



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Icarus ●●●(●●●)●●●-●●●

ICARUS

www.elsevier.com/locate/icarus

Sulfurous acid (H₂SO₃) on Io?

Andreas F. Voegelé,* Thomas Loerting,¹ Christofer S. Tautermann, Andreas Hallbrucker, Erwin Mayer, and Klaus R. Liedl

Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Received 17 February 2003; revised 16 October 2003

Abstract

Sulfurous acid (H₂SO₃) has never been characterized or isolated on Earth. This is caused by the unfavorable conditions for H₂SO₃ within Earth's atmosphere due to the high temperatures, the high water content and the oxidizing environment. Kinetic investigations by means of transition state theory showed that the half-life of H₂SO₃ at 300 K is 1 day but at 100 K it is increased to 2.7 billion years. Natural conditions to form H₂SO₃ presumably require cryogenic SO₂ or SO₂/H₂O mixtures and high energy proton irradiation at temperatures around 100 K. Such conditions can be found on the Jupiter moons Io and Europa. Therefore, we calculated IR-spectra of H₂SO₃ which we compared with Galileo's spectra of Io and Europa. From the available data we surmise that H₂SO₃ is present on Io and probably but to a smaller extent on Europa.

© 2003 Elsevier Inc. All rights reserved.

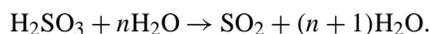
Keywords: Io; Satellites of Jupiter; Satellites, atmospheres; Spectroscopy

1. Introduction

Annually more than 100 millions of tons of sulfur are emitted into Earth's atmosphere. The majority of this sulfur is released as sulfur dioxide (SO₂) or dimethyl sulfide (DMS), which is subsequently oxidized in a multistep process to SO₂ (Graedel and Crutzen, 1994). Next, SO₂ is oxidized almost completely to SO₃ which is finally hydrated to sulfuric acid (H₂SO₄) (Stockwell and Calvert, 1983). However, it is quite remarkable that even though most of the sulfur species in atmosphere pass the stage of SO₂, the hydration product of SO₂ sulfurous acid (H₂SO₃) has never been found. In comparison, other acid anhydrides such as SO₃ or N₂O₅ (Wayne, 1991) are hydrated in atmosphere despite relatively high barriers for these reactions (Chen and Moore Plummer, 1985; Akhmatkaya et al., 1997; Hanway and Tao, 1998; Loerting and Liedl, 2000; Voegelé et al., 2003).

Thermodynamically it is well documented that H₂SO₃ is unstable by a few kcal mol⁻¹ compared to its dissoci-

ation products SO₂ and H₂O. Besides the thermodynamic instability, Li and McKee (1997) demonstrated theoretically that H₂SO₃ is catalytically destroyed by water molecules decreasing also the kinetic stability. This process becomes stronger with an increasing number of water molecules



However, similar to H₂SO₃ also carbonic acid (H₂CO₃) has long been believed to be a substance that is not characterizable because of its thermodynamic and kinetic instability. Yet, in the 1990s it was not only possible to prepare carbonic acid (Moore and Khanna, 1991; Hage et al., 1993; Brucato et al., 1997) but also to show its remarkable kinetic stability (Hage et al., 1998; Loerting et al., 2000). Different studies revealed, that H₂CO₃ is presumably present on Mars, in comets, and probably in interstellar icy grains (Brucato et al., 1997; Hage et al., 1998). The kinetic stability of H₂CO₃ was demonstrated by sublimation and recondensation studies of carbonic acid (Hage et al., 1998) and by transition state theory considerations (Loerting et al., 2000). Important requirements that favor the kinetic stability of carbonic acid are low temperatures and low humidity, otherwise H₂CO₃ is catalytically destroyed by water (Loerting et al., 2000) comparable to H₂SO₃.

Considering the similar findings between H₂CO₃ and H₂SO₃, one may think of conditions under which H₂SO₃

* Corresponding author.

E-mail address: andreas.voegelé@uibk.ac.at (A.F. Voegelé).

¹ Present Address: Department of Earth, Atmosphere and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Av., Cambridge, MA 02139-4307, USA.

is stable and in a next step characterizable as it was already possible for H_2CO_3 . In a recent study we have investigated the kinetic and thermodynamic properties of H_2SO_3 and we have shown that a sulfurous acid dimer is thermodynamically stable (Voegele et al., 2002). In this study, we reanalyze the stability of H_2SO_3 in more detail in comparison with H_2CO_3 . Conditions that favor the formation and existence of H_2SO_3 are discussed. Additionally, we deduce spectroscopic properties of H_2SO_3 which we compare with available spectroscopic data from our solar system and provide evidence for the existence of H_2SO_3 .

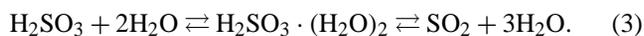
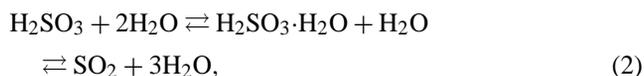
2. Methods

The details of the calculations and methods have been presented elsewhere (Loerting et al., 2000; Loerting and Liedl, 2001; Voegele et al., 2002), here we briefly summarize the concepts. Stationary points were calculated by hybrid density functional theory B3LYP/6-31 + G(d) and B3LYP/6-31G(d) (Stephens et al., 1994). The nature of the stationary points was confirmed by vibrational analysis. Saddle points were optimized with the three-structure quadratic synchronous transit guided approach (Peng et al., 1996). Reactant, product, and transition state were also calculated with the high-level method G3//B3LYP (Baboul et al., 1999). This method is accurate within $0.99 \text{ kcal mol}^{-1}$ average absolute deviation compared to an experimental test set of 299 energies which was taken from the G2/97 set. The maximum deviation in this test set was $3.8 \text{ kcal mol}^{-1}$. This range of deviation has to be considered when discussing the results.

Variational transition state theory (VTST) including tunneling corrections was applied to calculate reaction rates (Eyring, 1935; Truhlar, 1995). The potential energy surface (PES) was calculated by hybrid density functional theory B3LYP with the 6-31 + G(d) basis set which is a good description of the PES for our purpose (Märker et al., 1997). The minimum energy path, which is the path of least energy connecting products and reactants, was described in internal mass-weighted coordinates using the Page–McIver algorithm (Page and McIver, 1988) at a step size of $0.05 \text{ amu}^{1/2} \text{ bohr}$. Vibrational analysis was performed every third step. The PES was interpolated to the high-level G3//B3LYP points according to an interpolation scheme which also maps the harmonic frequencies and moments of inertia onto the high-level data (Hu et al., 1994; Chuang and Truhlar, 1997). Quantum mechanical corrections were applied to the VTST result using the small-curvature tunneling (Baldrige et al., 1989) and large-curvature tunneling corrections (Liu et al., 1993; Fernández-Ramos and Truhlar, 2001). SCT is considered by means of the centrifugal dominant small curvature semiclassical adiabatic ground state tunneling method according to the concept of Marcus and Coltrin (Marcus and Coltrin, 1977; Skodje et al., 1981; Baldrige et al., 1989). The LCT correction assumes that

tunneling occurs by using a series of straight line connections between reactant and the product valley in the reaction swath. The large curvature ground state approximation version 4 (LCG4) (Fernández-Ramos and Truhlar, 2001) was used. The approximation that best describes tunneling is determined according to the microcanonical optimized multi-dimensional tunneling (μOMT) method. As a result we obtained unimolecular reaction rate constants with tunneling corrections $k_{\text{uni}}^{\mu\text{OMT, VTST}}$.

From the obtained unimolecular reaction rate constants, which assume that the reaction complex has already formed, we calculated higher-molecular rate constants for the mechanisms which include formation of the preassociation-complex:



Similarly the reverse reactions, i.e., the hydration reactions of SO_2 , were calculated. These reaction rate constants are obtained according to our previous studies (Loerting and Liedl, 2000; Voegele et al., 2003):

$$k_n = K^{\text{preass}} k_{\text{uni}}^{\mu\text{OMT, VTST}} \quad (4)$$

with K^{preass} representing the preassociation constant for forming the complex. The rate constant k_n was converted into correct units by multiplication with the factor $f = (1.363 \times 10^{-22} T)^n \text{ cm}^{3n} \text{ atm}^n$. With the VTST approach there is no difference from the kinetic point of view between mechanism (1) and mechanism (2), since for a VTST calculation only information of the reaction complex and the transition state are used. VTST defines the “free” or not complexed water molecule to be infinitely far away, so there is no influence of this molecule on the calculation.

Stationary points were calculated with the Gaussian98 program package (Frisch et al., 1998) and VTST calculations were performed with Polyrate9.0 (Corchado et al., 2002b) and Gaussrate9.0 (Corchado et al., 2002a). Vibrational frequencies were determined at the MP2/aug-cc-pVTZ (Møller and Plesset, 1934; Dunning, 1989) level of theory. These harmonic frequencies were multiplied by a scale factor to better account for anharmonic effects (for both considerations see Table 2).

Half-lives of H_2SO_3 and H_2CO_3 were calculated from the reaction rate constants of decomposition. The investigated systems are either the free acid, the monohydrate or the dihydrate. In all cases the decomposition reaction is described as a unimolecular reaction. To determine the half-lives ($t_{1/2}$) we used the unimolecular rate constants of the VTST approach ($k_{\text{uni}}^{\mu\text{OMT, VTST}}$) and converted it according to the formula (Atkins, 1994)

$$t_{1/2} = \frac{\ln 2}{k_{\text{uni}}^{\mu\text{OMT, VTST}}}$$

3. Results and discussion

We have investigated the half-life of H_2SO_3 as a function of temperature and as a function of the water concentration and compared it with H_2CO_3 . In detail, the reactions of H_2SO_3 with $n = 0, 1$, and 2 water molecules in the temperature range 75–350 K were investigated according to the mechanisms



A detailed characterization with reaction mechanisms, reaction rates, isotope effects and tunneling contributions is presented elsewhere (Voegelé et al., 2002).

The catalytic influence of an increasing water concentration is enormous. Whereas the decomposition reaction of pure H_2SO_3 in the absence of water (reaction (5)) has a reaction barrier of $30.0 \text{ kcal mol}^{-1}$, the influence of one catalytic water molecule lowers the barrier (reaction (6)) to $17.4 \text{ kcal mol}^{-1}$. In a reaction complex with a second water molecule (reaction (7)), the barrier is only $9.0 \text{ kcal mol}^{-1}$ at the G3//B3LYP level of theory.

Figure 1 shows the expected half-life of H_2SO_3 as a function of temperature and depending on the number of water molecules in the vicinity of the system. For comparison, the half-life of H_2CO_3 is also shown for the same reaction mechanisms. Relatively, the stability of H_2SO_3 increases slightly more with increasing temperature than of H_2CO_3 . Nevertheless, the half-life of H_2SO_3 is generally a few orders of magnitude smaller. At 298 K, for instance, the half-life of pure H_2SO_3 is 24 h, whereas of H_2CO_3 it is 180000 years. In the presence of water (1:1 complex of $\text{H}_2\text{SO}_3:\text{H}_2\text{O}$ and of $\text{H}_2\text{CO}_3:\text{H}_2\text{O}$, respectively) the half-lives lower to 3 ms and

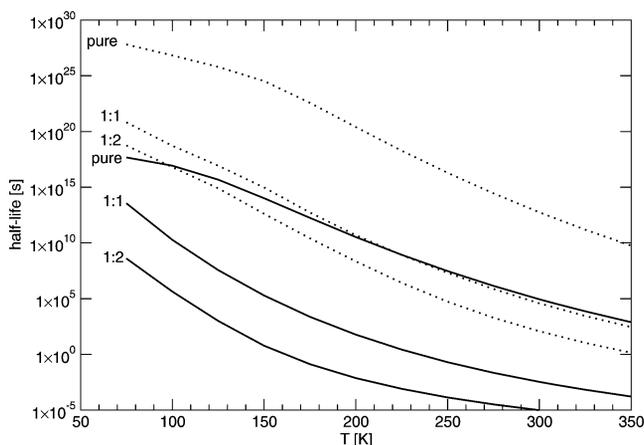


Fig. 1. Comparison of the half-lives of H_2SO_3 (solid lines) and H_2CO_3 (dotted lines) as a function of temperature. “Pure” stands for H_2SO_3 or H_2CO_3 alone, whereas the numbers beside the lines indicate the ratio of $\text{H}_2\text{SO}_3:\text{H}_2\text{O}$ and $\text{H}_2\text{CO}_3:\text{H}_2\text{O}$, respectively. (The half-lives were re-computed from the data taken from Loerting et al. (2000) for H_2CO_3 and from Voegelé et al. (2002) for H_2SO_3 according to the formula $t_{1/2} = \ln 2 / k_{\text{uni}}^{\text{VTST}}$.)

10 h, respectively. A second water molecule (1:2 complex) lowers the half-lives to 10 μs and 120 s, respectively. However, at 100 K the stability of H_2SO_3 is as high as 2.7 billion years which is four orders of magnitude more stable than the 0.18 million years of H_2CO_3 at room temperature. At 150 K the half-life of H_2SO_3 is still more than 3 million years which is more than enough for characterization since H_2CO_3 could experimentally be shown to be stable for quite a long period at room temperature (Loerting et al., 2000). Formation of the H_2SO_3 hydrates turned out to be energetically favored by at least $9.9 \text{ kcal mol}^{-1}$ for the monohydrate compared to $\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$; higher hydrates are even more favored. We were not able to locate a barrier between the separated molecules and the complex so we surmise that complex formation is barrierless. The rate of formation is therefore controlled diffusively and depends mainly on the present water concentration. Considering the reverse reactions $\text{H}_2\text{SO}_3 \cdot \text{H}_2\text{O}_n \rightarrow \text{H}_2\text{SO}_3 + n\text{H}_2\text{O}$ (complex dissociation) which seem barrierless, the rate constants of these reactions can only be estimated from the energy differences and the diffusional limit. From this considerations we calculate that the reaction rate constant $k_{\text{uni}}^{\text{TST}}$ for $n = 1$ is around $< 10^{-9} \text{ s}^{-1}$ (at 100 K) which is comparable to the rate constant of $\text{H}_2\text{SO}_3:\text{H}_2\text{O}$ decomposition into $\text{SO}_2 + 2\text{H}_2\text{O}$ (complex decomposition) with a $k_{\text{uni}}^{\text{VTST}}$ of $4 \times 10^{-11} \text{ s}^{-1}$. For higher hydrates complex decomposition predominate over complex dissociation due to two effects. First, formation of higher hydrate complexes is energetically favored and thus the dissociation rate is lower. Secondly, the decomposition rate constants increase for higher hydrate complexes making this type of reaction more important. Considering higher than first order reactions makes an evaluation possible to find out whether it is possible that such higher complexes form. Also the reverse consideration is possible to evaluate how fast the complexes dissociate (see Table 1). Knowing the water and the SO_2 concentration allows to find out which complexes are present.

Considering the findings on the half-life of H_2SO_3 , it becomes clear that Earth’s atmosphere does not provide conditions where it is possible to isolate H_2SO_3 . While the half-life of 24 h for pure H_2SO_3 would be enough for isolation, the catalytic influence of water prohibits the existence of this molecule (Voegelé et al., 2002). Additionally, Earth’s atmosphere has a very high oxidation potential and oxidants like the $\bullet\text{OH}$ radical react with SO_2 at very high rates to form higher oxides of sulfur (Lee et al., 1990; Wayne, 1991). Besides, intuitively one might expect that H_2SO_3 might form by the reaction of $\text{SO}_2 + \text{H}_2\text{O}$, however the rate of this reaction is not competitive with the rate of SO_2 oxidation (Loerting and Liedl, 2000) and it is energetically disfavored as indicated in Fig. 2. The barrier for this hydration reaction is very high and one cannot presume this reaction to proceed. Thus, required conditions to find sulfurous acid are low temperatures, low humidity and a nonoxidizing environment which are clearly not present on Earth.

Table 1

Reaction rate constants including formation of the reaction complex (a) for the formation of the sulfurous acid hydrate complexes followed by dissociation into an SO₂-water complexes (i-iii), and (b) for the formation of the SO₂-water complexes followed by formation of the sulfurous acid hydrate complexes (iv-ix)

| | Reaction | Rate constant, k_n | Units |
|------|--|------------------------|--|
| i | $a + w \rightleftharpoons a \cdot w \rightarrow b \cdot 2w$ | 5.87×10^{-42} | $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| ii | $a + 2w \rightleftharpoons a \cdot w + w \rightarrow b \cdot 2w + w$ | 5.87×10^{-42} | $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| iii | $a + 2w \rightleftharpoons a \cdot 2w \rightarrow b \cdot 3w$ | 5.86×10^{-44} | $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ |
| iv | $b + w \rightleftharpoons b \cdot w \rightarrow a$ | 1.23×10^{-72} | $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| v | $b + 2w \rightleftharpoons b \cdot w + w \rightarrow a + w$ | 1.23×10^{-72} | $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| vi | $b + 2w \rightleftharpoons b \cdot 2w \rightarrow a \cdot w$ | 2.52×10^{-71} | $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ |
| vii | $b + 3w \rightleftharpoons b \cdot w + 2w \rightarrow a + 2w$ | 1.23×10^{-72} | $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| viii | $b + 3w \rightleftharpoons b \cdot 2w + w \rightarrow a \cdot w + w$ | 2.52×10^{-71} | $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ |
| ix | $b + 3w \rightleftharpoons b \cdot 3w \rightarrow a \cdot 2w$ | 6.36×10^{-79} | $\text{cm}^9 \text{ molecule}^{-3} \text{ s}^{-1}$ |

In reactions (i), (v), (vii), and (viii) one or two water molecules are only observers and thus do not contribute to the overall mechanism. Symbols: a = H₂SO₃, b = SO₂, w = H₂O.

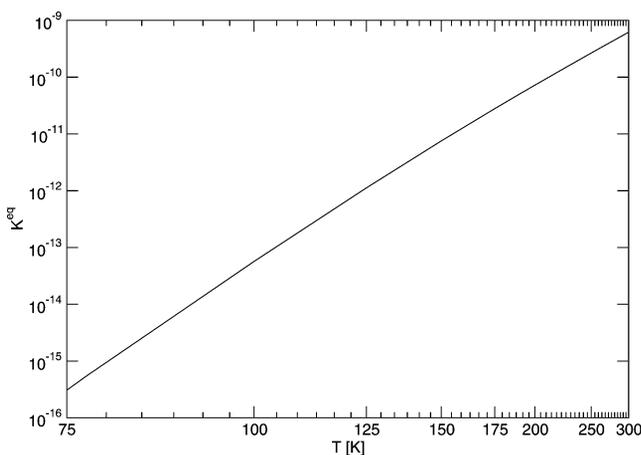


Fig. 2. Linearized representation of the equilibrium constant K^{eq} for formation of H₂SO₃ from SO₂ and H₂O. At 100 K the standard state free energy for the reaction (ΔG^0) is 6.0 kcal mol⁻¹ and at 150 K ΔG^0 is 7.6 kcal mol⁻¹ (see also Voegelé et al. (2002)).

Several solar system bodies like planets and/or their satellites have more or less dense atmospheres that also contain sulfur species. Venus, for instance contains almost the same concentrations of SO₂ and H₂O (Esposito, 1984; Na et al., 1990), but has a low concentration of oxidants. So in principal the reaction of SO₂ + H₂O to form H₂SO₃ would be possible. Yet, Venus' atmosphere is extremely dense and the temperatures there are very high with surface temperatures of up to 720 K (Wayne, 1991) caused by a strong greenhouse effect (Solomon et al., 1999; Prinn, 2001). Therefore, possibly present H₂SO₃ would decompose immediately.

A closer look at the jovian satellites reveals that at least three of the four "galilean" satellites, namely Europa, Callisto, and Io, contain measurable amounts of sulfur in their atmospheres (Showman and Malhotra, 1999). A better part of Callisto's surface is covered by water-ice and Callisto experiences strong temperature fluctuations (Showman and Malhotra, 1999). The presence of SO₂ has been demon-

strated but the relatively high temperatures (Noll et al., 1997) make formation and existence of H₂SO₃ unlikely.

On Europa, a cold and icy Jupiter moon with temperatures as low as 90 K (Urquhart and Jakosky, 1996), large amounts of sulfur, mainly in the form of SO₂, sulfate rock, and H₂SO₄ were found. These sulfur species are believed to have two different origins. On the one hand, it is supposed that sulfur compounds come from the inner core of Europa. On the other hand, it is assumed that relatively large amounts of sulfur are transported from Jupiter's inner satellite Io to the atmosphere of Europa. Part of this sulfur is deposited as H₂SO₄, MgSO₄, and Na₂SO₄ (Cheng, 1984; Kargel, 1998; McCord et al., 1998; Carlson et al., 1999)

The overall amount of SO₂ is not very high on Europa and it is difficult to guess whether the present conditions are promising for the existence of sulfurous acid. In spite of very large water concentrations compared to SO₂, the extremely low temperatures of 90 K in some regions would allow the existence of H₂SO₃ for a considerably long period (see Fig. 1). Figure 1 also reveals that the effect of a lowering in the half-life becomes smaller with an increasing number of water molecules. This is the case for both H₂SO₃ and H₂CO₃ and has been investigated in detail for H₂CO₃ (Tautermann et al., 2002). Extrapolating this effect for H₂SO₃ means that at 100 K the half-life of H₂SO₃ should be in the range of days, even if H₂SO₃ is embedded in H₂O. This period should be sufficient for characterization. Additionally, supposing that H₂SO₃ is present at the surface and in the gas-phase, we will not expect it to be surrounded by many water molecules as is the case in liquid solution. However, if H₂SO₃ is present on Europa at all then only in cold regions with temperatures around 90 K and not in "hot" regions around 140 K. Still it remains to be clarified how sulfurous acid might form on Europa. Experiments that successfully produced H₂CO₃ help us to evaluate suitable conditions. In these experiments pure CO₂, CO₂/H₂O mixtures or HCO₃⁻ samples were irradiated by proton or high energy irradiation to provide the necessary activation energy to

Table 2
Fundamental infrared harmonic vibrational frequencies in cm^{-1} of H_2SO_3

| Vibration | H_2SO_3 | | | SO_2 -monohydrate | | | SO_2 | | |
|------------|----------------------------------|--------------------------------|-------|----------------------------------|--------------------------------|-----|----------------------------------|--------------------------------|-----|
| | Unscaled (cm^{-1}) | Scaled (cm^{-1}) | I^* | Unscaled (cm^{-1}) | Scaled (cm^{-1}) | I | Unscaled (cm^{-1}) | Scaled (cm^{-1}) | I |
| ν_1 | 3698.88 | 3513.94 | 118 | 3926.82 | 3730.48 | 85 | 1305.55 | 1240.27 | 139 |
| ν_2 | 3697.16 | 3512.30 | 54 | 3803.24 | 3613.08 | 18 | 1099.40 | 1044.43 | 16 |
| ν_3 | 1254.52 | 1191.79 | 174 | 1628.11 | 1546.70 | 73 | 493.45 | 468.78 | 24 |
| ν_4 | 1107.90 | 1052.51 | 13 | 1309.00 | 1243.55 | 154 | | | |
| ν_5 | 1082.30 | 1028.19 | 59 | 1111.88 | 1056.29 | 19 | | | |
| ν_6 | 779.61 | 740.63 | 156 | 500.80 | 475.76 | 25 | | | |
| ν_7 | 769.25 | 730.79 | 355 | 243.66 | 231.48 | 10 | | | |
| ν_8 | 484.56 | 460.33 | 16 | 217.12 | 206.26 | 172 | | | |
| ν_9 | 442.02 | 419.92 | 45 | 129.60 | 123.12 | 57 | | | |
| ν_{10} | 407.47 | 387.10 | 114 | 102.84 | 97.70 | 53 | | | |
| ν_{11} | 339.61 | 322.63 | 30 | 89.37 | 84.90 | 42 | | | |
| ν_{12} | 125.50 | 119.23 | 20 | 19.53 | 18.55 | 2 | | | |

The vibrations were determined at the MP2/aug-cc-pVTZ level of theory. Unfortunately, ab initio vibrational frequencies in cm^{-1} especially for higher wave numbers are larger than the frequencies observed experimentally (Scott and Radom, 1996). Thus, the harmonic frequencies are usually multiplied by a scale factor f that accounts for anharmonic effects. For Møller-Plesset theory, the best f is around 0.95 (Scott and Radom, 1996). Therefore, frequencies multiplied by f are entitled “scaled”, whereas the raw data are entitled “unscaled”. These values can be seen as lower and upper limits, respectively. Scaled values should be used for higher frequencies, whereas unscaled values should be more accurate for lower frequencies.

* I : intensity in km mol^{-1} .

form H_2CO_3 (Moore and Khanna, 1991; Hage et al., 1993; Brucato et al., 1997). On Europa SO_2 is most likely present as a hydrate ($\text{SO}_2/\text{H}_2\text{O}$ mixture) or probably as a bisulfite ion (HSO_3^-). Similarly, the present high energy and proton irradiation on Europa could provide the necessary activation energy to form H_2SO_3 (Cooper et al., 2001). However, since sulfur is only a minor constituent of Europa, only very small traces of H_2SO_3 might be present. It is, however, unlikely at the moment to identify such small amounts of H_2SO_3 with currently available technology.

Jupiter’s innermost of the galilean satellites, Io, is covered by a compact layer of sulfur-compounds, mainly SO_2 (Pearl et al., 1979). This crust shows much resurfacing due to a high rate of volcanism but most of all due to the high gravitational forces Io encounters from Jupiter (Smith et al., 1979). Io is the driest of the four galilean Jupiter moons and temperatures around 90 to 100 K are discussed in nonvolcanic regions (Pearl et al., 1979). The low water content and the low temperatures make Io an ideal environment for H_2SO_3 . Additionally, at the conditions present on Io formation of the H_2SO_3 hydrate is unlikely. First, the water concentration is very low and secondly, the rate of $\text{H}_2\text{SO}_3 \cdot \text{H}_2\text{O}$ decomposition into $\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$ is comparably fast to decomposition into $\text{SO}_2 + 2\text{H}_2\text{O}$. Whereas in contrast to Europa the formation of H_2SO_3 from $\text{SO}_2/\text{H}_2\text{O}$ is less likely on Io, there is another possible route via dry SO_2 . Formation of H_2SO_3 might be accomplished in a similar manner as Brucato et al. (1997) synthesized carbonic acid from pure CO_2 by proton irradiation. Incoming protons hit the surface and are incorporated into the SO_2 crust (Cooper et al., 2001). This bombardment with energy and protons provides enough energy that reactions that form H_2SO_3 are facilitated. Brucato et al. (1997) demonstrated in their proton irradiation experiment of CO_2 that the reaction products are mainly H_2CO_3 and CO . This

implies a mechanism where the $\text{C}=\text{O}$ double bond is disrupted in CO_2 ; a similar mechanism might occur for SO_2 . The presence of SO_2 -hydrates would allow the same mechanism to form H_2SO_3 as described for Europa to a small extent.

Whether or not H_2SO_3 is present on Io or possibly on Europa can at the moment only be verified spectroscopically. The proposed mechanisms by which H_2SO_3 might be formed can also only be testified by experiments in combination with spectroscopic methods. Therefore, we determined the harmonic infrared-frequencies of sulfurous acid which are summed up in Table 2. Additionally, we provide theoretical spectroscopic data for SO_2 and SO_2 -monohydrate for comparison with the experimental results. Nash and Betts (1995) and Khanna et al. (1988) performed detailed spectroscopic studies of SO_2 phases at conditions comparable to those present on Io. For SO_2 -ice fundamental vibrations where determined to be at 1305, 1134, and 522 cm^{-1} . Considering that ab initio harmonic frequencies tend to be too large at higher wave numbers and slightly too small at low wave numbers (Scott and Radom, 1996), the agreement between theoretical values (unscaled) and experiment is quite good. Moore (1984) performed proton irradiation studies at low temperatures on SO_2 -ice films which were characterized by IR spectroscopy between 2900 and 400 cm^{-1} ; Moore (1984) proposed that SO_3 and a few other compounds are formed. Clearly, SO_3 is formed under these conditions. However, after irradiation new bands were observed which were assigned partially tentatively and reconsideration might be useful, namely those at 1205–1215, 1072, 750, and 468 cm^{-1} . The region of the experimental spectrum between 1150 and 1300 cm^{-1} is poorly resolved and considering the strong background of these data, one cannot exclude $\nu_3(\text{H}_2\text{SO}_3)$ to be present there. Unfortunately, ν_4 and ν_5 of

H_2SO_3 are in the same region as ν_2 of SO_2 . Still, the band at 1072 is in the $\nu_5(\text{H}_2\text{SO}_3)$ region and can serve as a first indicator. The new, very broad, and strong band at 750 cm^{-1} compared to unirradiated SO_2 is also in good agreement with ν_6 and $\nu_7(\text{H}_2\text{SO}_3)$. Similarly, the 468 cm^{-1} band has a shoulder, which is in good agreement with $\nu_9(\text{H}_2\text{SO}_3)$. Additionally, considering the findings of Nash and Betts (1995) it is probable that the used SO_2 samples of Moore (1984) are different to the conditions present on Io. However, for a really authentic assignment, spectra with higher resolution are needed in the full range of $300\text{--}3800\text{ cm}^{-1}$ which would also include ν_1 , ν_2 , ν_{11} , and ν_{12} .

To analyze whether H_2SO_3 is present on Europa or Io, we investigated the available IR spectra of the two satellites. The currently best available data for Europa and Io were obtained by Galileo's near-infrared mapping spectrometer (NIMS) (Carlson et al., 1996, 1997, 1999; Lopes-Gautier et al., 2000). These measurements are in the wavelength region $15000\text{--}3500\text{ cm}^{-1}$ for Europa and $4000\text{--}2000\text{ cm}^{-1}$ for Io. Relative to the fundamentals of H_2SO_3 , we are restricted to a region where only ν_1 and ν_2 of H_2SO_3 might be found. Comparing our spectroscopic data with the Europa spectrum in Fig. 8 of Carlson et al. (1996) one can hardly identify characteristic features at or below 3700 cm^{-1} because below this wavenumber the resolution is extremely poor. It is even difficult to assign a SO_2 -hydrate because of the poor resolution even though there should be a high concentration of SO_2 -hydrates present on Europa. On account of this it is difficult to compare our spectroscopic data with those available for Europa. However, since we expected only a small amount of H_2SO_3 there, even a higher resolution of the spectroscopic data of Europa might not help identifying H_2SO_3 from a circulating spacecraft.

Inspection of the IR-spectra of Io provided by Lopes-Gautier et al. (2000) (Suppl. material) and Sandford et al. (1994) showed a strong, broad band between 3560 and 3590 cm^{-1} which was compared to pure laboratory SO_2 spectra where this band was assigned to be a combination of several fundamentals. However, compared to the pure laboratory spectra the intensity of this band is much stronger and therefore this band might be an overlap with H_2SO_3 vibrations in the same region. Yet, to clearly assign the vibrational characteristics spectra of both Io and Europa, additional spectroscopic data with a higher resolution are required. Also a more precise determination of the present concentrations of H_2O and SO_2 would be useful for a detailed description which hydrate complexes could form and thus, how long sulfurous acid would be stable.

Only the atmospheres of Europa and Io appear to be environments where conditions for the existence of H_2SO_3 are fulfilled. On other satellites and planets such as Mars, Earth, or Venus either the atmospheres are too hot, or the concentration of sulfur species is too small, or the water content is too high as far as we know. On Europa the expected amount of H_2SO_3 will be small but it should be present there whereas on Io the proposed amount should be higher. While carbonic

acid was synthesized by high energy and proton irradiation of cryogenic $\text{CO}_2/\text{H}_2\text{O}$ mixtures (Moore and Khanna, 1991) or of pure solid CO_2 (Brucato et al., 1997), and protonation of bicarbonate and carbonate (Hage et al., 1993; Hage et al., 1998), conditions that are presumably present on Mars and on comets, similar conditions should allow formation of H_2SO_3 and are present on Io and on Europa. The lifetimes of H_2SO_3 on these satellites are considerable long and due to the high proton/irradiation impact there should be a steady state between formation and decomposition. The incoming particle flux (e^- , H^+) which is around $10^7\text{--}10^8\text{ cm}^{-2}\text{ s}^{-1}$ (Cooper et al., 2001) allows only an upper limit estimation for H_2SO_3 formation. However, with the physical and chemical properties present on Io we surmise that sulfurous acid might be present and detectable there; sulfurous acid might be present in traces on Europa but it will be hardly detectable with current technology.

Acknowledgments

This study was supported by the Austrian Science Fund (project number P14357-TPH).

References

- Akhmatskaya, E.V., Apps, C.J., Hillier, I.H., Masters, A.J., Watt, N.E., Whitehead, J.C., 1997. Formation of H_2SO_4 from SO_3 and H_2O , catalyzed in water clusters. *Chem. Commun.*, 707–708.
- Atkins, P.W., 1994. *Physical Chemistry*, fifth ed. Oxford Univ. Press, Oxford.
- Baboul, A.G., Curtiss, L.A., Redfern, P.C., Raghavachari, K., 1999. Gaussian-3 theory using density functional geometries and zero-point energies. *J. Chem. Phys.* 110, 7650–7657.
- Baldrige, K.K., Gordon, M.S., Steckler, R., Truhlar, D.G., 1989. Ab initio reaction paths and direct dynamics calculations. *J. Phys. Chem.* 93, 5107–5119.
- Brucato, J.R., Palumbo, M.E., Strazzula, G., 1997. Carbonic acid by ion implantation in water/carbon dioxide ice mixtures. *Icarus* 125, 135–144.
- Carlson, R.W., Anderson, M.S., Johnson, R.E., Smythe, W.D., Hendrix, A.R., Barth, C.A., Soderblom, L.A., Hansen, G.B., McCord, T.B., Dalton, J.B., Clark, R.N., Shirley, J.H., Ocampo, A.C., Matson, D.L., 1999. Hydrogen peroxide on the surface of Europa. *Science* 283, 2062–2064.
- Carlson, R.W., Johnson, R.E., Anderson, M.S., 1999. Sulfuric acid on Europa and the radiolytic sulfur cycle. *Science* 286, 97–99.
- Carlson, R.W., Smythe, W., Baines, K., Barbinis, E., Becker, K., Burns, R., Calcutt, S., Calvin, W., Clark, R., Danielson, G., Davies, A., Drossart, P., Encrenaz, T., Fanale, F., Granahan, J., Hansen, G., Herrera, P., Hibbitts, C., Hui, J., Irwin, P., Johnson, T., Kamp, L., Kieffer, H., Leader, F., Lellouch, E., Lopes-Gautier, R., Matson, D., McCord, T., Mehlman, R., Ocampo, A., Orton, G., Segura, M.R.-S.M., Shirley, J., Soderblom, L., Stevenson, A., Taylor, F., Torson, J., Weir, A., Weissman, P., 1996. Near-infrared spectroscopy and spectral mapping of Jupiter and the galilean satellites: results from Galileo's initial orbit. *Science* 274, 385–388.
- Carlson, R.W., Smythe, W.D., Lopes-Gautier, R.M.C., Davies, A.G., Kamp, L.W., Mosher, J.A., Soderblom, L.A., Leader, F.E., Mehlman, R., Clark, R.N., Fanale, F.P., 1997. The distribution of sulfur dioxide and other infrared absorbers on the surface of Io. *Geophys. Res. Lett.* 24, 2479–2482.

- Cheng, A.F., 1984. Escape of sulfur and oxygen from Io. *J. Geophys. Res.* 89, 3939–3944.
- Chen, T.S., Moore Plummer, P.L., 1985. Ab initio MO investigation of the gas-phase reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$. *J. Phys. Chem.* 89, 3689–3693.
- Chuang, Y.-Y., Truhlar, D.G., 1997. Improved dual-level direct dynamics method for reaction rate calculations with inclusion of multidimensional tunneling effects and validation for the reaction of H with trans- N_2H_2 . *J. Phys. Chem. A* 101, 3808–3814.
- Cooper, J.F., Johson, R.E., Mauk, B.H., Garrett, H.B., Gehrels, N., 2001. Energetic ion and electron irradiation of the icy galilean satellites. *Icarus* 149, 133–159.
- Corchado, J.C., Chuang, Y.-Y., Coitino, E.L., Truhlar, D.G., 2002a. Gaussrate9.0. Univ. of Minnesota, Minneapolis.
- Corchado, J.C., Chuang, Y.-Y., Fast, P.L., Villá, J., Hu, W.-P., Liu, Y.-P., Lynch, G.C., Nguyen, K.A., Jackels, C.F., Melissas, V.S., Lynch, B.J., Rossi, I., Coitino, E.L., Fernandez-Ramos, A., Pu, J., Albu, T.V., Steckler, R., Garrett, B.C., Isaacson, A.D., Truhlar, D.G., 2002b. Polyrate9.0. Univ. of Minnesota, Minneapolis.
- Dunning Jr., T.H., 1989. Gaussian basis sets for use in correlated molecular calculations: I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* 90, 1007–1023.
- Esposito, L.W., 1984. Sulfur dioxide: episodic injection shows evidence for active Venus volcanisms. *Science* 223, 1072–1074.
- Eyring, H., 1935. The activated complex in chemical reactions. *J. Chem. Phys.* 3, 107–115.
- Fernández-Ramos, A., Truhlar, D.G., 2001. Improved algorithm for corner cutting tunneling calculations. *J. Chem. Phys.* 114, 1491–1496.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., Pople, J.A., 1998. Gaussian98, Revision A.9. Gaussian, Inc., Pittsburgh, PA.
- Graedel, T.E., Crutzen, P.J., 1994. *Chemie der Atmosphäre, Bedeutung für Klima und Umwelt. Spektrum/Akademischer Verlag, Heidelberg/Berlin/Oxford.*
- Hage, W., Hallbrucker, A., Mayer, E., 1993. Carbonic-acid: synthesis by protonization of bicarbonate and FTIR spectroscopic characterization via a new cryogenic technique. *J. Am. Chem. Soc.* 115, 8427–8431.
- Hage, W., Liedl, K.R., Hallbrucker, A., Mayer, E., 1998. Carbonic-acid in the gas-phase and its astrophysical relevance. *Science* 279, 1332–1335.
- Hanway, D., Tao, F.-M., 1998. A density functional theory and ab initio study of the hydrolysis of dinitrogen pentoxide. *Chem. Phys. Lett.* 285, 459–466.
- Hu, W.-P., Liu, Y.-P., Truhlar, D.G., 1994. Variational transition-state theory and semiclassical tunneling calculations with interpolated corrections: a new approach to interfacing electronic structure theory and dynamics for organic reactions. *J. Chem. Soc. Faraday Trans.* 90, 1715–1725.
- Kargel, J.S., 1998. The salt of Europa. *Science* 280, 1211–1212.
- Khanna, R.K., Zhao, G., Ospina, M.J., Pearl, J.C., 1988. Crystalline sulfur dioxide: crystal field splittings, absolute band intensities, and complex refractive indices derived from infrared spectra. *Spectrochim. Acta A* 44, 581–586.
- Lee, Y.-Y., Kao, W.-C., Lee, Y.-P., 1990. Kinetics of the reaction $\text{OH} + \text{SO}_2$ in He, N_2 , and O_2 at low pressure. *J. Phys. Chem.* 94, 4534–4540.
- Li, W.-K., McKee, M.L., 1997. Theoretical study of OH and H_2O addition to SO_2 . *J. Phys. Chem. A* 101, 9778–9782.
- Liu, Y.-P., Lynch, G.C., Truong, T.N., Lu, D.-H., Truhlar, D.G., Garrett, B.C., 1993. Molecular modeling of the kinetic isotope effect for the [1,5]-sigmatropic rearrangement of *cis*-1,4-pentadiene. *J. Am. Chem. Soc.* 115, 2408–2415.
- Loerting, T., Liedl, K.R., 2000. Toward elimination of discrepancies between theory and experiment: the rate constant of the atmospheric conversion of SO_3 to H_2SO_4 . *Proc. Natl. Acad. Sci. USA* 97, 8874–8878.
- Loerting, T., Liedl, K.R., 2001. Water-mediated proton transfer: a mechanistic investigation on the example of the hydration of sulfur oxides. *J. Phys. Chem. A* 105, 5137–5145.
- Loerting, T., Tautermann, C., Kroemer, R.T., Kohl, I., Hallbrucker, A., Mayer, E., Liedl, K.R., 2000. On the surprising kinetic stability of carbonic-acid (H_2CO_3). *Angew. Chem. Int. Ed.* 39, 891–894.
- Lopes-Gautier, R., Douté, S., Smythe, W.D., Kamp, L.W., Carlson, R.W., Davies, A.G., Leader, F.E., McEwen, A.S., Geissler, P.E., Kieffer, S.W., Keszhelyi, L., Barbini, E., Mehlman, R., Segura, M., Shirley, J., Soderblom, L.A., 2000. A close-up look at Io from Galileo's near-infrared mapping spectrometer. *Science* 288, 1201–1204.
- Marcus, R.A., Coltrin, M.E., 1977. A new tunneling path for reactions such as $\text{H} + \text{H}_2 \rightleftharpoons \text{H}_2 + \text{H}$. *J. Chem. Phys.* 67, 2609.
- Märker, C., Schleyer, P.v. R., Liedl, K.R., Ha, T.-K., Quack, M., Suhm, M.A., 1997. A critical analysis of electronic density functionals for structural, energetic, dynamic and magnetic properties of hydrogen fluoride clusters. *J. Comput. Chem.* 18, 1695–1719.
- McCord, T.B., Hansen, G.B., Fanale, F.B., Carlson, R.W., Matson, D.L., Johnson, T.V., Smythe, W.D., Crowley, J.K., Martin, P.D., Ocampo, A., Hibbitts, C.A., Granahan, J.C., the NIMS Team, 1998. Salts in Europa's surface detected by Galileo's near infrared mapping spectrometer. *Science* 280, 1242–1245.
- Møller, C., Plesset, M.S., 1934. Note on an approximation treatment for many-electron systems. *Phys. Rev.* 46, 618–622.
- Moore, M.H., 1984. Studies of proton-irradiated SO_2 at low temperatures: implications for Io. *Icarus* 59, 114–128.
- Moore, M.H., Khanna, R.K., 1991. Infrared and mass spectral studies of proton irradiated $\text{H}_2\text{O} + \text{CO}_2$ ice: evidence for carbonic acid. *Spectrochim. Acta A* 47, 255–262.
- Na, C.Y., Esposito, L.W., Skinner, T.E., 1990. International ultraviolet explorer observation of Venus SO_2 and SO. *J. Geophys. Res.* 95, 7485–7491.
- Nash, D.B., Betts, B.H., 1995. Laboratory infrared spectra (2.3–23 μm) of SO_2 phases: applications to Io surface analysis. *Icarus* 117, 402–419.
- Noll, K.S., Johnson, R.E., McGrath, M.A., Caldwell, J.J., 1997. Detection of SO_2 on Callisto with the Hubble Space Telescope. *Geophys. Res. Lett.* 24, 1139–1142.
- Page, M., McIver Jr., J.W., 1988. On evaluating the reaction path hamiltonian. *J. Chem. Phys.* 88, 922–935.
- Pearl, J., Hanel, R., Kunde, V., Maguire, W., Fox, K., Gupta, S., Ponnampereuma, C., Raulin, F., 1979. Identification of gaseous SO_2 and new upper limits for other gases on Io. *Nature* 280, 755–758.
- Peng, C., Ayala, P.Y., Schlegel, H.B., 1996. Using redundant internal coordinates to optimize equilibrium geometries and transition states. *J. Comput. Chem.* 17, 49–56.
- Prinn, R.G., 2001. Climate change on Venus. *Nature* 412, 36–37.
- Sandford, S.A., Geballe, T.R., Salama, F., Goorvitch, D., 1994. New narrow infrared absorption features in the spectrum of Io between 3600 and 3100 cm^{-1} (2.8–3.2 μm). *Icarus* 110, 292–302.
- Scott, A.P., Radom, L., 1996. Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *J. Phys. Chem.* 100, 16502–16513.
- Showman, A.P., Malhotra, R., 1999. The galilean satellites. *Science* 286, 77–84.
- Skodje, R.T., Truhlar, D.G., Garrett, B.C., 1981. A general small-curvature approximation for transition-state-theory transmission coefficients. *J. Phys. Chem.* 85, 3019–3023.
- Smith, B.A., Shoemaker, E.M., Kieffer, S.W., Cook II, A.F., 1979. The role of SO_2 in volcanism on Io. *Nature* 280, 738–743.

- Solomon, S.C., Bullock, M.A., Grinspoon, D.H., 1999. Climate change as a regulator of tectonics on Venus. *Science* 286, 87–90.
- Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J., 1994. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* 45, 11623–11627.
- Stockwell, W.R., Calvert, J.G., 1983. The mechanism of the HO–SO₂ reaction. *Atmos. Environ.* 17, 2231–2235.
- Tautermann, C.S., Voegele, A.F., Loerting, T., Kohl, I., Hallbrucker, A., Mayer, E., Liedl, K.R., 2002. Towards the experimental decomposition rate of carbonic acid (H₂CO₃) in aqueous solution. *Chem. Eur. J.* 8, 66–73.
- Truhlar, D.G., 1995. Chapter Direct Dynamics Method for the Calculation of Reaction Rates. Kluwer, Dordrecht. pp. 229–255.
- Urquhart, M.L., Jakosky, B.M., 1996. Constraints on the solid-state greenhouse effect on the icy galilean satellites. *J. Geophys. Res.* 101, 21169–21176.
- Voegele, A.F., Tautermann, C.S., Loerting, T., Hallbrucker, A., Mayer, E., Liedl, K.R., 2002. About the stability of sulfurous acid (H₂SO₃) and its dimer. *Chem. Eur. J.* 8, 5644–5651.
- Voegele, A.F., Tautermann, C.S., Loerting, T., Liedl, K.R., 2003. Toward elimination of discrepancies between theory and experiment: the gas-phase reaction of N₂O₅ with H₂O. *Phys. Chem. Chem. Phys.* 5, 487–495.
- Wayne, R.P., 1991. *Chemistry of Atmospheres. An Introduction to the Chemistry of Atmospheres of Earth, the Planets, and their Satellites*, second ed. Clarendon, Oxford.