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Sulfur Dioxide and Water: Structures and Energies of the Hydrated Species $SO_2 \cdot nH_2O$, $[HSO_3]^- \cdot nH_2O$, $[SO_3H]^- \cdot nH_2O$, and $H_2SO_3 \cdot nH_2O$ (n = 0–8)

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The structures of a large number of hydrates of sulfur dioxide ($SO_2 \cdot nH_2O$), of the sulfonate ion ($[HSO_3]^- \cdot nH_2O$), of the tautomeric hydrogensulfite anion ($[SO_3H]^- \cdot nH_2O$), and of sulfurous acid ($H_2SO_3 \cdot nH_2O$) with up to eight water molecules attached to these species have been optimized at the B3LYP/6-31G(2df,p) level of theory (DFT). The calculated vibrational frequencies allow the definite assignment of certain characteristic modes, and in this way a convincing interpretation of published spectra of aqueous SO_2 as well as of SO_2 adsorbed on very cold ice crystals has been achieved for the first time. Single-point calculations at the G3X(MP2) level of theory were used to calculate the binding energies of the water molecules in $SO_2 \cdot nH_2O$ as well as the relative stabilities of the isomeric anionic species $[HSO_3]^- \cdot nH_2O$ and $[SO_3H]^- \cdot nH_2O$. Generally, the water molecules tend to stick together forming clusters, whereas the particular sulfur-containing molecule remains at the surface of the water cluster, but it is always strongly hydrogen-bonded. Only when there are more than six water molecules are the anions more or less completely surrounded by water molecules. DFT calculations erroneously predict that the gaseous hydrated sulfonate ions are more stable than the isomeric hydrogensulfite ions, even when hydrated with six water molecules. However, if these hydrated species are calculated as being embedded in a polar continuum simulating the aqueous phase, the hydrogensulfite ions are more stable than the sulfonate ions, in agreement with various spectroscopic observations on aqueous sulfite solutions. On the other hand, at the higher G3X(MP2) level, the gaseous hydrated hydrogensulfite anions are more stable than the corresponding sulfonate ions only if the number of water molecules is larger than four, whereas for the weakly hydrated anions the order of relative energies is reversed. The possible implications of these results for the enzymatic oxidation of "sulfite ions" ($[HSO_3]^-$ and $[SO_3H]^-$) by sulfite oxidase are discussed. The conversion of $SO_2 \cdot 6H_2O$ into its isomer $H_2SO_3 \cdot 5H_2O$ is predicted to be exothermic (ΔH°_{298} = –56.1 kJ mol^{-1}) and exergonic (ΔG°_{298} = –22.5 kJ mol^{-1}).

Introduction

Sulfur dioxide is a major component of the global sulfur cycle[1] and also an important industrial product.[2] Its role in the formation of acid rain is well known,[3] and in certain regions of this planet SO_2 is still a major air pollutant. Probably the most important reaction of SO_2 in the environment is its interaction with water. Because of the highly polar nature of both SO_2 and H_2O the solubility of SO_2 in water is quite substantial (10% by weight at 20 °C/1 bar SO_2 pressure).[4] It is generally accepted that such solutions contain mainly solvated SO_2 and only minor concentrations of ions originating from the proton transfer reactions (1) and (2).

$$SO_2 + 2\ H_2O = [H_3O]^+ + [SHO_3]^- \qquad (1)$$

$$[SHO_3]^- + H_2O = [H_3O]^+ + [SO_3]^{2-} \qquad (2)$$

In these equations $[SHO_3]^-$ stands for the two isomers of this anion; the hydrogensulfite anion $[SO_3H]^-$ with the hydrogen atom attached to one of the oxygen atoms and the sulfonate ion $[HSO_3]^-$ containing an S–H bond.[5] The latter ion has been isolated as salts of rubidium[6] and cesium,[6,7] and the anion was found to be of C_{3v} symmetry. In contrast, the hydrogensulfite anion has never been isolated in a solid salt since on attempts to crystallize its salts from aqueous solutions it undergoes the condensation reaction (3) resulting in the disulfite anion, also known as pyrosulfite.

$$2\ [SO_3H]^- = [S_2O_5]^{2-} + H_2O \qquad (3)$$

It is self-evident that the above equilibrium reactions are strongly pH- and/or concentration-dependent. The disulfite anion is of C_s symmetry with an S–S bond. Thus, aqueous SO_2 contains quite a variety of species, and it has become customary to summarize the two tautomeric monoanions $[SO_3H]^-$ and $[HSO_3]^-$ as $[SHO_3]^-$ if the actual connectivity is of no importance or is simply not known. Obviously, the chemical properties of the monoanions $[SO_3H]^-$ and $[HSO_3]^-$ including their pK_a values will be quite different. Unfortunately, this aspect is often ignored in the technical literature.

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Several quantum-chemical calculations have shown that the two isolated (gaseous) monoanions $[SO_3H]^-$ and $[HSO_3]^-$ are of comparable energy, and the sulfonate anion is the global minimum structure.[8–12] At the QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) level of theory, the highest level applied so far, the hydrogensulfite anion was found to be less stable by 16.3 kJ mol^{-1} ($\Delta H°_{298}$).[12] This order of energies also remained when the influence of a polar environment was simulated by using either the Onsager reaction-field method (SCRF)[10] or Tomasi's PCM method of a polar continuum (but without re-optimization of the geometry).[13] In the case of the gaseous species only the direct hydration of $[SO_3H]^-$ and $[HSO_3]^-$ with four water molecules resulted in a clear advantage of the hydrogensulfite anion over the isomeric sulfonate, by 60.7 kJ mol^{-1} at the B3LYP/6-31+G(d,p) level of theory.[11] However, the structures of these solvated anions were not described in detail, and it is not clear whether the global minimum structures were found. In addition, the vibrational spectra of the hydrated anions were not reported. Below, we will show that these DFT results at the B3LYP/6-31+G(d,p) level do not persist at higher levels of theory.

In contrast to most of the mentioned theoretical results, all experimental studies showed that the solvated hydrogensulfite $[SO_3H(aq)]^-$ is the dominating monoanion in aqueous sulfite solutions. Thus, ^{17}O NMR measurements of acidic sodium sulfite solutions by Horner and Connick resulted in an $[SO_3H(aq)]^-/[HSO_3(aq)]^-$ ratio (Q_1) of 4.9.[14] The evaluation of Raman spectra of aqueous sulfite by Littlejohn et al. yielded a ratio Q_1 of 5.0,[15] and from a XANES study of solutions of SO_2 and sulfite at various pH values this ratio was derived by Risberg et al.[16] as 2.6 ± 0.5 (all data at 25 °C). The differing ionic strength of the investigated systems as well as the differing accuracy of the applied methods may be responsible for the slightly differing results. On increasing temperatures Q_1 decreases as expected.[15] The isomerization of $[HSO_3(aq)]^-$ to $[SO_3H(aq)]^-$ proceeds primarily by proton removal from $[HSO_3(aq)]^-$.[5]

The above results show that the hydrated anions $[SO_3H(aq)]^-$ and $[HSO_3(aq)]^-$ have reversed relative stabilities compared to the unsolvated gaseous S^{IV} species. To confirm this conclusion and to find out the origin of the reversed stabilities on a molecular basis, we have carried out theoretical studies both on hydrated SO_2 and H_2SO_3 molecules (as precursors) as well as on the hydrated anions $[SO_3H(aq)]^-$ and $[HSO_3(aq)]^-$ by using between one and eight water molecules per sulfur atom. In particular, we wanted to find out how many water molecules are needed to favor the hydrogensulfite ion thermodynamically over the sulfonate tautomer. As in our previous work,[12,17] the high-level G3X(MP2) theory[18] was applied, which reproduces the thermodynamic properties of sulfur compounds very well. Almost 40 molecules and ions have been studied at this level in the present work.

The hydration of SO_2 by up to three water molecules has been studied before, both experimentally and theoretically. Certain bands in the IR spectra of SO_2/H_2O mixtures trapped in inert matrices at low temperatures have been assigned to 1:1, 1:2, and 2:1 complexes between the two components.[19–22] The structure of the 1:1 complex was determined by microwave spectroscopy.[23] The geometry has the planes of the two monomer units tilted by about 45° from a parallel orientation with the oxygen atom of H_2O closest to the S atom of SO_2 at an S···O distance of 282.4(2) pm. This structure is basically in agreement with quantum chemical calculations at various levels of theory (see Figure 1),[22,24,25,26] but as we will show below the experimental tilt angle between the two monomers needs to be discussed. The structures of other SO_2 hydrates have been studied theoretically only;[22,25,27] this work will also be discussed below.

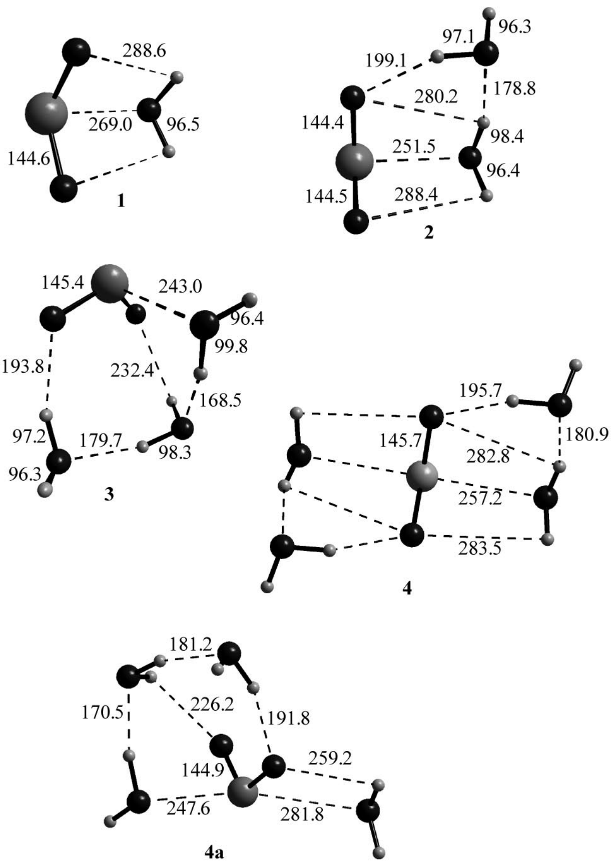

Figure 1. Structures of the solvates of composition $SO_2·nH_2O$ (n = 1–4), calculated at the B3LYP/6-31G(2df,p) level of theory (internuclear distances in pm; local minima are generally marked as "**a**"). The tetrahydrate **4** is of C_2 symmetry.

Results and Discussion

Reference Calculations

To find a suitable theoretical method for the hydrates of SO_2 and $[SHO_3(aq)]^-$ yielding reliable thermodynamic data we have chosen the cyclic water trimer $(H_2O)_3$ as a reference compound since many of the investigated molecules contain similar hydrogen-bonded structures as this species. The most stable isomer of $(H_2O)_3$ is of C_1 symmetry with two

Table 1. Negative absolute energies *E* and enthalpies *H* (both in Hartree) of the hydrates $SO_2 \cdot nH_2O$ as well as of their free components. The dipole moments μ calculated at the B3LYP/6-31G(2df,p) level are given in Debye.

Species	E_e (B3LYP/6-31G(2df,p))	E°_{298} (G3X/MP2)	H°_{298} (G3X/MP2)	μ
H_2O	76.42608	76.34357	76.33979	1.85
$(H_2O)_3$	229.31624	229.04349	229.03536	1.30
SO_2	548.62589	548.05232	548.04824	2.10
$SO_2 \cdot H_2O$ (**1**)	625.06305	624.40010	624.39246	1.49
$SO_2 \cdot 2H_2O$ (**2**)	701.51097	700.75225	700.74242	1.62
$SO_2 \cdot 3H_2O$ (**3**)	777.95898	777.10462	777.09242	1.68
$SO_2 \cdot 4H_2O$ (**4**)	854.39432	853.45254	853.43655	0.33
$SO_2 \cdot 4H_2O$ (**4a**)	854.39338	853.45157	853.43528	3.09
$SO_2 \cdot 6H_2O$ (**5**)	1007.28563	1006.15686	1006.13553	1.00
$SO_2 \cdot 6H_2O$ (**5a**)	1007.28390	1006.15720	1006.13551	3.15

hydrogen atoms oriented up and one hydrogen atom down from the plane defined by the three oxygen atoms.[28] The binding energy D_e of this molecule, that is the energy change for the dissociation reaction $(H_2O)_3 \rightarrow 3H_2O$, is well known. The most recent experimental value at equilibrium is 67.2 kJ mol^{-1}[29] whereas high-level theoretical calculations predicted values between 65.9[30] and 68.2 kJ mol^{-1}.[31] A systematic study of the water oligomers by Dunn et al.[32] demonstrated that of the following methods the G3 theory gave the best agreement with the experimental results on the water trimer (D_e data given in parentheses, in kJ mol^{-1}): CBS-QB3 (63.8), CBS-APNO (65.7), G2 (63.5), and G3 (65.9). However, the G3 method uses a geometry optimization at the rather low HF/6-31G(d) level of theory. In the case of $(H_2O)_3$ this level does not reproduce the experimental structure very well. For example, the three shortest O···O distances are calculated as 286.2, 287.5, and 285.9 pm (this work) compared to the averaged experimental value of 277.6 pm.[29] The more economical G3X(MP2) theory[18] uses the geometry optimized at the B3LYP/6-31G(2df,p) level, which in the case of $(H_2O)_3$ results in a much better agreement with the experimental data, as demonstrated by the O···O distances of 276.5 (twice) and 277.1 pm. By this method the binding energy of $(H_2O)_3$ at equilibrium is obtained as 60.6 kJ mol^{-1}, a result that is still in reasonable agreement with the experimental value. The absolute energies and enthalpies are given in Table 1. Therefore, we decided to use the G3X(MP2) method as a compromise both for the structural and the thermodynamic characterization of the various hydrates of SO_2, of the two tautomeric anions of composition $[SHO_3]^-$, and of sulfurous acid. Since we are mainly interested in the energy *differences*, e.g., between $[HSO_3(aq)]^-$ and $[SO_3H(aq)]^-$, small systematic errors in the energy calculations will probably compensate each other.

In previous studies these hydrates have sometimes been investigated by using various density functional theory methods without any improvements by additional single-point energy calculations. To check the reliability of such treatments we studied the molecule $(H_2O)_3$ by using the B3LYP functional with the basis sets 6-31G(2df,p) and 6-31+G(d,p) both for the geometry optimization as well as for the energy calculation. With these methods the dissociation energy (D_e) of the water trimer is predicted as 99.7 kJ mol^{-1} (2df,p) and 75.1 kJ mol^{-1} (d,p), respectively. These results are far off the experimental value of 67.2 kJ mol^{-1}.[29] Therefore, one has to conclude that the DFT binding energies are unreliable in this case.

Hydrates of SO_2

The structures of SO_2 and of the hydrates $SO_2 \cdot nH_2O$ (n = 1–4), calculated at the B3LYP/6-31G(2df,p) level of theory, are shown in Figure 1; the atomic coordinates are listed in the Supporting Information.

The absolute energies and enthalpies as well as the dipole moments of the SO_2 hydrates obtained at the B3LYP/6-31G(2df,p) and G3X(MP2) levels of theory are presented in Table 1. As discussed above, the monohydrate $SO_2 \cdot H_2O$ (**1**) consists of two almost parallel oriented dipole molecules without any sign of hydrogen bonding (symmetry C_s). Atoms of opposite charge approach each other, and the shortest intermolecular distance d(S···O) = 269.0 pm is in fair agreement with the experimental value of 282.4 pm.[23] This non-bonding distance is much longer than a corresponding single S–O bond as in dimethyl sulfoxylate MeO–S–OMe (162.5 pm[33]), for example, but shorter than the sum of the van der Waals radii (315 pm). Otherwise, the geometries of the two components SO_2 and H_2O are rather undisturbed in the complex compared to the separate molecules. The angle between the two molecular planes – and this is also the angle between the two dipole moment vectors – is calculated as 14.0°, whereas 45° have been derived from microwave spectra. The latter value seems to be too large, since the dipole moment μ_c of the molecule calculated from the dipole moments of the two free components by using a tilt angle of 45° is 1.31 D,[23] considerably smaller than the experimental dipole moment of 1.984(2) D derived from the Starck effect on the spectra.[23] A smaller tilt angle yields a larger vector sum of the dipole moments. Thus, we believe that our theoretically predicted tilt angle is more reliable, especially since other theoretical methods also resulted in a nearly parallel arrangement of the two monomers.[24,25,26] As a consequence of this relatively loose sandwich structure, the G3X(MP2) binding enthalpy at 298 K is only 11.6 kJ mol^{-1}. In the following, all enthalpies ΔH°_{298} will be given at this level of theory unless noted otherwise.

Attempts to optimize a structure with a second water molecule linked to the unoccupied side of $SO_2 \cdot H_2O$ to create a kind of "double sandwich" were unsuccessful. Instead, after geometry optimization, the additional H_2O molecule was linked to the first one by a rather short $O\cdots H$ bond (178.8 pm) forming an additional strong hydrogen bond to the SO_2 unit. The intermolecular $S\cdots O$ distance discussed above decreased from 269.0 pm in **1** to 251.5 pm in **2**. The binding enthalpy of **2** compared to the three separate molecules is now much higher ($38.3\,kJ\,mol^{-1}$) than with the monohydrate ($11.6\,kJ\,mol^{-1}$). The structure of **2** is basically in agreement with the results of Hirabayashi et al. who used the MP2/6-311++G(2d,2p) level of theory for the geometry optimization.[22] However, all the MP2 bond lengths are slightly larger than our DFT data.

In the trihydrate $SO_2 \cdot 3H_2O$ (**3**) the third H_2O molecule also prefers to bind to the two other water molecules and in addition to one of the oxygen atoms of the SO_2 unit, which then has three H_2O molecules on one side of its molecular plane (Figure 1). The intermolecular $S\cdots O$ distance decreases further, to 243.0 pm, and the binding enthalpy increases to $65.1\,kJ\,mol^{-1}$. Interestingly, the binding energy per water molecule increases with the water content, from $11.6\,kJ\,mol^{-1}$ for $n = 1$ to $19.2\,kJ\,mol^{-1}$ for $n = 2$ to $21.7\,kJ\,mol^{-1}$ for $n = 3$. For this reason, three molecules of $SO_2 \cdot H_2O$ are less stable than one molecule of $SO_2 \cdot 3H_2O$ plus two molecules of SO_2, by $30.2\,kJ\,mol^{-1}$. This remarkable result may have implications for the hydration of SO_2 under very dry conditions as in the upper atmosphere of the earth. With four and more water molecules the binding enthalpy per H_2O molecule seems to stabilize at approximately $20\,kJ\,mol^{-1}$ since 19.1 and $21.1\,kJ\,mol^{-1}$ have been calculated for $n = 4$ and 6, respectively. On the other hand, the change in binding energy during the stepwise addition of one water molecule after another ($n \rightarrow n+1$) does not show any definite trend. For the most stable of the first four hydrates of SO_2 ($n = 1$–4) the following data have been calculated: 11.6, 26.7, 26.8, and $11.4\,kJ\,mol^{-1}$.

Our structure of $SO_2 \cdot 3H_2O$ (**3**) was obtained with several differing starting geometries. Thus, we trust that we obtained the global minimum structure. However, this structure differs slightly from the corresponding trihydrate structure calculated by Hirabayashi et al.[22] in which only three $O\cdots H$ hydrogen bonds are shown and one oxygen atom of SO_2 is not involved in any hydrogen bonding, which seems rather unlikely.

With an increasing number of water molecules the number of possible geometrical arrangements increases. For the composition $SO_2 \cdot 4H_2O$ two energy minima were located on the potential energy surface (PES), which differ by only $2.5\,kJ\,mol^{-1}$. The corresponding structures are shown in Figure 1. The more stable isomer **4** is of C_2 symmetry and characterized by four short $O\cdots H$ bonds and four long $O\cdots H$ contacts (ca. 280 pm) as well as by a triple-decker conformation of the central $H_2O/SO_2/H_2O$ unit. Two hydrogen atoms are not engaged in any hydrogen bonding. In the less stable isomer **4a** three water molecules are on one side of the SO_2 plane and connected by $O\cdots H$ bonds, whereas the fourth H_2O unit is attached to the SO_2 molecule by just a dipole–dipole attraction.

All hydrates of SO_2 discussed so far have at least one water molecule attached to the SO_2 unit in such a way that the $S\cdots O$ distance is less than 260 pm. This also holds for the hexahydrate $SO_2 \cdot 6H_2O$ (**5**), the structure of which is shown in Figure 2. This complex has two $S\cdots O$ bonds of length 246.5 and 252.2 pm and six $O\cdots H$ bonds shorter than 192 pm, but four hydrogen atoms do not take part in hydrogen bonding. The bond angle O=S=O is 113.9° and the $O\cdots S\cdots O$ angle is 144.5° resulting in a distorted pseudo-trigonal-bipyramidal coordination of the sulfur atom with the formal S=O double bonds in equatorial positions. As far as the water molecules are concerned, the cyclic structures of the SO_2 hydrates with up to 50% of free hydrogen atoms not engaged in hydrogen bonding very much resemble the cyclic structures of the water oligomers $(H_2O)_n$ with $n = 3$–5.[28] An isomer of $SO_2 \cdot 6H_2O$ (**5a**) with a slightly different arrangement of three of the water molecules is just $0.5\,kJ\,mol^{-1}$ (ΔH°_{298}) less stable (Figure 2). The small enthalpy difference between the isomeric hydrates **4**/**4a** and **5**/**5a** lends confidence to the assumption that our most stable structures either represent the particular global minimum or are very close to this in energy.

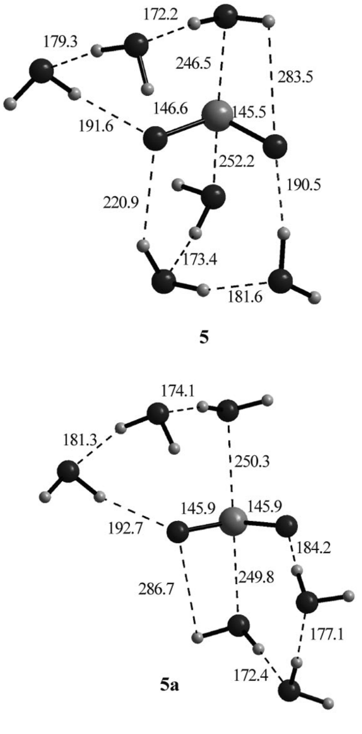

Figure 2. Structures corresponding to global or local energy minima of the solvates of composition $SO_2 \cdot 6H_2O$, calculated at the B3LYP/6-31G(2df,p) level of theory (internuclear distances in pm; the less stable structure is marked as "**a**").

The structure of $SO_2 \cdot 6H_2O$ (**5**) can be used to understand the formation of sulfurous acid (H_2SO_3) and its anions $[HSO_3]^-$ and $[SO_3H]^-$ from SO_2 in water. The shortest hydrogen bond of **5** has a length of 172.2 pm. If the bridging proton "jumps" over to the neighboring water molecule forming a cation $[H_3O]^+$ and if the resulting hydroxide anion simultaneously moves towards the sulfur atom of SO_2 shortening the S···O distance from 246.5 pm in **5** to ca. 170 pm, the result would be a solvated ion pair, $[H_3O][SO_3H]$. This seems to be the most natural pathway for the nucleophilic attack of water on SO_2. Results for sulfurous acid will be reported below after the discussion of the anions.

The fundamental vibrations of the hydrates investigated in this work were calculated at the B3LYP/6-31G(2df,p) level of theory. For the structures shown in Figures 1–8 and Figure S1 the frequencies were all real. The three fundamental modes of SO_2 are only slightly affected by an increasing number of surrounding water molecules. As expected, the wavenumbers of the two SO stretching modes (asymmetric/symmetric) decrease on solvation, from 1381/1171 cm^{-1} in free SO_2 to 1364/1170 cm^{-1} in $SO_2·H_2O$ and 1343/1160 cm^{-1} in $SO_2·2H_2O$ to 1325/1158 cm^{-1} in $SO_2·3H_2O$ (unscaled values). On the other hand, the O=S=O bending mode shifts on hydration from 515 cm^{-1} in free SO_2 to slightly higher wavenumbers, but, as the number of water units increases, this mode is more and more coupled to other vibrations of the cluster-like hydrates and therefore can no longer be considered a characteristic fundamental of SO_2. These trends are in agreement with the IR spectra of $SO_2(H_2O)_n$ complexes recorded in an argon matrix.[22]

Hydrates of the Sulfonate Ion $[HSO_3]^-$

The free sulfonate anion is of C_{3v} symmetry and offers plenty of lone pairs at the oxygen atoms to bind water molecules by hydrogen bonds. The atomic charges of these oxygen atoms calculated by a natural population analysis (NPA) are –1.01, and as a consequence the hydrates of the sulfonate and hydrogensulfite anions contain less OH groups that are not involved in hydrogen bonding than the hydrates of SO_2. On the other hand, the negative NPA charge on the sulfonate hydrogen atom (–0.12) prevents the formation of a hydrogen bond to the oxygen atom of a neighboring water molecule, at least as long as there is a limited number of H_2O units. When we tried to optimize a structure with an H_2O molecule connected to the S–H terminal of one of the smaller hydrates discussed below, it always moved to the S–O bonds or to the other water molecules to form a stronger O···H–O rather than a much weaker O···H–S bond. Only with eight water molecules was an internuclear SH···O distance of 234.5 pm calculated, which may be interpreted as a long and bent hydrogen bond (see below and Figure S1).

The addition of an increasing number of water molecules to the sulfonate anion results in structures quite different from those of the hydrates of SO_2. The larger atomic charge on the oxygen atoms now favors hydrogen bonds with a single H_2O molecule as shown in Figure 3.

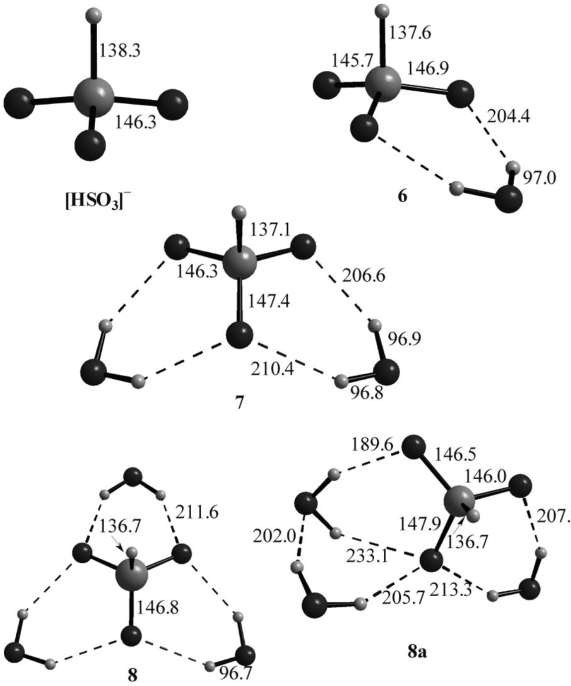

Figure 3. Structures of the sulfonate ion and of its hydrates of composition $[HSO_3]^-·nH_2O$ (n = 1–3), calculated at the B3LYP/6-31G(2df,p) level of theory (the less stable trihydrate is marked as "**a**"; internuclear distances in pm). The naked anion $[HSO_3]^-$ as well as the trihydrate **8** are of C_{3v} symmetry; the mono- and the dihydrate are of C_s symmetry.

The monohydrate $[HSO_3]^-·H_2O$ (**6**) is of C_s symmetry with two relatively long O···H bonds with a length of 204.4 pm. As a consequence of this cyclic structure, the H–O–H bond angle of the water molecule decreased from 104.5° in free H_2O to 97.0°, whereas the two O···H–O angles are 145.6°. The dihydrate $[HSO_3]^-·2H_2O$ (**7**) is also of C_s symmetry and structurally similar to the monohydrate with two cyclic units O···H–O–H···O and with O···H bond lengths that are 206.6 and 210.4 pm.

The trihydrate **8** is of similar geometry but of C_{3v} symmetry with three cyclic $SO_2···H_2O$ units (Figure 3). The six O···H bonds of **8** are equivalent and have a length of 211.6 pm. An isomeric structure **8a** with two of the water molecules attached to each other and also to the sulfonate anion and with the third H_2O linked to the anion in a similar fashion as in the monohydrate is slightly less stable, by 6.4 kJ mol^{-1}. This asymmetrical structure contains six O···H hydrogen bonds with lengths between 189.6 and 233.1 pm.

The most stable structure of $[HSO_3]^-·4H_2O$ (**9**) can be derived from the structure of the most stable trihydrate **8** by connecting an additional water molecule to both the sulfonate anion and to one of the already existing H_2O units as shown in Figure 4. The isomeric structure **9a** can be derived from the less stable trihydrate **8a** in a similar fashion. This isomer **9a** is only 6.6 kJ mol^{-1} less stable than **9** ($\Delta H°_{298}$) at the G3X(MP2) level.

The structures of the pentahydrate **10** (Figure 4) and of two isomeric hexahydrates of $[HSO_3]^-$ (**11**, **11a**; Figure 5) are in line with the previous discussion. They all contain

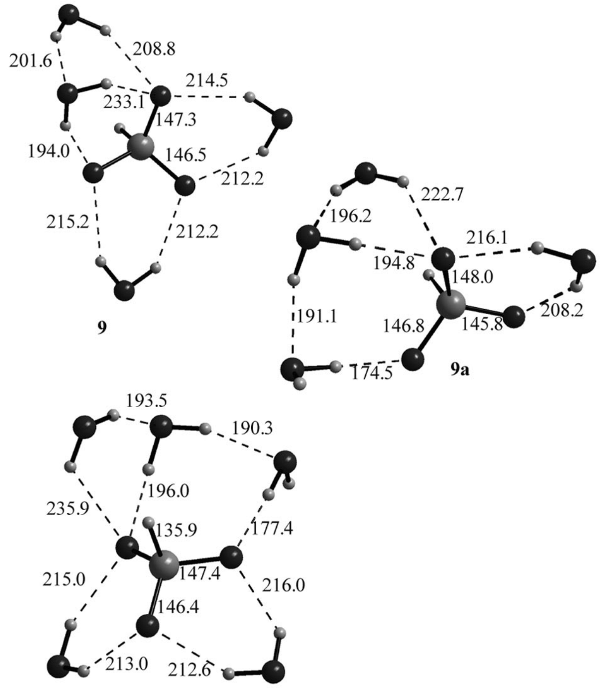

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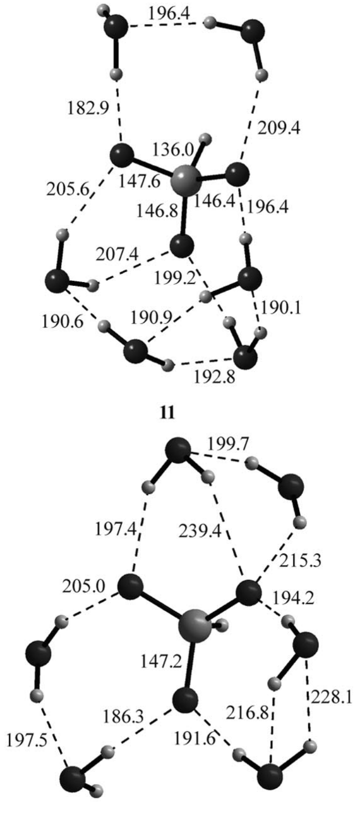
Figure 4. Structures of the hydrated sulfonate anions of composition $[HSO_3]^-\cdot nH_2O$ (n = 4–5), calculated at the B3LYP/6-31G(2df,p) level of theory (the less stable species is marked as "**a**"; internuclear distances in pm).



11a

Figure 5. Structures of two isomeric hexahydrates of the sulfonate anion, calculated at the B3LYP/6-31G(2df,p) level of theory (the less stable species is marked as "**a**"; internuclear distances in pm). There are no SH···O interactions.

just one OH group that is not involved in hydrogen bonding. The isomer **11a** is ΔH°_{298} = 19.6 kJ mol^{-1} less stable than **11** (3.3 kJ mol^{-1} per H_2O unit).

The octahydrate $[HSO_3]^-\cdot 8H_2O$ (**12**) was studied only in an exploratory manner, since we are not sure whether we obtained the global minimum structure of this rather complex species. The structure of **12** is given in the Supporting Information (Figure S1); it is characterized by a weak SH···O hydrogen bond with a length of 234.5 pm in addition to 15 OH···O bonds with lengths of <250 pm.

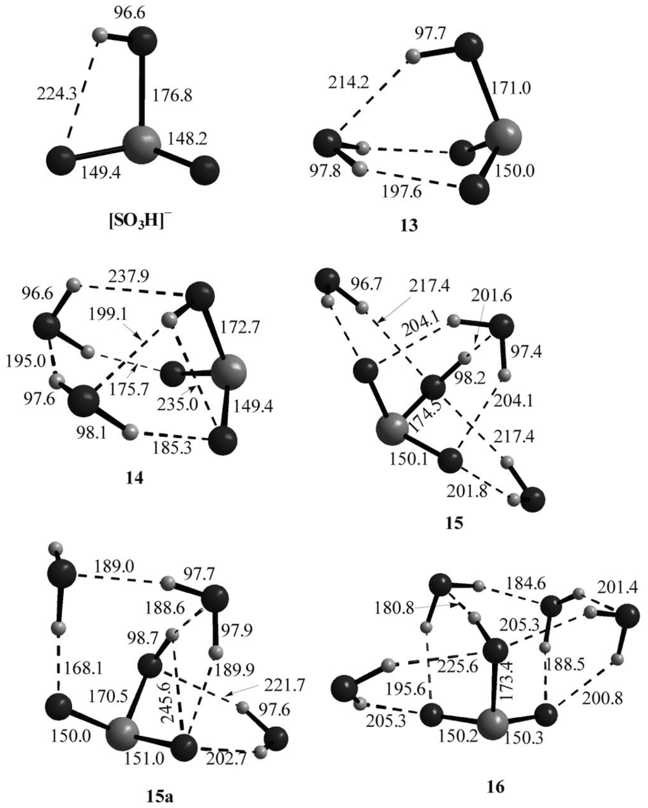
In all the hydrates $[HSO_3]^-\cdot nH_2O$ (n = 0–6) the structure of the central $[HSO_3]^-$ anion is only slightly disturbed by the hydration. For example, if one compares the structures of the two C_{3v}-symmetrical species $[HSO_3]^-$ and $[HSO_3]^-\cdot 3H_2O$ (**8**) the S–O distances increase on hydration by only 0.5 pm, the S–H bond length decreases by 1.6 pm, the O–S–O angles decrease by 0.6°, and the O–S–H angles increase by 0.9°.

Hydrates of the Hydrogensulfite Ion $[SO_3H]^-$

The free hydrogensulfite anion of connectivity $O_2S–O–H$ is not of C_s symmetry as might be expected. As a result of a weak intramolecular hydrogen bond of length 224.3 pm the symmetry is C_1 with two quite different O=S–O–H torsion angles of +19.3° and –96.6° (Figure 6). In this anion there are not only the three oxygen atoms available for hydrogen bonding to neighboring water molecules, but in addition the polar OH group can bind to the oxygen atoms of H_2O units by its positively charged hydrogen atom. And this is what is observed in all hydrates of hydrogensulfite, as shown in Figures 6 and 7. An indication of a weak S···H–O interaction was found only with eight water molecules (see below).

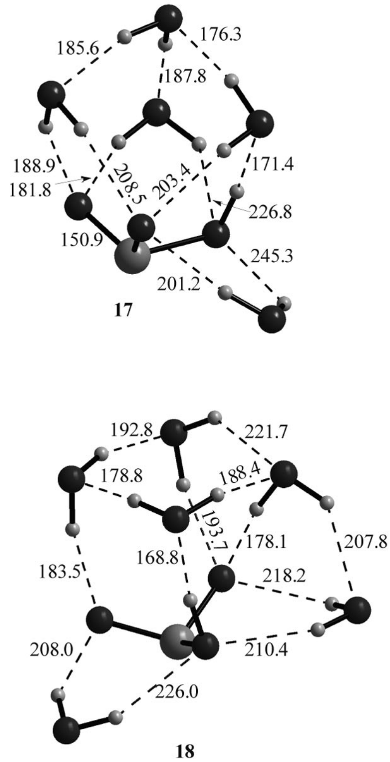
The monohydrate $[SO_3H]^-\cdot H_2O$ (**13**) is of C_s symmetry with two O···H bonds (197.6 pm) between the water hydrogen atoms and the SO_2 unit of the anion but with an additional O···H bond (214.2 pm) between the hydrogen atom of the anion and the lone pair of the water oxygen atom (Figure 6). The two O=S–O–H torsion angles are ±57.1°. As a result of this symmetrical geometry the two intra-anionic non-bonding O···H distances have increased from 224.3 pm in free $[SO_3H]^-$ to 256.0 pm in $[SO_3H]^-\cdot H_2O$. In the following only O···H contacts shorter than 250 pm will be considered as hydrogen bonds.

In the dihydrate $[SO_3H]^-\cdot 2H_2O$ (**14**) the anion has practically the same conformation as in the free ion with O=S–O–H torsion angles of +19.3° and –95.7° (Figure 6). Consequently, there again exists an intra-anionic O···H bond (235.0 pm). The two water molecules are connected to each other by one O···H bond (195.0 pm), but in addition there are four hydrogen bonds to the anion. Thus, altogether six hydrogen bonds are formed with bond lengths in the range 175.7–237.9 pm, and only the sulfur atom does not take part in this hydrogen-bonding network. The rather differing O···H bond lengths are mainly the result of the varying O–H···O bond angles, which in turn are enforced by the cluster-like geometry of this dihydrate that has no symmetry at all.



$[SO_3H]^-$ 13 14 15 15a 16

Figure 6. Structures of the hydrogensulfite anion and of its hydrates of composition $[SO_3H]^-\cdot nH_2O$ (n = 1–4), calculated at the B3LYP/6-31G(2df,p) level of theory (the less stable trihydrate is marked as "**a**"; internuclear distances in pm). The monohydrate **13** and the trihydrate **15** are of C_s symmetry, all other species are asymmetrical.



17 18

Figure 7. Structures of the two most stable hydrogensulfite hydrates of composition $[SO_3H]^-\cdot nH_2O$ (n = 5 and 6), calculated at the B3LYP/6-31G(2df,p) level of theory (internuclear distances in pm). There are no OH···S interactions.

Two isomers of the trihydrate $[SO_3H]^-\cdot 3H_2O$ corresponding to minima on the potential energy surface have been located (Figure 6). The more stable form (**15**) is of C_s symmetry with all hydrogen atoms involved in bonds to the three oxygen atoms of the $[SO_3H]^-$ anion. The asymmetrical isomer **15a** is characterized by seven hydrogen bonds with only one hydrogen atom not taking part in the O···H network. The G3X(MP2) enthalpy difference between **15** and **15a** is just 0.6 kJ mol^{-1}. The structure of the tetrahydrate $[SO_3H]^-\cdot 4H_2O$ (**16**) is also asymmetric and is stabilized by nine hydrogen bonds with lengths of 180.8–225.6 pm (Figure 6).

The structures of the penta- and hexahydrates of $[SO_3H]^-$ (**17**, **18**) are asymmetric, but generally in line with the previous discussion (Figure 7). Two additional isomeric hexahydrates **18a**, **18b** have been identified that are 7.5 and 15.3 kJ mol^{-1}, respectively, less stable than **18**. All hydrogen atoms of **18** are involved in hydrogen bonds of lengths <226.0 pm, which make this structure more stable than the corresponding hydrate of the sulfonate anion (see below). The shortest of these H bonds (length 168.8 pm) originates from the OH group of the anion. The structure of the anion has changed considerably compared to free hydrogensulfite. The terminal SO bond lengths are 149.8 and 152.4 pm compared to 148.2 and 149.4 pm in the free anion. On the other hand, the length of the formal S–OH single bond decreased from 176.8 pm in the free anion to 168.6 pm in **18**.

The structure of the octahydrate $[SO_3H]^-\cdot 8H_2O$ (**19**) is given in the Supporting Information (Figure S1). It is characterized by an OH···S internuclear distance of 276.1 pm in addition to 16 OH···O bonds of length <250 pm. Below we will show that the sulfur atom of the hydrogensulfite hydrates bears a charge of approximately +1.7 units, which probably prevents the formation of hydrogen bonds despite the lone-pair electrons located on that atom.

Thermodynamics of the Hydrated Anions $[HSO_3(aq)]^-$ and $[SO_3H(aq)]^-$

The thermodynamic properties of the hydrates of both the sulfonate and the hydrogensulfite anion very much depend on the method of calculation and on the basis set used. The absolute energies as well as the enthalpies are given in Table 2. For example, at the B3LYP/6-31G(2df,p) level (hereafter termed as DFT) the energy difference between the two unsolvated gaseous anions $[HSO_3]^-$ and $[SO_3H]^-$, at the potential energy minimum, is 12.5 kJ mol^{-1} in favor of the sulfonate ion; this value increases to 19.5 kJ mol^{-1} at the G3X(MP2) level, despite identical geometries (see Table 2).

Table 2. Negative absolute energies E and enthalpies H (both in Hartree) of the hydrates $[HSO_3]^-\cdot nH_2O$ and $[SO_3H]^-\cdot nH_2O$ as well as of their free components. The dipole moments μ calculated at the B3LYP/6-31G(2df,p) level are given in Debye.

Species	E_e (B3LYP/6-31G(2df,p))	E°_{298} (G3X/MP2)	H°_{298} (G3X/MP2)	μ
$[HSO_3]^-$ (C_{3v})	624.50447 624.60916 (PCM)	623.87680	623.87214	2.16
$[HSO_3]^-\cdot H_2O$ (**6**)	700.95915 701.05296 (PCM)	700.24148	700.23366	2.44
$[HSO_3]^-\cdot 2H_2O$ (**7**)	777.41030	776.60397	776.59280	2.39
$[HSO_3]^-\cdot 3H_2O$ (C_{3v}) (**8**)	853.85858	852.96459	852.94986	2.45
$[HSO_3]^-\cdot 3H_2O$ (C_1) (**8a**)	853.86209	852.96214	852.94815	1.44
$[HSO_3]^-\cdot 4H_2O$ (**9**)	930.30868	929.32154	929.30389	1.06
$[HSO_3]^-\cdot 4H_2O$ (**9a**)	930.31124	929.31811	929.30139	2.19
$[HSO_3]^-\cdot 5H_2O$ (**10**)	1006.75698	1005.67664	1005.65628	2.03
$[HSO_3]^-\cdot 6H_2O$ (**11**)	1083.22016 1083.29808 (PCM)	1082.03600	1082.01460	4.52
$[HSO_3]^-\cdot 6H_2O$ (**11a**)	1083.20262 1083.28092 (PCM)	1082.02998	1082.00713	1.57
$[HSO_3]^-\cdot 8H_2O$ (**12**)	1236.11737	1234.74594	1234.71912	3.85
$[SO_3H]^-$ (C_1)	624.49972 624.60543 (PCM)	623.86938	623.86378	1.24
$[SO_3H]^-\cdot H_2O$ (**13**)	700.96355 701.05553 (PCM)	700.23408	700.22635	0.54
$[SO_3H]^-\cdot 2H_2O$ (**14**)	777.42162	776.59606	776.58585	1.16
$[SO_3H]^-\cdot 3H_2O$ (**15**)	853.86640	852.95636	852.94221	0.73
$[SO_3H]^-\cdot 3H_2O$ (**15a**)	853.87109	852.95576	852.94243	2.33
$[SO_3H]^-\cdot 4H_2O$ (**16**)	930.32759	929.31608	929.30028	1.54
$[SO_3H]^-\cdot 5H_2O$ (**17**)	1006.78245	1005.67751	1005.65900	1.31
$[SO_3H]^-\cdot 6H_2O$ (**18**)	1083.23304 1083.30542 (PCM)	1082.03596	1082.01487	3.36
$[SO_3H]^-\cdot 6H_2O$ (**18a**)	1083.22901	1082.03365	1082.01202	2.83
$[SO_3H]^-\cdot 6H_2O$ (**18b**)	1083.22688	1082.03039	1082.00901	2.36
$[SO_3H]^-\cdot 8H_2O$ (**19**)	1236.13767	1234.74939	1234.72349	3.49

The findings for the hydrates are similar. At the DFT level all the hydrates of $[SO_3H]^-$ are more stable than those of $[HSO_3]^-$, even for $n = 1$. In contrast, at the G3X(MP2) level the situation is more complex. Up to $n = 4$ the hydrates of the sulfonate ion are all more stable than those of the hydrogensulfite ion. The enthalpy difference at 298 K varies between 19.2 kJ mol^{-1} for $n = 1$, 18.2 kJ mol^{-1} for $n = 2$ and 19.5 kJ mol^{-1} for $n = 3$, but the tetrahydrate $[HSO_3]^-\cdot 4H_2O$ (**9**) is only 9.5 kJ mol^{-1} more stable than its isomer $[SO_3H]^-\cdot 4H_2O$ (**16**). With five and six water molecules the stability of the hydrated anions is reversed. On the basis of its enthalpy at 298 K, the pentahydrate $[SO_3H]^-\cdot 5H_2O$ (**17**) is by 7.1 kJ mol^{-1} more stable than its sulfonate isomer **10**, but with the hexahydrates **18** and **11** the enthalpy difference is just 0.7 kJ mol^{-1} in favor of the hydrogensulfite **18**. Thus, it seems that at least five molecules of H_2O are needed to confirm the experimentally established order of relative stabilities of these solvated anions.

The reason for this order of relative stabilities can be seen from the data in Table 3, which contains the binding enthalpies (*B.E.*) of the water molecules in the various hydrates of the anions $[HSO_3]^-$ and $[SO_3H]^-$. As expected, the binding enthalpies per water molecule (*B.E./n*) decrease with increasing hydration because of the distribution of the negative ion charge over a larger molecule, but this decrease is larger for the sulfonate ion than for the hydrogensulfite anion. Therefore, the hydration stabilizes the latter over the former for $n > 4$ since the difference in binding enthalpies (*B.E.*2 – *B.E.*1) exceeds the difference of the free unsolvated ion enthalpies (21.9 kJ mol^{-1} at 298 K) for $n > 4$, in agreement with the experimental findings discussed in the Introduction.

Table 3. Binding enthalpies (*B.E.*)[a] at 298 K of the most stable hydrates of the sulfonate and hydrogensulfite anions with respect to their separate components $[SHO_3]^-$ and nH_2O, calculated at the G3X(MP2) level of theory (n: number of water molecules). The binding enthalpies per water molecule (*B.E./n*) decrease with increasing water content n.

n	1	2	3	4	5	6
*B.E.*1 ($[HSO_3]^-\cdot nH_2O$)	57.0	107.9	153.2	190.6	223.7	272.3
*B.E.*1/*n*	57.0	54.0	51.1	47.7	44.7	45.4
*B.E.*2 ($[SO_3H]^-\cdot nH_2O$)	59.8	111.5	155.1	203.1	252.8	295.0
*B.E.*2/*n*	59.8	55.8	51.7	50.8	50.6	49.2
*B.E.*2 – *B.E.*1	+2.1	+3.6	+1.9	+12.5	+29.1	+22.7

[a] Reaction enthalpies for the dissociation of the hydrates into their $n + 1$ components.

As mentioned above, at the B3LYP/6-31G(2df,p) level the energy difference at the potential energy minimum between the two anions $[HSO_3]^-$ and $[SO_3H]^-$ is 12.5 kJ mol^{-1} in favor of the sulfonate ion. This energy difference shrinks to 9.8 kJ mol^{-1} if the PCM method is applied by using the gas-phase geometries without further optimization and a dielectric constant of 80 for liquid water. This order of relative energies is reversed in the case of the monohydrates, since $[SO_3H]^-\cdot H_2O$ (**6**) is by 6.7 kJ mol^{-1} more stable in the polar continuum than $[HSO_3]^-\cdot H_2O$ (**13**). In the case of the two hexahydrates the hydrogensulfite **18** is more stable than the sulfonate **11** in a polar continuum, by 19.3 kJ mol^{-1} (see Table 2). The latter results are in line with the experimental observations mentioned in the Introduction. Thus, one has to conclude that the DFT energies of the *gaseous* species are unreliable in this case, and only the DFT-PCM or G3X(MP2) calculations of the hydrates yield relative stabilities in agreement with the various experiments.

Voegele et al. studied the reaction energies and activation barriers for the conversion of gaseous sulfonate to hydrogensulfite anions, both without water and with one or two water molecules of hydration.[13] The structures of the mono- and dihydrates calculated by these authors at the B3LYP/6-31+G(d) level are very different from our structures and cannot correspond to the global minima structures since the number of hydrogen bonds is much smaller than with our structures. These authors did not confirm that the vibrational frequencies of their hydrate structures were all real. We therefore conclude that the reaction energies and activation energies (barrier heights) calculated from these artificial structures are of little physical significance. In addition, only DFT energies were reported, which are unreliable as outlined above.

Biochemical Implications

Sulfur dioxide and sulfite ions are toxic to plants, microorganisms as well as animals. The detoxification strategies of organisms use either the reduction of sulfite to sulfide (catalyzed by Fe_4S_4-containing enzymes called sulfite reductases[34]) or the oxidation of sulfite to sulfate by the molybdoenzyme sulfite oxidase.[35] In the oxidized form of this enzyme the molybdenum atom is of oxidation number +6 and coordinated by three thiolate groups as well as by two terminal oxygen atoms, i.e. $(RS)_3Mo(=O)_2$. The interaction of the $[SO_3H]^-$ ion with the catalytic center may occur either by connecting one of its terminal and strong negatively charged oxygen atoms to the metal atom establishing a coordinate O→Mo bond. Alternatively, the three-coordinate and positively charged sulfur atom of $[SO_3H]^-$ may bind to one of the terminal oxygen atoms of the metal center because of their opposite atomic charges (O→S). After this primary interaction, an oxygen transfer reaction between Mo and S takes place forming a sulfate anion and leaving the molybdenum atom in the oxidation state +4. Sarkar et al.[34] have tried to decide between the above-described coordination alternatives by using calculated atomic charges of model complexes and the naked $[SO_3H]^-$ anion and came to the conclusion that the hydrogensulfite ion is linked to the molybdenum atom by a metal–oxygen rather than a sulfur–oxygen bond. However, the sulfonate anion, as well as the water of hydration, was not taken into account in these studies. Therefore, we have calculated the NPA atomic charges of the two isomeric $[SHO_3]^-$ ions as well as of their mono- and hexahydrates. The data in Table 4 demonstrate that both the water of hydration and the polar continuum have almost no impact on the atomic charges of the terminal oxygen atoms of $[SO_3H]^-$, which are calculated as –1.7±0.1. However, the positive charge on the sulfur atom increases from 1.67 in the gas phase to 1.68 in the polar continuum to 1.72 for the gaseous monohydrate **13** and further to 1.78 for the gaseous hexahydrate **18**. Thus, the ion is polarized and, therefore, activated by the network of hydrogen bonds. The total charge of the $[SO_3H]^-$ unit of **18** is only –0.87, i.e. 0.13 electrons have been transferred to the water molecules. In the case of the sulfonate ion neither the polar continuum nor the water of hydration changes the charge on the terminal oxygen atoms noticeably. In the case of the hexahydrate **11**, 0.14 electrons have been transferred from the $[HSO_3]^-$ unit to the water molecules. Since the atomic charges on the oxygen atoms of **11** (–1.05) are practically identical to those of the hydrogensulfite isomer **18** (–1.07), it can be expected that both ions interact with the molybdenum center of the sulfite reductase by a coordinate O→Mo bond. The reaction mechanism of the enzymatic sulfite oxidation may therefore be more complex than previously thought.

Table 4. Atomic charges of the sulfonate and hydrogensulfite ions both in the gas phase and in a polar continuum as well as of the gaseous mono- and hexahydrates, calculated by a natural population analysis (NPA) at the B3LYP/6-31G(2df,p) level.

Atom	S	$O_{terminal}$	O(H)	H
$[HSO_3]^-$ (gas phase)	+2.29	–1.06	–	–0.12
$[HSO_3]^-$ (PCM)	+2.27	–1.08	–	–0.03
$[HSO_3]^-\cdot H_2O$ (**6**)	+2.30	–1.06	–	–0.09
$[HSO_3]^-\cdot 6H_2O$ (**11**)	+2.30	–1.05	–	–0.01
$[SO_3H]^-$ (gas phase)	+1.67	–1.06	–0.99	+0.44
$[SO_3H]^-$ (PCM)	+1.68	–1.08	–1.00	+0.49
$[SO_3H]^-\cdot H_2O$ (**13**)	+1.72	–1.06	–0.99	+0.47
$[SO_3H]^-\cdot 6H_2O$ (**18**)	+1.78	–1.07±0.02	–1.02	+0.50

The interaction of the hydrated hydrogensulfite anion with the Mo-cofactor deeply "buried" inside the enzyme evidently requires that most of the water molecules are stripped of the anion. This endothermic process is expected to influence the thermodynamics of the enzymatic reaction studied by Sarkar et al.[36] who used only gas-phase model species without any solvation. On the other hand, the walls of the pocket containing the Mo-cofactor binding site are formed by amino acids with various polar groups[35] that are also suitable for forming hydrogen bonds to the two tautomeric sulfite anions $[SHO_3]^-$. Which of the two anions is oxidized at a higher rate under these conditions remains to be found out.

Vibrational Spectra of $[HSO_3]^-\cdot nH_2O$ and $[SO_3H]^-\cdot nH_2O$

The calculated vibrational spectra of the hydrates of the sulfonate and hydrogensulfite anions may be compared with the experimental Raman spectra of aqueous sulfite solutions to confirm the assignment of those fundamental modes that have previously been used to derive the molar ratio of the two isomeric anions as outlined in the Introduction. Unfortunately, most of the vibrations of the hydrated anions are strongly coupled with each other due to the low molecular symmetry. Nevertheless, certain trends can be derived.

The SH stretching mode of the sulfonate ion $[HSO_3]^-$ shifts on hydration from 2310 cm^{-1} in the free ion to 2369 cm^{-1} ($n = 1$), 2415 cm^{-1} ($n = 2$), 2454 cm^{-1} ($n = 3$), and 2488 cm^{-1} ($n = 4$) to 2530 cm^{-1} for the higher hydrates with $n = 5$ and 6 (unscaled values). For aqueous $Na[HSO_3]$ this mode is observed at 2535 cm^{-1} and for solid $Cs[HSO_3]$ at 2573 cm^{-1}.[16] These data are in line with our result showing that the SH group is not involved in any hydrogen bonding.

A different trend is calculated for the symmetric SO_3 stretching mode of $[HSO_3]^-$, which moves slightly from 1046 cm^{-1} for the free ion to 1041 cm^{-1} ($n = 1$), 1038 cm^{-1} ($n = 2$), 1034 cm^{-1} ($n = 3$), 1037 cm^{-1} ($n = 4$), 1032 cm^{-1} ($n = 5$), and 1040 cm^{-1} ($n = 6$) to 1028 cm^{-1} for $n = 8$. The experimental value for solid $Cs[HSO_3]$ is 1025 cm^{-1},[16] but for aqueous $Na[HSO_3]$ the assignment is uncertain. At pH values close to 4.0 such solutions exhibit two neighboring Raman lines at 1053 and 1025 cm^{-1}. Whereas Littlejohn et al.[15] assigned these lines to the symmetric stretching mode of the SO_3 group of the sulfonate ion (1053 cm^{-1}) and to the corresponding mode of the SO_2 unit of the hydrogensulfite anion (1025 cm^{-1}), Risberg et al.[16] preferred the reverse assignment. Our calculations support the assignment by Littlejohn et al., since the two octahydrates clearly show the sulfonate ion to exhibit the higher wavenumber for the symmetric SO stretching vibrations (see also below). Furthermore, the intensity ratio of these Raman lines, $Q_2 = I(1025)/I(1053)$, has been reported to decrease with increasing temperature.[15] Since the sulfonate ion is the less stable species in water, its equilibrium concentration will increase on heating. Thus, the 1053 cm^{-1} line should be assigned to $\nu_s(SO_3)$ of this ion.

In the case of the hydrogensulfite hydrates $[SO_3H]^-\cdot nH_2O$ the frequency assignments are more difficult because of the low symmetry of the central anion and the resulting coupling between modes of similar frequency. However, the symmetric SO_2 stretching mode may be identified from the calculated data. For the solvates with $n > 4$, its wavenumber is nearly identical to the corresponding mode of the isomeric sulfonate anions. For free $[SO_3H]^-$ a wavenumber of 1019 cm^{-1} is calculated for $\nu_s(SO_2)$, which on hydration of the anion moves slightly from 1032 cm^{-1} ($n = 1$) to 1038 cm^{-1} ($n = 2$) and 1037 cm^{-1} ($n = 4$) to 1019 cm^{-1} for $n = 8$. A Raman line at 1025 cm^{-1} for aqueous $Na[SHO_3]$ has previously been assigned to this mode[15] (see the discussion above).

Recently, the interaction of SO_2 with liquid water[37] and with very cold ice crystals[38] has been studied by IR spectroscopy. Besides the fundamental and combination vibrations of H_2O and SO_2 a number of additional but very weak absorption bands in the region 1000–1250 cm^{-1} have been observed and interpreted as an indication of the formation of ionic species such as $[HSO_3(aq)]^-$ and $[SO_3H(aq)]^-$. The well-known absorption bands of $[SO_3]^{2-}$ and $[S_2O_5]^{2-}$[39] were absent in these spectra. To assign the observed weak features we compare the published spectra with those calculated for the two hexahydrates of $[HSO_3]^-\cdot 6H_2O$ (**11**) and $[SO_3H]^-\cdot 6H_2O$ (**18**), which for the regions 900–1400 cm^{-1} are given in Tables 5 and 6. In this region, the hexahydrate of SO_2 (**5**) has just three absorption bands at 966 (0.10), 1140 (0.09), and 1278 (0.36) cm^{-1} (relative IR intensities in parentheses). These signals originate basically from a wagging motion of H_2O (966 cm^{-1}) and from the symmetric and asymmetric SO stretching modes of SO_2.

Table 5. Vibrational frequencies of the hexahydrate $[HSO_3]^-\cdot 6H_2O$ in the region 900–1400 cm^{-1} together with relative IR intensities, calculated at the B3LYP/6-31G(2df,p) level of theory (unscaled values; ν: stretching, δ: bending, ω: wagging mode).

Wavenumber [cm^{-1}]	Relative IR intensity [arbitrary units]	Assignment	Aqueous SO_2[37] [cm^{-1}]
1036	0.13	$\nu_s(SO_3)$	1047
1061	0.03	$\omega(H_2O)$	
1114	0.00	$\delta(HSO) + \nu_s(SO_3)$	
1141	0.01	$\delta(HSO) + \nu_{as}(SO_3)$	
1217	0.63	$\nu_{as}(SO_3) + \delta(HSO)$	1203
1244	0.53	$\nu_{as}(SO_3) + \delta(HSO)$	1224

Table 6. Vibrational frequencies of the hexahydrate $[SO_3H]^-\cdot 6H_2O$ in the region 900–1400 cm^{-1} together with relative IR intensities, calculated at the B3LYP/6-31G(2df,p) level of theory (unscaled values; ν: stretching, δ: bending, τ: torsion, ω: wagging mode).

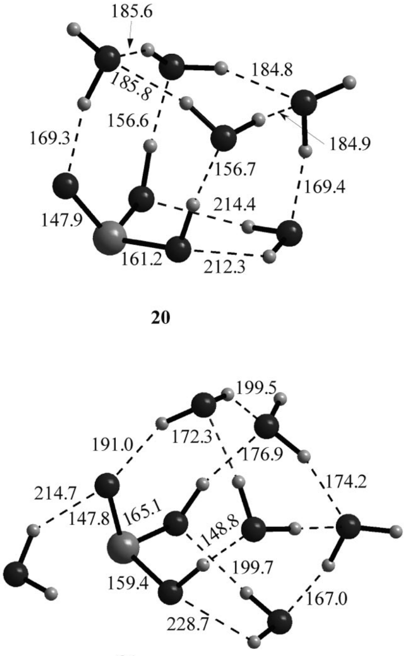
Wavenumber [cm^{-1}]	Relative IR intensity [arbitrary units]	Assignment	Aqueous SO_2[37] [cm^{-1}]
988	0.09	$\nu_s(SO_2) + \delta(HSO)$	
1005	0.40	$\nu_s(SO_2) + \omega(H_2O)$	1021
1075	0.10	$\nu_{as}(SO_2) + \tau(S–OH)$	1063
1106	0.32	$\nu_{as}(SO_2) + \tau(S–OH)$	
1356	0.05	$\delta(SOH)$	

The data in Table 5 show that the vibrations $\delta(HSO)$ and $\nu_{as}(SO_3)$, which are degenerate in the free sulfonate ion, split into two neighboring components in the hexahydrate **11**, which is of C_1 symmetry.

For aqueous SO_2 the mentioned novel IR absorptions have been observed at 1021, 1047, 1063, 1203, and 1224 cm^{-1}[37], which on the basis of the data in Tables 5 and 6 can all be ascribed to a mixture of solvated sulfonate and hydrogensulfite anions without the need for any further species (see the fourth columns of Tables 5 and 6). The spectra of SO_2 monolayers on deep-frozen ice crystals exhibit a broad absorption region between 1000 and 1064 cm^{-1} as well as a similar feature at 1120 cm^{-1}.[38] These bands also fit the expectations from a solvated sulfonate-hydrogensulfite mixture as given in Tables 5 and 6. Thus, the aqueous SO_2 solution can now be considered as spectroscopically well understood. The fact that disulfite has not been observed in these systems can be explained by the low concentration of the two monoanions, which make reaction (3) unfavorable. In the case of SO_2 adsorbed on ice crystals there is a possibility that in addition to the monoanions the undissociated sulfurous acid is present. This aspect will be discussed below.

Hydrates of Sulfurous Acid H_2SO_3

In previous publications only the lower hydrates of SO_2 with n = 1–3 have been studied with regard to a proton-shift reaction with the formation of hydrated sulfurous acid.[27] We have tried to generate a hydrated ion-pair $[H_3O]$-$[SO_3H]$ from the structure of $SO_2·6H_2O$ (**5**) by shifting two protons, and also from $[SO_3H]^-·nH_2O$ [n = 5 (**17**), 6 (**18**)] by protonation of the water molecule that is farthest away from the anion. However, all these attempts were unsuccessful, since the structure optimizations led to hydrates of undissociated sulfurous acid, $H_2SO_3·nH_2O$ [n = 5 (**20**), 6 (**21**)]. The structures of these species are shown in Figure 8; their energies are given in Table S1 in the Supporting Information.



20

21

Figure 8. Structures of the hydrates **20** and **21** of sulfurous acid calculated at the B3LYP/6-31G(2df,p) level of theory (internuclear distances in pm). Species **20** is nearly of C_s symmetry.

The most stable pentahydrate of H_2SO_3 (**20**) forms a cluster-like structure that is practically of C_s symmetry and has all water molecules on the same side of the acid molecule with 10 hydrogen bonds and only two dangling H atoms. The two torsion angles τ(HOS=O) are ±32.5°. The binding energy per water molecule (40.9 $kJ\,mol^{-1}$) is larger than that of the SO_2 hydrates discussed above (ca. 20 $kJ\,mol^{-1}$) but smaller than the corresponding hydrates of the monoanions of the acid (45–50 $kJ\,mol^{-1}$; Table 3). Interestingly, the conversion of $SO_2·6H_2O$ (**5**) into its isomer $H_2SO_3·5H_2O$ (**20**) is exothermic ($\Delta H°_{298}$ = –56.1 $kJ\,mol^{-1}$) and exergonic ($\Delta G°_{298}$ = –22.5 $kJ\,mol^{-1}$).[40] In addition, two less symmetrical isomers of $H_2SO_3·5H_2O$ (**20a**, **20b**) corresponding to energy minima of the PES have been identified (see Table S1). The hexahydrate **21** is characterized by 11 hydrogen bonds and three dangling H atoms.

The molecular vibrations of the hydrated sulfurous acid molecules are even more coupled than those of the hydrated anions. This is probably due to the strong hydrogen bonds between the acidic OH group and the surrounding water molecules. As a consequence, even the stretching mode of the formal S=O double bond is calculated at quite different wavenumbers as the following data show: 1140 (**20**), 1080 (**20a**), 1164 (**20b**), 1137 (**21**) cm^{-1}. This vibration is always coupled with bending or torsion modes of the SOH groups. For the free molecule H_2SO_3 the S=O stretch is predicted at 1256 cm^{-1} (coupled with δ_{SOH}). In the region 900–1400 cm^{-1} the hydrates also exhibit SOH bending, O=SOH torsion, and HOH wagging modes, which make it difficult to decide whether or not sulfurous acid molecules are a component of the samples prepared by adsorbing SO_2 on the surface of cold ice crystals as discussed above. However, the prediction that the conversion of hydrated SO_2 into hydrates of H_2SO_3 is exothermic and exergonic indicates that H_2SO_3 is likely to be present on such surfaces in addition to its anions.

The OH stretching modes of the asymmetrical H_2SO_3 hydrates are strongly coupled to stretching modes of the water molecules. Therefore, the corresponding signals in the vibrational spectra of **20a**, **20b**, and **21** are not very characteristic. Only the C_s-symmetrical species **20** is predicted to have two nearly pure SO–H stretching modes at 2755 (a′) and 2665 cm^{-1} (a″); both are expected to be of high IR intensity. The S–OH stretching modes of this hydrate are calculated at 840 (a′) and 814 cm^{-1} (a″), but their IR intensities are low. For free H_2SO_3 the O–H stretching vibrations are predicted at 3709 (a′) and 3706 cm^{-1} (a″). The large wavenumber shift of these modes on hydration proves the strength of the corresponding hydrogen bonds.

Conclusions

With an increasing number of water molecules SO_2 forms cluster-like hydrates, in which the components are strongly hydrogen-bonded with an average binding energy per H_2O molecule of about 20 $kJ\,mol^{-1}$ at the G3X(MP2) level of theory. As with the microsolvation of other neutral molecules such as H_2S,[41] the SO_2 unit remains at the surface of the water cluster, since the sulfur atom does not take part in the hydrogen-bonding network as long as the number of water molecules remains as small as six. The calculated vibrational spectra of the species $SO_2·nH_2O$ are in agreement with the very few reported IR spectra of the corresponding complexes between SO_2 and H_2O (n = 1, 2); the higher hydrates of SO_2 have not yet been studied spectroscopically. The isomerization of $SO_2·6H_2O$ to solvated sulfurous acid $H_2SO_3·5H_2O$ is predicted to be exothermic and exergonic.

The solvated sulfonate ions $[HSO_3]^-·nH_2O$ and the tautomeric hydrogensulfite anions $[SO_3H]^-·nH_2O$ were studied for the first time with up to eight water molecules. For n > 3 several isomeric structures were obtained, in which the arrangement of the water molecules differs. Whereas at the

B3LYP/6-31G(2df,p) level the hydrated sulfonate anions are predicted to always be less stable than the corresponding hydrogensulfite ions, this result does not persist at the higher G3X(MP2) level of theory. At this level only the hydrogensulfite ions with more than four water molecules are more stable than the sulfonate species, in agreement with experimental studies on aqueous sulfite solutions. The main reason for this reversal of relative energy is the larger binding energy per water molecule for the $[SO_3H]^-·nH_2O$ species. By using the polar continuum model (PCM), the energies of *all* hydrogensulfite hydrates are lower than those of the sulfonate hydrates, but the relative energies of free ions are reversed as in the gas phase. Several literature reports on the structures and relative stabilities of the tautomeric species $[HSO_3]^-·nH_2O$ and $[SO_3H]^-·nH_2O$ based on DFT calculations are shown to be in error.

The symmetrical SO stretching vibrations of the two types of solvated anions are in agreement with the reported Raman and IR spectra of $Cs[HSO_3]$ and of aqueous sodium sulfite solutions at pH values of about 4. Our computed spectra of these anions allowed the assignment of absorption bands in the published IR spectra of aqueous SO_2 and of SO_2 adsorbed on ice nanocrystals at 128 K.

Computational Details

The structures and energies of the various complexes were examined according to the G3X(MP2) theory[18] by using the GAUSSIAN 03[42] program package. This composite method corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy calculations together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2)[43] theory with three important changes: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large basis set for the second-row atoms at the Hartree–Fock level. All three features are particularly important for the proper description of sulfur-containing species as examined in this work. In the light of the rather large basis set, no basis set superposition corrections were carried out. Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real. The wavenumbers given are unscaled. For all investigated species a charge density analysis was performed by using the natural bond orbital (NBO) approach based on the B3LYP/6-31G(2df,p) wavefunction.[44] Such atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[45] As far as gas-phase species are concerned, all relative energies and enthalpies reported in the text correspond to the G3X(MP2) level, whereas all reported structural parameters correspond to the B3LYP/6-31G(2df,p) level. Some of the investigated complexes are characterized by large dipole moments. Therefore, it was to be expected that the thermodynamics of such species in the solid state and in polar solvents would be quite different from that in the gas phase. In order to study the influence of a polar environment, calculations according to Tomasi's polar continuum model (PCM)[46] were carried out at the B3LYP/6-31G(2df,p) level. In this model the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ε). The solute is assumed to be embedded in a cavity of the medium. The permanent dipole of the solute induces a dipole in the medium, which in turn interacts with the molecular dipole leading to stabilization. A dielectric constant of 80.0 was used for the PCM calculations to represent the aqueous phase, but no geometry optimization was performed.

Supporting Information (see footnote on the first page of this article): Atomic coordinates of all calculated species, absolute energies of sulfurous acid (Table S1) and figures of the octahydrates of the sulfonate and hydrogensulfite anions.

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