonation to the weaker SO bond in HSO^-. Therefore, H_2SO (ΔG°_{298} = 1394 kJ mol^{-1}) is as strong a proton donor as nitrous acid HNO_2 (ΔG°_{298} = 1396 kJ mol^{-1}) while H_2OS (ΔG°_{298} = 1294 kJ mol^{-1}) is as strong as hydrogen iodide HI (ΔG°_{298} = 1294 kJ mol^{-1}).[31] The acidities obtained at the CBS-Q and G2(MP2) levels (Table 4) differ by 0.5% or less from the G2 data.

Compounds of Composition [H_2S,O_2]

The geometries of the four most stable acids of composition [H_2,S,O_2], HOSOH (C_2), HOSOH (C_s), HS(O)OH, and $H_2S(O)_2$, are well-known at the MP2(full)/6-31G(d) level[6a] and have not been refined any further in this work. The absolute enthalpies and Gibbs free enthalpies of these species of their anions $HS(O)O^-$ and $HOSO^-$ are given in Table 5; the relative stabilities are presented in Table 6. Compared to the previous work, the order of relative stabilities has not changed. The acidities of the three representative structures are shown in Table 7.

Table 5. Enthalpies and Gibbs free energies (negative a. u.) of the acids HOSOH, $H_2S(O)_2$, and HS(O)OH, and of their anions $HOSO^-$ and HSO_2^-, at 298 K

	Species	Symmetry	CBS-Q	G2(MP2)	G2
	HOSOH	C_2	549.187809	549.161874	549.172641
	HOSOH	C_s	549.185684	549.160021	549.170764
H°	$H_2S(O)_2$	C_{2v}	549.168559	549.140765	549.149404
	HS(O)OH	C_1	549.180762	549.154377	549.163664
	$HOSO^-$	C_1	548.632001	548.604945	548.617037
	HSO_2^-	C_1	548.653483	548.625411	548.635399
	HOSOH	C_2	549.217689	549.191849	549.202616
	HOSOH	C_s	549.216266	549.190699	549.201442
G°	$H_2S(O)_2$	C_{2v}	549.197793	549.170047	549.178686
	HS(O)OH	C_1	549.210937	549.184628	549.193914
	$HOSO^-$	C_1	548.662513	548.635543	548.647635
	HSO_2^-	C_1	548.682752	548.654719	548.664707

Table 6. Relative enthalpies and Gibbs free energies (kJ mol^{-1}) of the acids HOSOH, $H_2S(O)_2$, and HS(O)OH, and of their anions $HOSO^-$ and HSO_2^- at 298 K

Species	CBS-Q		G2(MP2)		G2	
	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}
HOSOH (C_2)	0	0	0	0	0	0
HOSOH (C_s)	5.6	3.7	4.9	3.0	4.9	3.1
$H_2S(O)_2$	50.5	52.2	55.4	57.2	61.0	62.8
HS(O)OH	18.5	17.7	19.7	19.0	23.6	22.8
HSO_2^-	0	0	0	0	0	0
$HOSO^-$	56.4	53.1	53.7	50.3	48.2	44.8

Table 7. Gas-phase acidities (kJ mol^{-1}) of HOSOH, $H_2S(O)_2$, and HS(O)OH at 298 K

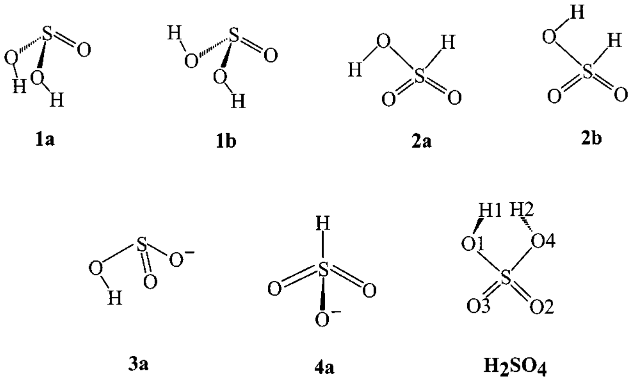
Species	CBS-Q		G2(MP2)		G2	
	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}
HOSOH	1465	1426	1468	1430	1465	1426
$H_2S(O)_2$	1359	1324	1359	1325	1356	1321
HS(O)O*H*	1391	1359	1395	1363	1393	1361
*H*S(O)OH	1447	1412	1449	1414	1442	1406

The most stable isomer HOSOH (C_2 symmetry) is of lowest acidity (ΔG°_{298} = 1426 kJ mol^{-1}), comparable to hydrogen cyanide, HCN (ΔG°_{298} = 1420 kJ mol^{-1}). The chain of C_s symmetry is by only 3 kJ mol^{-1} less stable and therefore of practically identical acidity. The asymmetric species HS(O)OH is, by 23 kJ mol^{-1}, less stable than HOSOH (C_2). The OH acidity of this acid (ΔG°_{298} = 1361 kJ mol^{-1}) is, by 45 kJ mol^{-1}, higher than its SH acidity. This is because the anion $HS(O)O^-$ is more stable than $HOSO^-$. The least stable of the isomers considered here, the tetrahedral molecule $H_2S(=O)_2$ (ΔG°_{298} = 1321 kJ mol^{-1}) is as strong an acid as trifluoroacetic acid, CF_3COOH (ΔG°_{298} = 1324 k] mol^{-1}). No experimental acidity data on [H_2,S,O_2] compounds are available for comparison, but it is obvious now that the acidities based on the earlier MP4/6-31G(d)//MP2(fu)/6-31G(d) calculations which were mentioned in the Introduction are too low by 55–90 kJ mol^{-1}.

Sulfurous Acid, $(HO)_2SO$, and Sulfonic Acid, $HS(O)_2OH$

Although sulfurous acid is mentioned in all inorganic chemistry textbooks, its gas-phase geometry has never been studied on a correlated level of theory. The best previous data for $(HO)_2SO$ and $HS(O)_2OH$ are those by Squires,[10b] calculated with the HF/6-31++G(d,p) basis set. The situation for the anions is better: their geometries were determined at the MP2/6-311+G(2df,p) level.[10c] Therefore, we have optimised the structures of the two acids and their anions at the MP2/6-311++G(3df,2p) level. The results are shown in Table 8 The bond lengths of the acids differ by up to 2%, the bond angles by up to 3° and the torsion angles by up to 6° from the best previous data.

The molecule $(HO)_2SO$ can exist as two conformers which both have positive vibrational eigenvalues at all levels of theory investigated. These species are termed as *syn,syn* (**1a**) and *syn,anti* (**1b**) to indicate the orientation of the OH groups (see Figure 1). Their molecular symmetries are C_s and C_1, respectively. The cage-like molecule **1a** represents the global minimum on the energy hypersurface, but **1b** is only slightly less stable (Table 9).



1a **1b** **2a** **2b** **3a** **4a** **H_2SO_4**

Figure 1. Conformation of the acids of composition [H_2,S,O_3] and of their anions, as well as numbering of atoms in the H_2SO_4 molecule

In a similar fashion, the molecule $HS(O)_2OH$ exists as a *syn* (**2a**) and an *anti* conformer (**2b**) which both are of C_1 symmetry. However, **2b** has one negative eigenvalue of the

Table 8. Geometries of the acids $(HO)_2SO$ and $HS(O)_2OH$, and of their anions $HOSO_2^-$ and HSO_3^-, optimised at the MP2/6-311++G(3df, 2p) level (internuclear distances in pm, bond angles and torsion angles in °)

Species	Symmetry	*d*(H1O1)	*d*(H2O3)	*d*(SH1)	*d*(SO1)	*d*(SO2)	*d*(SO3)	α(SO1H1)	α(SO3H2)	α(O1SO2)	α(O1SO3)	τ(H1O1SO2)	τ(H1O1SO3)	τ(H2O3SO2)
1a, $(HO)_2SO$	C_s (*syn, syn*)	97.2	97.2		161.9	145.4	161.9	107.9	107.9	105.8	105.5	20.4	89.6	–89.6
1b, $(HO)_2SO$	C_1 (*syn, anti*)	96.8	97.2		163.9	144.2	162.0	108.6	108.3	102.3	98.7	–178.0	71.0	–36.3
2a, $HS(O)_2OH$	C_1 (*syn*)		96.8	133.9	141.9	142.8	158.8		108.3	123.6	108.1			–12.5
3a, $HOSO_2^-$	C_1 (*syn*)	96.8			175.3	147.5	148.9	99.9		102.8	98.7	–107.6	8.6	
4a, HSO_3^-	C_{3v}			135.4	145.8	145.8	145.8			114.6				

Table 9. Enthalpies and Gibbs free energies (negative a. u.) of the acids $(HO)_2SO$ and $HS(O)_2OH$ and of their anions $HOSO_2^-$ and HSO_3^- at 298 K

	Species	Symmetry	CBS-Q	G2(MP2)	G2	QCISD(T)
H°	**1a**, $(HO)_2SO$	C_s (*syn, syn*)	624.356818	624.321537	624.332814	624.266937
	1b, $(HO)_2SO$	C_1 (*syn, anti*)	624.355635	624.320072	624.331614	624.265569
	2a, $HS(O)_2(OH)$	C_1 (*syn*)	624.345341	624.308397	624.319712	624.254688
	3a, $HOSO_2$	C_1 (*syn*)	623.842567	623.805453	623.818487	623.751103
	4a, HSO_3	C_{3v}	623.851352	623.811820	623.824084	623.757324
G°	**1a**, $(HO)_2SO$	C_s (*syn, syn*)	624.389897	624.354714	624.365991	624.300412
	1b, $(HO)_2SO$	C_1 (*syn, anti*)	624.388558	624.353148	624.364690	624.298709
	2a, $HS(O)_2(OH)$	C_1 (*syn*)	624.377507	624.340561	624.351876	624.286837
	3a, $HOSO_2^-$	C_1 (*syn*)	623.876716	623.838523	623.851120	623.784615
	4a, HSO_3^-	C_{3v}	623.881168	623.841713	623.853977	623.787285

Table 10. Relative enthalpies and Gibbs free energies (kJ mol^{-1}) of the acids $(OH)_2SO$ and $HS(O)_2OH$ and of their anions $HOSO_2^-$ and HSO_3^-

Species	CBS-Q		G2(MP2)		G2		QCISD(T)	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
1a, $(HO)_2SO$	0	0	0	0	0	0	0	0
1b, $(HO)_2SO$	3.1	3.5	3.8	4.1	3.2	3.4	3.6	4.5
2a, $HS(O)_2OH$	30	33	34	37	34	37	32	36
3a, $HOSO_2^-$	21.8	11.7	16.7	8.4	15.8	7.5	16.3	7.0
4a, HSO_3^-	0	0	0	0	0	0	0	0

Hesse matrix if the vibrational data are calculated at the MP2(full)/6-31G(d) level. At the MP2/6-311++G(d,p) level all eigenvalues are positive, but the lowest wavenumber is only 12 cm^{-1}. Furthermore, the MP2/6-311++G(3df,2p) energy of **2b** was found to be higher, by 6 kJ mol^{-1}, than that of **2a** (at 0 K without ZPE correction). Therefore, the species **2b** will not be considered further. The relative enthalpies and Gibbs free enthalpies are listed in Table 10.

Deprotonation of **1a** and **1b** may theoretically result in two conformations of the anion $HOSO_2^-$, but only one (**3a** in Figure 1) has all eigenvalues positive. This species is of C_1 symmetry. Deprotonation of **2a** at the oxygen atom results in the C_{3v} symmetric anion HSO_3^- (**4a**) which is more stable than **3a** (Table 10).

The gas-phase acidities of sulfurous and sulfonic acids were calculated before,[6h][10] but only ΔH values were given. Our data in Table 11 agree with the previous results, but in addition we present $\Delta G°$ values as well as the results obtained at the QCISD(T) level. There is a very good agreement between these different levels of theory. We therefore trust that the theoretical data are reliable; the following data of sulfurous acid **1a** seem to be the best: $\Delta H°_{298} = 1361$, $\Delta G°_{298} = 1326$ kJ mol^{-1}. An experimental deprotonation enthalpy of $\Delta G°_{298} = 1377 \pm 13$ kJ mol^{-1} was reported by Squires.[10b] However, this author already discussed the possibility that the decomposition of sulfurous acid during the mass spectrometric measurement may be responsible for the deviation of the experimental value from his theoretical result ($\Delta H°_{298} = 1380$ kJ mol^{-1}) obtained at the MP4(sdq)/6-31++G(d,p)//HF/6-31++G(d,p) level.

Table 11. Gas-phase acidities (kJ mol^{-1}) of $(HO)_2SO$ and $HS(O)_2OH$ at 298 K

Species	CBS-Q		G2(MP2)		G2		QCISD(T)	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
$(HO)_2SO$	1355	1320	1361	1327	1358	1324	1361	1326
$HS(O)_2OH$ (*H* of OH)	1303	1275	1310	1282	1307	1279	1312	1284
$HS(O)_2OH$ (*H* of SH)	1326	1287	1327	1290	1322	1287	1328	1291

As the data in Table 11 show, the acidity of sulfurous acid matches that of trifluoroacetic acid ($\Delta G°_{298} = 1324$ kJ mol^{-1}) and that of nitric acid HNO_3 ($\Delta G°_{298} = 1330$ kJ mol^{-1}), while sulfonic acid is even stronger: the SH acidity is comparable to that of hydrogen iodide, HI, ($\Delta G°_{298} = 1294$ kJ mol^{-1}) and the

OH acidity is close to that of metaphosphoric acid, HPO_3 ($\Delta G°_{298}$ = 1270 kJ mol^{-1}).[31]

Sulfuric Acid, H_2SO_4

The highest level of theory at which the acidity of H_2SO_4 has been studied previously was MP2/6-311++G(d,p)//6-31+G(d).[17e] Structure calculations were carried out at the MP2(full)/6-31+G(d)[17c] and MP2/6-311+G(d,p)[32] levels of theory. In addition, density functional calculations at the B3LYP/6-311++G(2d,2p) level were published.[33] We have recalculated the structure at the MP2/6-311++G(3df,2p) level, and compare the results with the experimental structure in Table 12. There is a remarkably good agreement between the two sets of data. The bond lengths differ by less than 1%, and the bond angles by less than 1.5°. Only the two torsion angles HOSO deviate by ca. 8° from the experimental values. The geometrical parameters of the hydrogen sulfate anion calculated at the same level are also given in Table 12.

Table 12. Calculated geometry of H_2SO_4 (C_2) and of its anion HSO_4^- (C_s, *trans*) optimised at the MP2/6-311++G(3df, 2p) level; comparison with the experimental structure (internuclear distances in pm, bond angles and torsion angles in degrees); for numbering of atoms, see Figure 1

	H_2SO_4 calc.	H_2SO_4 exp.[a]	HSO_4^- calc.
d(H1O1)	96.8	97(1)	96.3
d(SO1)	158.3	157(1)	166.1
d(SO2)	141.9	142(1)	145.4
d(SO3)	141.9	142(1)	145.4
d(SO4)	158.3	157(1)	144.6
α(SO1H1)	108.7	108.5(1.5)	104.3
α(O1SO2)	108.8	108.6(0.5)	104.1
α(O1SO4)	102.1	101(1)	101.3
α(O2SO3)	124.3	123(1)	113.7
α(O2SO4)	105.3	106.4(0.5)	115.6
τ(H1O1SO2)	28.7	21(1)	59.7
τ(H1O1SO4)	–82.3	–91(1)	–59.7

[a] Ref.[16]

The energies of H_2SO_4 and its monoanion were calculated by the standard CBS-Q, G2(MP2), and G2 methods (Table 13). However, it was found that the minimal energy conformation of the anion depends on the basis set. At the MP2(fu)/6-31G(d) [G2] level a conformation of C_1 symmetry was found as the global minimum. At the higher levels MP2/6-31G(d′) [CBS-Q], MP2/6-311++G(d,p), and MP2/6-311++G(3df,2p), the only energy minimum found was that of a structure of C_s symmetry, characterised by a *trans* configuration of the four atoms HOSO located in the plane of symmetry. Therefore, the energies of H_2SO_4 and HSO_4^- were also calculated at these levels. To check whether the calculated acidities can be improved further, we carried out QCISD(T)/6-311++G(3df,2p) energy calculations. However, the results were practically identical with those at the G2 and G2(MP2) levels. These calculated acidities of H_2SO_4 at 298 K perfectly agree with the experimental value measured at 368 K (Table 14).

Table 13. Enthalpies and Gibbs free energies (negative a. u.) of H_2SO_4 and of its anion HSO_4^- at 298 K

	Species	Symmetry	CBS-Q	G2(MP2)	G2	QCISD(T)
H°	H_2SO_4	C_2	699.513641	699.467221	699.481180	699.400683
	HSO_4^-	C_s (*trans*)	699.021094			698.905698
	HSO_4^-	C_1		698.971814	698.986743	
G°	H_2SO_4	C_2	699.547213	699.501036	699.514996	699.434332
	HSO_4^-	C_s (*trans*)	699.055240			698.939772
	HSO_4^-	C_1		699.006334	699.021262	

Table 14. Gas-phase acidities (kJ mol^{-1}) of H_2SO_4 at 298 K

	CBS-Q	G2(MP2)	G2	QCISD(T)	exp.[a]
$\Delta H°_{298}$	1299	1307	1305	1306	1295 ± 11
$\Delta G°_{298}$	1264	1271	1268	1270	1265 ± 10

[a] Ref.[20]

Discussion

In Figure 2, the acidities of the nine investigated oxo acids of sulfur are listed and compared with the acidities of well-known inorganic and simple organic proton donors. The weakest of the

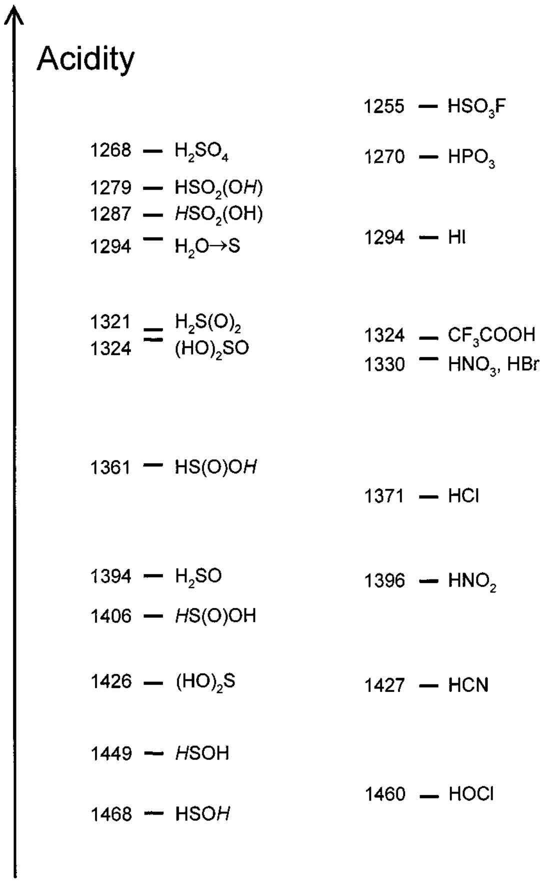


Figure 2. Gas-phase acidities of the sulfur oxo acids [H_2,S,O_n] (n = 1–4) relative to the acidities of other inorganic and organic proton donors; the values of $\Delta G°_{298}$ (kJ mol^{-1}) for the deprotonation reaction are given

sulfur acids (sulfenic acid HSO*H*) is as weak a proton donor as HOCl, while sulfuric acid is the strongest of the sulfur oxo acids investigated in this work.

From Figure 2 it can be seen that there is no simple relationship between the oxidation number of the sulfur atom and the OH or SH acidities. The oxidation numbers vary between 0 and +6. However, if only compounds that are structurally related are compared, a clear trend is seen, namely that higher acidities are found with increasing sulfur oxidation number (or number of oxygen atoms). This is demonstrated by the examples shown in Table 15.

Table 15. Influence of the number of oxygen atoms on the gas-phase acidities of sulfur oxo acids

Series (n = 0–2)	Species	$\Delta G°_{298}$ [kJ mol^{-1}]
$H_2S(=O)_n$	H_2S	1443
	$H_2S=O$	1394
	$H_2S(=O)_2$	1321
$(HO)_2S(=O)_n$	$(HO)_2S$	1426
	$(HO)_2S=O$	1324
	$(HO)_2S(=O)_2$	1268
$\mathit{H}S(=O)_nOH$	$\mathit{H}SOH$	1449
	$\mathit{H}S(=O)OH$	1406
	$\mathit{H}S(=O)_2OH$	1287

A surprising result of this study is the rather high acidities of some of the so-called lower oxo acids of sulfur, such as sulfurous acid $(HO)_2SO$ and, in particular, of sulfonic acid, $HS(O)_2OH$, which is almost as strong as sulfuric acid. Even the S*H* acidity of this acid is higher than that of all the hydrogen halides. In the vapour phase these two oxo acids are unstable with respect to H_2O and SO_2, but their formation in the earth's atmosphere (acid rain) and in certain industrial processes is out of question, since the anions $HOSO_2^-$ and HSO_3^- are stable and these must be in equilibrium with the corresponding acids. If any of the two acids is formed from the corresponding anion, its decomposition into H_2O and SO_2 may be hindered by a substantial energy barrier, as the mass spectrometric observation of $(HO)_2SO$[11] demonstrates.

Several authors have tried to model the behaviour of sulfur oxo acids in water by calculating these molecules inside of or connected to a cluster of water molecules.[33][34] It seems that this is a promising procedure to obtain acidities for aqueous solutions by purely theoretical methods. We will report such calculations on the lower oxo acids of sulfur in a separate publication.

Summary

Nine sulfur oxo acids of composition $[H_2,S,O_n]$ with n = 1–4 were investigated by ab initio MO calculations at the CBS-Q, G2(MP2), and G2 levels of theory, to obtain the enthalpies and Gibbs free energies of the deprotonation reactions in the gas phase at 298 K. As expected, sulfuric acid is the strongest and sulfenic acid HSO*H* is the weakest proton donor. The OH acidity of sulfonic acid, $HS(O)_2O\mathit{H}$, is only slightly lower than that of sulfuric acid, while sulfurous acid, $(HO)_2SO$, is about as strong as nitric acid, $HONO_2$, or hydrogen bromide, HBr. The elusive water → sulfide, $H_2O \rightarrow S$, is also a strong proton donor, comparable to hydrogen iodide, HI. These results are of relevance to the chemistry of sulfur compounds in the earth's atmosphere, where species such as H_2S are oxidised by oxygen atoms, hydrogen peroxide or ozone to give various oxo acids of sulfur. Their acidity then determines the interaction with water molecules which may result in the formation of acid rain and aerosols.[35]

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