Sulfurous acid (H$_2$SO$_3$) on Io?

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Received 17 February 2003; revised 16 October 2003

Abstract

Sulfurous acid (H$_2$SO$_3$) has never been characterized or isolated on Earth. This is caused by the unfavorable conditions for H$_2$SO$_3$ 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 H$_2$SO$_3$ at 300 K is 1 day but at 100 K it is increased to 2.7 billion years. Natural conditions to form H$_2$SO$_3$ presumably require cryogenic SO$_2$ or SO$_2$/H$_2$O 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 H$_2$SO$_3$ which we compared with Galileo’s spectra of Io and Europa. From the available data we surmise that H$_2$SO$_3$ is present on Io and probably but to a smaller extent on Europa.

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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 (SO$_2$) or dimethyl sulfide (DMS), which is subsequently oxidized in a multistep process to SO$_2$ (Graedel and Crutzen, 1994). Next, SO$_2$ is oxidized almost completely to SO$_3$ which is finally hydrated to sulfuric acid (H$_2$SO$_4$) (Stockwell and Calvert, 1983). However, it is quite remarkable that even though most of the sulfur species in atmosphere pass the stage of SO$_2$, the hydration product of SO$_2$ sulfurous acid (H$_2$SO$_3$) has never been found. In comparison, other acid anhydrides such as SO$_3$ or N$_2$O$_5$ (Wayne, 1991) are hydrated in atmosphere despite relatively high barriers for these reactions (Chen and Moore Plummer, 1985; Akhmatskaya et al., 1997; Hanway and Tao, 1998; Loerting and Liedl, 2000; Voegele et al., 2003).

Thermodynamically it is well documented that H$_2$SO$_3$ is unstable by a few kcal mol$^{-1}$ compared to its dissociation products SO$_2$ and H$_2$O. Besides the thermodynamic instability, Li and McKee (1997) demonstrated theoretically that H$_2$SO$_3$ is catalytically destroyed by water molecules decreasing also the kinetic stability. This process becomes stronger with an increasing number of water molecules

H$_2$SO$_3$ + nH$_2$O → SO$_2$ + (n + 1)H$_2$O.

However, similar to H$_2$SO$_3$ also carbonic acid (H$_2$CO$_3$) 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 H$_2$CO$_3$ 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 H$_2$CO$_3$ 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 H$_2$CO$_3$ is catalytically destroyed by water (Loerting et al., 2000) comparable to H$_2$SO$_3$.

Considering the similar findings between H$_2$CO$_3$ and H$_2$SO$_3$, one may think of conditions under which H$_2$SO$_3$...
is stable and in a next step characterizable as it was already possible for H$_2$CO$_3$. In a recent study we have investigated the kinetic and thermodynamic properties of H$_2$SO$_3$ 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$_2$SO$_3$ in more detail in comparison with H$_2$CO$_3$. Conditions that favor the formation and existence of possible for H$_2$CO$_3$. In a recent study we have investigated is stable and in a next step characterizable as it was already stable (Voegele et al., 2002). In this study, we reanalyze the stability of H$_2$SO$_3$ in more detail in comparison with H$_2$CO$_3$. Conditions that favor the formation and existence of H$_2$SO$_3$ are discussed. Additionally, we deduce spectroscopic properties of H$_2$SO$_3$ which we compare with available spectroscopic data from our solar system and provide evidence for the existence of H$_2$SO$_3$.

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 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 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 amu$^{1/2}$ 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 (Baldridge 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; Baldridge 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 multidimensional tunneling (µOMT) method. As a result we obtained unimolecular reaction rate constants with tunneling corrections $k_{\text{uni}}$.

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:

\begin{align}
\text{H}_2\text{SO}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{SO}_3\cdot\text{H}_2\text{O} \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}, \\
\text{H}_2\text{SO}_3 + 2\text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{SO}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{SO}_2 + 3\text{H}_2\text{O}, \\
\text{H}_2\text{SO}_3 + 2\text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{SO}_3 \cdot (\text{H}_2\text{O})_2 \rightarrow \text{SO}_2 + 3\text{H}_2\text{O}. 
\end{align}

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):

\begin{equation}
\frac{k_r}{k_\text{uni}} = K^{\text{press}}k_{\mu\text{OMT}, \text{VTST}}
\end{equation}

with $K^{\text{press}}$ representing the preassociation constant for forming the complex. The rate constant $k_r$ was converted into correct units by multiplication with the factor $f = (1.363 \times 10^{-22}T)^n$ cm$^3$ 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$_2$SO$_3$ and H$_2$CO$_3$ 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 $(k_{\text{uni}}^{\mu\text{OMT}, \text{VTST}})$ and converted it according to the formula (Atkins, 1994)

\begin{equation}
t_{1/2} = \frac{\ln 2}{k_r^{\mu\text{OMT}, \text{VTST}}}
\end{equation}
3. Results and discussion

We have investigated the half-life of \( \text{H}_2\text{SO}_3 \) as a function of temperature and as a function of the water concentration and compared it with \( \text{H}_2\text{CO}_3 \). In detail, the reactions of \( \text{H}_2\text{SO}_3 \) with \( n = 0, 1, \) and 2 water molecules in the temperature range 75–350 K were investigated according to the mechanisms

\[
\begin{align*}
\text{H}_2\text{SO}_3 & \rightarrow \text{SO}_2 + \text{H}_2\text{O}, \\
\text{H}_2\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}, \\
\text{H}_2\text{SO}_3 + 2\text{H}_2\text{O} & \rightarrow \text{SO}_2 + 3\text{H}_2\text{O}.
\end{align*}
\]

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

The catalytic influence of an increasing water concentration is enormous. Whereas the decomposition reaction of pure \( \text{H}_2\text{SO}_3 \) in the absence of water (reaction (5)) has a reaction barrier of 50.8 kcal mol\(^{-1}\), the influence of one catalytic water molecule lowers the barrier (reaction (6)) to 30.8 kcal mol\(^{-1}\). In a reaction complex with a second water molecule (reaction (7)), the barrier is already 9.0 kcal mol\(^{-1}\) at the G3//B3LYP level of theory.

Figure 1 shows the expected half-life of \( \text{H}_2\text{SO}_3 \) 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 \( \text{H}_2\text{CO}_3 \) is also shown for the same reaction mechanisms. Relatively, the stability of \( \text{H}_2\text{SO}_3 \) increases slightly with increasing temperature than of \( \text{H}_2\text{CO}_3 \). Nevertheless, the half-life of \( \text{H}_2\text{SO}_3 \) is generally a few orders of magnitude smaller. At 298 K, for instance, the half-life of pure \( \text{H}_2\text{SO}_3 \) is 24 h, whereas of \( \text{H}_2\text{CO}_3 \) 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 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 \( \text{H}_2\text{SO}_3 \) is as high as 2.7 billion years which is four orders of magnitude more stable than the 0.18 million years of \( \text{H}_2\text{CO}_3 \) at room temperature. At 150 K the half-life of \( \text{H}_2\text{SO}_3 \) is still more than 3 million years which is more than enough for characterization since \( \text{H}_2\text{CO}_3 \) could experimentally be shown to be stable for quite a long period at room temperature (Loerting et al., 2000). Formation of the \( \text{H}_2\text{SO}_3 \) hydrates turned out to be energetically favored by at least 9.9 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 diffusionally and depends mainly on the present water concentration. Considering the reverse reactions \( \text{H}_2\text{SO}_3: \text{H}_2\text{O}_n \rightarrow \text{SO}_2 + n\text{H}_2\text{O} \) (complex dissociation) which seem barrierless, the rate constants of these reactions can only be estimated from the energy differences and the diffusional limit. From these considerations we calculate that the reaction rate constant \( k_{\text{TST}} \) for \( n = 1 \) is around \( 10^{-9} \text{ s}^{-1} \) (at 100 K) which is comparable to the rate constant of \( \text{H}_2\text{SO}_3: \text{H}_2\text{O}_n \) decomposition into \( \text{SO}_2 + 2\text{H}_2\text{O} \) (complex decomposition) with a \( k_{\text{TST}} \) 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 \( \text{SO}_2 \) concentration allows to find out which complexes are present.

Considering the findings on the half-life of \( \text{H}_2\text{SO}_3 \), it becomes clear that Earth’s atmosphere does not provide conditions where it is possible to isolate \( \text{H}_2\text{SO}_3 \). While the half-life of 24 h for pure \( \text{H}_2\text{SO}_3 \) would be enough for isolation, the catalytic influence of water prohibits the existence of this molecule (Voegle et al., 2002). Additionally, Earth’s atmosphere has a very high oxidation potential and oxidants like the \(*\text{OH}\) radical react with \( \text{SO}_2 \) at very high rates to form higher oxides of sulfur (Lee et al., 1990; Wayne, 1991). Besides, intuitively one might expect that \( \text{H}_2\text{SO}_3 \) 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 \( \text{SO}_2 \) 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.
the same concentrations of SO$_2$ and H$_2$O (Esposito, 1984; Malhotra, 1999). The presence of SO$_2$ has been demonstrated but the relatively high temperatures (Noll et al., 1997) make formation and existence of H$_2$SO$_3$ 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 SO$_2$, sulfate rock, and H$_2$SO$_4$ 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 H$_2$SO$_4$, MgSO$_4$, and Na$_2$SO$_4$ (Cheng, 1984; Kargel, 1998; McCord et al., 1998; Carlson et al., 1999).

The overall amount of SO$_2$ is not very high on Europa and it is difficult to guess whether the present conditions are promising for the existence of sulfuric acid. In spite of very large water concentrations compared to SO$_2$, the extremely low temperatures of 90 K in some regions would allow the existence of H$_2$SO$_3$ 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 H$_2$SO$_3$ and H$_2$CO$_3$ and has been investigated in detail for H$_2$CO$_3$ (Tautermann et al., 2002). Extrapolating this effect for H$_2$SO$_3$ means that at 100 K the half-life of H$_2$SO$_3$ should be in the range of days, even if H$_2$SO$_3$ is embedded in H$_2$O. This period should be sufficient for characterization. Additionally, supposing that H$_2$SO$_3$ 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 H$_2$SO$_3$ 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 sulfuric acid might form on Europa. Experiments that successfully produced H$_2$CO$_3$ help us to evaluate suitable conditions. In these experiments pure CO$_2$, CO$_2$/H$_2$O mixtures or HCO$_3^-$ samples were irradiated by proton or high energy irradiation to provide the necessary activation energy to

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 SO$_2$ and H$_2$O (Esposito, 1984; Na et al., 1990), but has a low concentration of oxidants. So in principal the reaction of SO$_2$ + H$_2$O to form H$_2$SO$_3$ 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 H$_2$SO$_3$ 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 SO$_2$ has been demonstrated but the relatively high temperatures (Noll et al., 1997) make formation and existence of H$_2$SO$_3$ unlikely.

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form \(H_2CO_3\) (Moore and Khanna, 1991; Hage et al., 1993; Moore et al., 1997). On Europa \(SO_2\) is most likely present as a hydrate (\(SO_2/H_2O\) 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). 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 \(H_2SO_3/H_2O\) decomposition into \(H_2SO_3 + H_2O\) is comparably fast to decomposition into \(SO_2 + 2H_2O\). Whereas in contrast to Europa the formation of \(H_2SO_3\) from \(SO_2\) 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 \(C=O\) 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 \(v_3(H_2SO_3)\) to be present there. Unfortunately, \(v_4\) and \(v_5\) of

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<th>Vibration</th>
<th>(H_2SO_3) Unscaled (cm(^{-1}))</th>
<th>(H_2SO_3) Scaled (cm(^{-1}))</th>
<th>(H_2SO_3) (\nu^*)</th>
<th>(SO_2)-monohydrate Unscaled (cm(^{-1}))</th>
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<td>89.37</td>
<td>84.90</td>
<td>42</td>
<td>121</td>
</tr>
<tr>
<td>(v_{12})</td>
<td>125.50</td>
<td>119.23</td>
<td>20</td>
<td>19.53</td>
<td>18.55</td>
<td>2</td>
<td>121</td>
</tr>
</tbody>
</table>

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\(^{-1}\).
H$_2$SO$_3$ are in the same region as $\nu_2$ of SO$_2$. Still, the band at 1072 is in the $\nu_4$(H$_2$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 $\nu_4$ and $\nu_7$(H$_2$SO$_3$). Similarly, the 468 cm$^{-1}$ band has a shoulder, which is in good agreement with $\nu_9$(H$_2$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 300–3800 cm$^{-1}$ which would also include $\nu_1$, $\nu_2$, $\nu_{11}$, and $\nu_{12}$.

To analyze whether H$_2$SO$_3$ 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 15000–3500 cm$^{-1}$ for Europa and 4000–2000 cm$^{-1}$ for Io. Relative to the fundamentals of H$_2$SO$_3$, we are restricted to a region where only $\nu_1$ and $\nu_2$ of H$_2$SO$_3$ 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$_2$SO$_3$ there, even a higher resolution of the spectroscopic data of Europa might not help identifying H$_2$SO$_3$ 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 than the incoming particle flux ($e^-$, H$^+$) which is around $10^7$–$10^8$ cm$^{-2}$ s$^{-1}$ (Cooper et al., 2001) allows only an upper limit estimation for H$_2$SO$_3$ 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


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