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## Possible identification of local deposits of Cl<sub>2</sub>SO<sub>2</sub> on Io from NIMS/Galileo spectra

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[1] Starting from the recent discovery of chlorine ions in Io's plasma torus, we searched for evidence of Cl-bearing species at the surface of the satellite. We have identified Cl<sub>2</sub>SO<sub>2</sub>, with possible contribution by ClSO<sub>2</sub>, as candidates for the absorber(s) of the 3.92 μm band locally present in NIMS/Galileo spectra of the reddish deposits south of Marduk's volcanic center. Low-temperature laboratory measurements of the infrared spectra of several Cl and S-bearing molecules in the solid state, coupled with radiative transfer modeling, first allowed us to select four candidate molecules. Their abundance and stability at Io's surface have been tested through formation, condensation, and destruction scenarios using volcanic and atmospheric models completed with chemical and thermodynamical data. In particular, the sublimation rates of solid Cl<sub>2</sub>SO<sub>2</sub> and SO<sub>2</sub> have been measured to study the selective condensation of these species. Cl<sub>2</sub>SO<sub>2</sub> diluted at ~1% in a millimeter thick layer of solid SO<sub>2</sub> is the favorite candidate for the 3.92 μm band. We strongly favor a formation process of this molecule by heterogeneous reaction of Cl atoms on SO<sub>2</sub> ice condensing on plume particles or at Io's surface. The high Cl<sub>2</sub>SO<sub>2</sub> abundance observed implies that a Cl-rich volcanic eruption ( $[\text{Cl} - (\text{Na} + \text{K})]/\text{S} > 0.015$ ) occurred at Marduk. ClSO<sub>2</sub> is a potential additional contributor to the band. Pure H<sub>2</sub>S is safely discarded as it is extremely unstable at Io's surface but an upper limit of 0.01% is derived for H<sub>2</sub>S diluted in SO<sub>2</sub>. Finally, chemical constraints allow us to firmly exclude H<sub>2</sub>S<sub>2</sub>. We also suggest that Cl<sub>2</sub>S may be an alternative explanation for the reddish coloration of some volcanic deposits. *INDEX TERMS:* 5410 Planetology: Solid Surface Planets: Composition; 5470 Planetology: Solid Surface Planets: Surface materials and properties; 5480 Planetology: Solid Surface Planets: Volcanism (8450); 6218 Planetology: Solar System Objects: Jovian satellites; 3934 Mineral Physics: Optical, infrared, and Raman spectroscopy; *KEYWORDS:* Io's surface composition, chlorine chemistry, Cl<sub>2</sub>SO<sub>2</sub>, H<sub>2</sub>S, infrared spectroscopy, NIMS-Galileo spectra

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### 1. Introduction

[2] Since 1979 SO<sub>2</sub> is the only molecule firmly identified at the surface of Io [Smythe *et al.*, 1979; Fanale *et al.*, 1979; Hapke, 1979]. Most of the numerous features observed in Io's spectra were attributed to this species by comparison with laboratory data from the midinfrared to the ultraviolet thus confirming without ambiguity its identification [Nash *et al.*, 1980; Howell *et al.*, 1989; Schmitt *et al.*, 1994, manuscript in preparation, 2003; Carlson *et al.*, 1997]. Several forms of allotropic sulfur (S<sub>2</sub>, S<sub>4</sub>, and S<sub>8</sub>), S<sub>2</sub>O and polysulfur oxides could explain some spectral features of Io's visible spectra [Moses and Nash, 1991; Hapke,

1989] and are strongly suspected at the satellite surface. Laboratory measurements have shown that SO<sub>2</sub> and S<sub>8</sub> could also explain two of the emission features seen in the midinfrared spectra recorded by the IRIS/Voyager 1 instrument [Hanel *et al.*, 1992; Pearl, 1988]. Detailed Galileo data analysis has shown that SO<sub>2</sub> and sulfur allotropes are dominant compounds of the chemical composition over most of the satellite surface [Geissler *et al.*, 1999; Douté *et al.*, 2001]. A few other molecules have been suggested to explain some of the remaining absorption and emission bands seen on Io's spectra. In the Iris spectra frozen SO<sub>3</sub> was also proposed by Khanna *et al.* [1995] to contribute to the two bands previously assigned to SO<sub>2</sub> and S<sub>8</sub>. However, their laboratory near-infrared spectra of SO<sub>3</sub> showed features around 4.03–4.08 μm which were not seen in the observational data. A weak 3.91 μm band observed on the

side of the strong 4.07  $\mu\text{m}$  band of solid SO<sub>2</sub> was first attributed to H<sub>2</sub>S, either pure [Nash and Howell, 1989] or diluted in SO<sub>2</sub> [Salama et al., 1990], but Schmitt et al. [1994, manuscript in preparation, 2003] showed that solid SO<sub>2</sub> could fully explain this feature. Schmitt et al. also reattributed to SO<sub>2</sub> two other near-infrared bands formerly explained by H<sub>2</sub>S [Lester et al., 1992] and CO<sub>2</sub> [Sandford et al., 1991]. The possible identification of H<sub>2</sub>O [Salama et al., 1994] met with the same fate [Dahmani and Khanna, 1996; Nash and Betts, 1998; B. Schmitt et al., manuscript in preparation, 2003]. Sodium and potassium have been also suspected to be present in some solid form because they were discovered in Io's torus [Brown, 1974]. The possible contribution of Na<sub>2</sub>S, NaHS, K<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> to Io's reflectance spectrum has been studied [Nash and Nelson, 1979; Nash, 1988; Howell et al., 1989] but none has been yet positively identified at the surface. The net result of these spectral studies is that there is either no or still controversial identifications to all the bands not attributed to SO<sub>2</sub>, the only molecule unquestionably condensed on Io's surface.

[3] The recent discovery of abundant chlorine ions in Io's plasma torus [Küppers and Schneider, 2000; Feldman et al., 2001] led us to consider a new family of candidates to explain some of the unidentified or controversial features of Io's surface spectra: Cl-bearing molecules. On the basis of Io's torus atomic abundances, a large number of molecules composed of S, O, Na, K, Cl, and H are predicted in Io's atmosphere by Zolotov and Fegley [1998a] and Fegley and Zolotov [2000] as the result of lava degassing and high temperature volcanic chemistry. Thirteen of the molecules predicted by Zolotov and Fegley [1998a] contain chlorine; therefore it is probable that some of these Cl-bearing species could be found at the surface of the satellite.

[4] Although they are not the dominant Cl compounds predicted by the chemical model under most of the physical conditions studied, we first decided to study the four infrared-active and commercially available molecules containing at least one Cl and one S atom: Cl<sub>2</sub>S, Cl<sub>2</sub>S<sub>2</sub>, Cl<sub>2</sub>SO and Cl<sub>2</sub>SO<sub>2</sub> (S. Rodriguez and B. Schmitt, Infrared spectra of chlorine-sulfur bearing species as pure solids and diluted in SO<sub>2</sub> ice: Implications for Io's surface composition, submitted to *Planetary and Space Sciences*, 2003) (hereinafter referred to as Rodriguez and Schmitt, submitted manuscript, 2003). No infrared spectrum is available in the literature for these four molecules in the solid state. Only gas phase or rare gas matrix IR spectra or liquid Raman spectra exist [Schinanouchi, 2000]. We also performed specific laboratory experiments on two "classical" candidates, H<sub>2</sub>S and SO<sub>3</sub>, for which a few solid state spectra have already been published [Reding and Hornig, 1957; Ferraro et al., 1980; Salama et al., 1990; Nelson and Smythe, 1986; Khanna et al., 1995].

[5] In this paper we focus on the analysis of one new infrared absorption band at 3.920  $\mu\text{m}$  we recently discovered locally in NIMS/Galileo spectro-images of Io [Schmitt and Rodriguez, 2000; Schmitt et al., 2001]. We will only describe the spectroscopic experiments with Cl<sub>2</sub>SO<sub>2</sub> and H<sub>2</sub>S necessary for the identification of this band. We will also present some sublimation experiments of SO<sub>2</sub> and Cl<sub>2</sub>SO<sub>2</sub> designed to determine their relative volatility. The detailed presentation of the laboratory experiments on the

six molecules listed above will be published in future papers (see Rodriguez and Schmitt (submitted manuscript, 2003) for the Cl-bearing molecules).

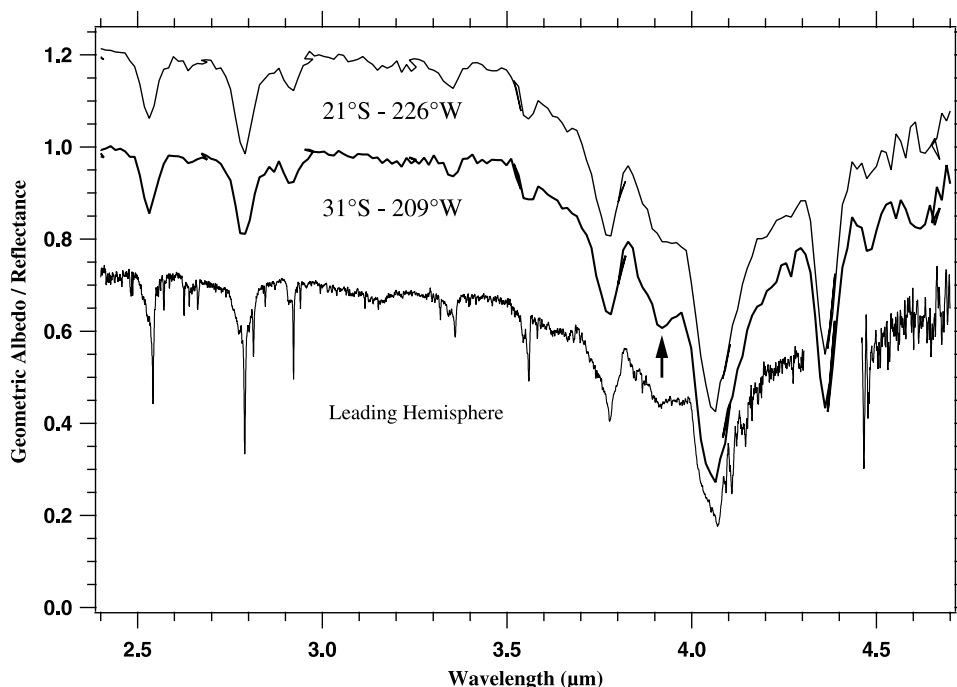
## 2. Observational Data

[6] The Io observations collected by the Galileo NIMS instrument cover the 0.7–5.2  $\mu\text{m}$  range at 0.025  $\mu\text{m}$  resolution [Carlson et al., 1992]. From these observations the only compound clearly identified so far at its surface is SO<sub>2</sub> (from a series of 8 absorption bands [Carlson et al., 1997]). A few other weaker absorption features widely distributed on Io have been observed [Carlson et al., 1997; Soderblom et al., 1999] but are still awaiting identification. During a systematic search a spectral absorption feature at 3.920  $\pm$  0.005  $\mu\text{m}$  appeared to be locally present in a few groups of pixels of the full spectral resolution data (INHRSPEC) acquired during the G2, C3, E4, E6, G7 and E14 orbits (September, November and December 1996, February and March 1997, March 1998) and caught our attention.

[7] We concentrated on the G2 data which have the best signal-to-noise ratio. After a careful check in the raw G2 data (i.e., detector pixels before spectral/geometrical reprojection) for possible energetic particle spikes, the occurrence of this band has been clearly confirmed in at least one area south of Marduk (centered around 31°S, 209°W). Only the 3.955  $\mu\text{m}$  channel was found to be partly affected by a "positive spike" in one detector pixel adjacent to the three detector pixels displaying the band. The spatial reprojection in Io geographic coordinates propagated part of this spike into some of the "end-product" pixels showing the 3.920  $\mu\text{m}$  band. A deconvolution and despiking procedure of the spectra has been developed by Soderblom et al. [1999] and applied to the data of the G2 orbit. The resulting spectra around Marduk are much less noisy and well corrected from the spike near the 3.920  $\mu\text{m}$  band. The average deconvolved reflectance spectrum of this region (five reprojected pixels covering about 350  $\times$  270 km<sup>2</sup>) measured during the G2 orbit is plotted in Figure 1 and compared to an average spectrum of a nearby area showing only SO<sub>2</sub> ice bands. The mean incidence, emergence, and phase angles of the averaged south Marduk observations are 31.5°, 33°, and 1.50°, respectively. The location of the pixels displaying the band are drawn on the SSI context image of the Marduk region (Figure 2). Spatial coregistration between NIMS G2 and SSI data are accurate within  $\pm 1^\circ$  (latitude and longitude).

[8] The independent observation of the band, but at lower signal to noise, covering about the same area (within NIMS pointing accuracy) in the E4, G7 and E14 data strengthens its occurrence. In particular in the E4 observation, recorded at higher spatial resolution than G2, the feature covers 8 contiguous pixels. Unfortunately the highest spatial resolution data, C3, are too noisy to firmly confirm the occurrence of the band. In the E6 data a few pixels near Marduk display the band but are shifted by about 6° in longitude, possibly due to a registration problem. In summary, within the above limitations, the available set of NIMS observations consistently displays the 3.920  $\mu\text{m}$  band with similar intensities in the region south of Marduk.

[9] It should be noted that the  $\nu_1 + \nu_3$  band of SO<sub>2</sub> (4.07  $\mu\text{m}$ ) has a wide "side-plateau" with small bumps in



**Figure 1.** The NIMS average reflectance spectrum (middle curve) south of Marduk (G2 orbit, center  $\sim 31^\circ\text{S}$ ,  $209^\circ\text{W}$ ; see Figure 2 for exact location) displaying the  $3.920\ \mu\text{m}$  band (arrow) compared to an average spectrum of a nearby area showing only  $\text{SO}_2$  ice bands (centered  $21^\circ\text{S}$ – $226^\circ\text{W}$ ; top curve with vertical shift:  $+0.15$ ). The ISO leading hemisphere spectrum of Io (Geometric albedo; bottom curve with vert. shift:  $-0.05$ ) is also shown at full spectral resolution as a “pure  $\text{SO}_2$  ice” reference in this range (B. Schmitt et al., manuscript in preparation, 2003). Note in this spectrum the weak  $\text{SO}_2$  band at  $3.92\ \mu\text{m}$  formerly attributed to  $\text{H}_2\text{S}$  on Io.

the  $3.85$ – $4.0\ \mu\text{m}$  range corresponding to combinations with phonon modes [Schmitt et al., 1994] that are easily observed in high spectral resolution full disk spectra (B. Schmitt et al., manuscript in preparation, 2003) (see Figure 1). They are these bumps that have been formerly attributed to pure solid  $\text{H}_2\text{S}$  [Nash and Howell, 1989] or diluted in  $\text{SO}_2$  [Salama et al., 1990]. The band at  $3.920\ \mu\text{m}$  we observe in the NIMS spectra is much stronger and is superimposed on the  $\text{SO}_2$  “bumpy plateau.” The depth of the  $3.920\ \mu\text{m}$  band relative to this “ $\text{SO}_2$  continuum” is about 5%.

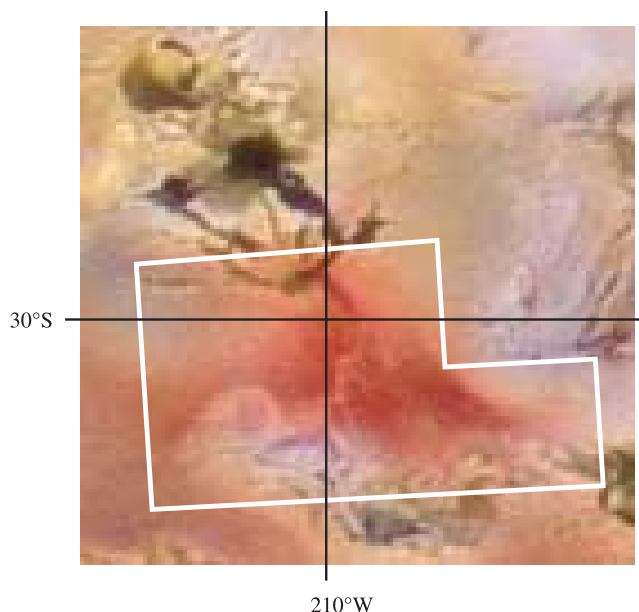
### 3. Laboratory Measurements

[10] Laboratory transmission spectra in the midinfrared ( $1.5$ – $25\ \mu\text{m}$ ) were obtained on thin films at  $1\ \text{cm}^{-1}$  resolution with our Fourier transform infrared spectrometer (Nicolet 800) fitted out with an ultra-high vacuum cryogenic optical cell. A brief description of the experimental setup and procedure can be found in Schmitt et al. [1994]. Thin films of solid  $\text{Cl}_2\text{SO}_2$  (sulfuryl chloride),  $\text{H}_2\text{S}$  and  $\text{SO}_2$  samples were synthesized in the vacuum optical cell by the technique of direct gas deposition on a CsI window.

[11] We performed experiments on pure solid samples as well as for these molecules diluted in solid  $\text{SO}_2$  (Figure 3). Gas phase spectra were also recorded for reference.

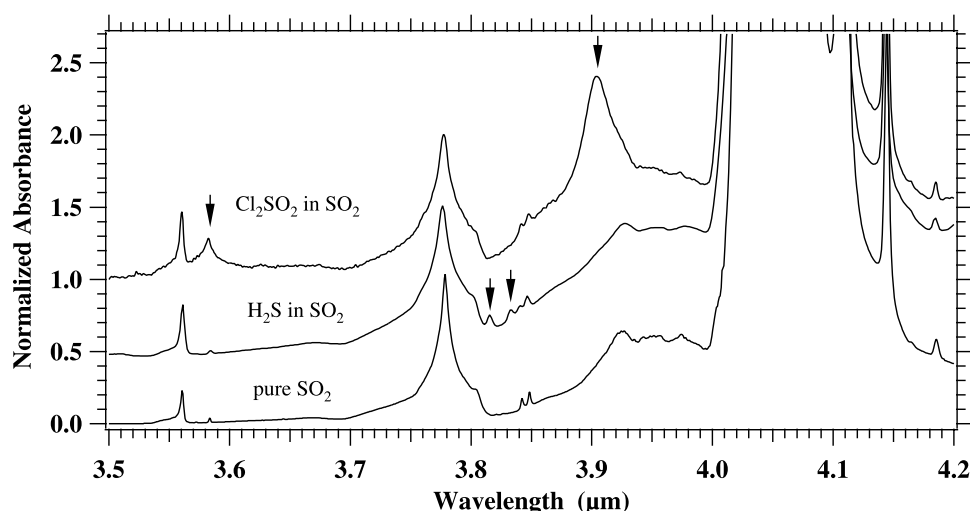
#### 3.1. $\text{Cl}_2\text{SO}_2$ Spectra

[12] Several successive deposits of pure  $\text{Cl}_2\text{SO}_2$  gas (liquid purity  $>99\%$ ) were made at  $120\ \text{K}$  ( $2$ – $15\ \mu\text{m}$  thick),



**Figure 2.** SSI context image of the Marduk region (cylindrical projection) [McEwen et al., 1998]. The image size is about  $15^\circ$  in longitude and  $17^\circ$  in latitude ( $420 \times 540\ \text{km}$ ). The location of the group of five NIMS G2 pixels clearly displaying a  $3.920\ \mu\text{m}$  band is shown as a white box. Note the good correlation with the red deposits.





**Figure 3.** Laboratory absorbance spectra of solid mixtures of 2%  $\text{Cl}_2\text{SO}_2$  in  $\text{SO}_2$  (100 K) and 2.8%  $\text{H}_2\text{S}$  in  $\text{SO}_2$  (130 K) compared to pure  $\text{SO}_2$  ice (125 K). The curves are offset by 0.5 unit for clarity. The arrows show the location of the  $\text{Cl}_2\text{SO}_2$  and  $\text{H}_2\text{S}$  bands.

then cooled to 100 K and slowly warmed by steps of 10 K until complete sublimation of the sample occurred around 160 K. After each deposit and each temperature step we recorded a mid-IR transmission spectrum of the sample. For the study of  $\text{Cl}_2\text{SO}_2$  diluted in  $\text{SO}_2$ , a gas mixture of 2.0% of  $\text{Cl}_2\text{SO}_2$  in  $\text{SO}_2$  ( $\text{SO}_2$  gas purity >99.9%) was first prepared in a glass bulb, then sent to the deposition tube of the optical cell and cocondensed in several steps on the infrared window at 100 K (thickness increasing from 0.5 to 185  $\mu\text{m}$  with condensation rates from 1 to 160  $\mu\text{m h}^{-1}$ ). This lower temperature was chosen because of the higher volatility of  $\text{SO}_2$ . The resulting solid sample was homogeneously and intimately mixed. Transmission spectra were also acquired with the same procedure until the sample totally sublimated (first  $\text{SO}_2$  around 130–140 K, then  $\text{Cl}_2\text{SO}_2$  around 160 K).

[13] Between 2.5 and 25  $\mu\text{m}$ , we observe about 25 absorption bands of various intensities and attribute them to 7 fundamental vibration modes of  $\text{Cl}_2\text{SO}_2$ , 10 combination modes (with only three below 5  $\mu\text{m}$ :  $2\nu_1$ ,  $\nu_1 + \nu_6$ , and  $2\nu_6$ ), and several isotopic bands (mainly from  $^{37}\text{Cl}$  and  $^{34}\text{S}$ ) (Rodriguez and Schmitt, submitted manuscript, 2003).

[14] The wavelength shifts between the band positions of the pure solid state and diluted state occur in both directions and range from weak to medium depending on the vibration mode. In particular the  $\nu_1 + \nu_6$  combination mode measured at 3.9015  $\mu\text{m}$  at 120 K in the pure solid state shifts to 3.9075  $\mu\text{m}$  upon dilution in  $\text{SO}_2$  at the same temperature. The position of this band is found to be strongly temperature sensitive in the diluted state ( $-0.2 \text{ nm K}^{-1}$ ) in comparison with the 15 times weaker sensitivity measured for pure  $\text{Cl}_2\text{SO}_2$ . There are also strong changes in the relative band intensities. This is particularly the case for the three combination modes of  $\nu_1$  and  $\nu_6$ : with similar intensities for pure  $\text{Cl}_2\text{SO}_2$ , the  $\nu_1 + \nu_6$  mode becomes markedly predominant when diluted in solid  $\text{SO}_2$  (Figures 3 and 4). The  $2\nu_1$  mode near 4.25  $\mu\text{m}$  is then barely distinguishable in the wing of

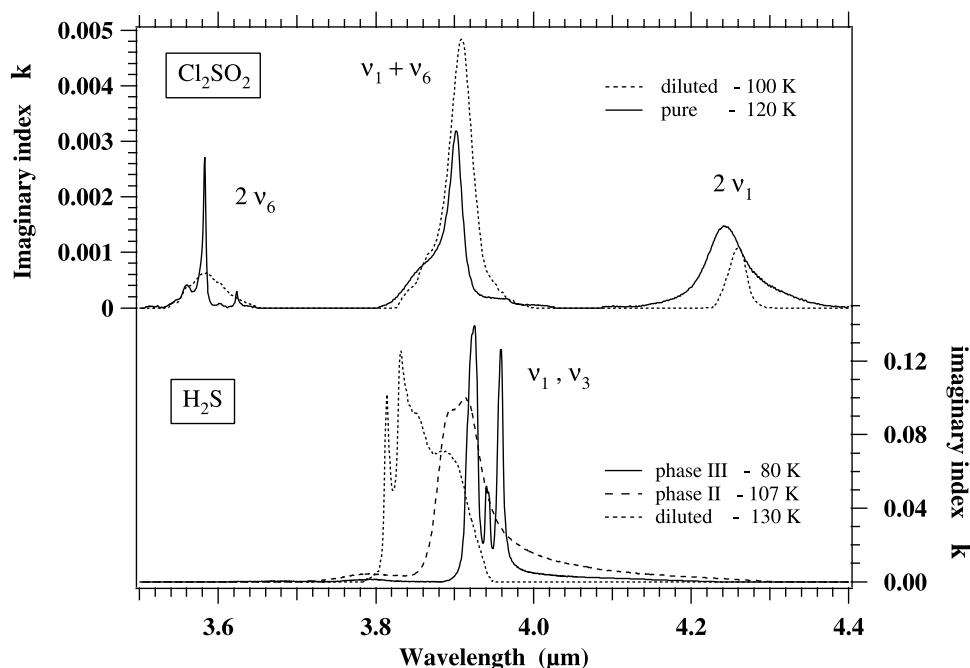
the  $\text{SO}_2$  band. Consequently, the  $\text{Cl}_2\text{SO}_2$  band positions and intensities are relevant indicators of the physical state (temperature and dilution state) of this molecule.

[15] We extracted the absorption coefficient of diluted  $\text{Cl}_2\text{SO}_2$  and normalized it to the density of pure  $\text{Cl}_2\text{SO}_2$  using a procedure and assumptions similar to the ones described by *Quirico et al.* [1999] for  $\text{CH}_4$  diluted in  $\text{N}_2$ . The main difference is that the  $\text{SO}_2$  absorptions strongly dominate the spectrum making their subtraction more difficult. The spectrum was normalized assuming that the molar integrated absorption coefficient of the  $\nu_1 + \nu_6$  band is the same for pure and diluted  $\text{Cl}_2\text{SO}_2$ . A density of  $2.36 \pm 0.35 \text{ g cm}^{-3}$  and a corresponding refractive index of  $1.675 \pm 0.12$  were also assumed for pure solid  $\text{Cl}_2\text{SO}_2$  (see the  $\text{Cl}_2\text{SO}_2$  sublimation section). With these assumptions the derived absorption coefficient spectrum is fully consistent with the values directly obtained using the thickness of the sample (185  $\mu\text{m}$ ) and the nominal concentration (2.0%) of the condensed  $\text{Cl}_2\text{SO}_2:\text{SO}_2$  gas mixture.

### 3.2. $\text{H}_2\text{S}$ Spectra

[16] Two pure  $\text{H}_2\text{S}$  samples (gas purity >99.7%) were condensed at temperatures of 15 and 80 K. Mid-IR spectra were recorded during step warmup to 90 K where  $\text{H}_2\text{S}$  rapidly sublimates under vacuum. In order to also obtain spectra at a temperature more relevant to daytime temperatures on Io we designed an experiment in which the sample is condensed and dynamically stabilized at 107 K by continuing deposition at a rate adjusted to compensate sublimation losses. Mid and near-IR spectra of  $\text{H}_2\text{S}$  mixed in  $\text{SO}_2$  have been also studied several years ago with a  $\text{SO}_2$  sample condensed with 2.8%  $\text{H}_2\text{S}$  and 4.7%  $\text{CO}_2$  [Schmitt *et al.*, 1994, 1998].

[17] The two strong and closely spaced stretching fundamental modes  $\nu_1$  and  $\nu_3$  dominate the 3–5  $\mu\text{m}$  spectrum of  $\text{H}_2\text{S}$ . Their absorption bands strongly change with temperature due to the occurrence of three different crystalline phases in the 80–130 K range [Anderson *et al.*, 1977]. Below 103.6 K the ordered phase III displays three sharp bands at 3.923  $\mu\text{m}$  ( $\nu_3$  mode), 3.941 and 3.957  $\mu\text{m}$  (both  $\nu_1$



**Figure 4.** Imaginary refractive index ( $k$ ) spectra of  $\text{Cl}_2\text{SO}_2$  and  $\text{H}_2\text{S}$  in the 3.5–4.4  $\mu\text{m}$  region. Upper part: pure  $\text{Cl}_2\text{SO}_2$  and diluted in  $\text{SO}_2$ . Lower part: two crystalline phases of pure  $\text{H}_2\text{S}$  and diluted in  $\text{SO}_2$ . For the diluted molecules the index is normalized to the density of the pure solids after subtraction of the absorption of the  $\text{SO}_2$  matrix.

mode) while the disordered phase II (below 126.2 K) has only one broad structured band centered around 3.906  $\mu\text{m}$  (Figure 4). At higher temperatures phase I is reported to display a very similar, although slightly narrower, single band at 3.910  $\mu\text{m}$  [Reding and Hornig, 1957]. All these bands are only very slightly temperature sensitive, within a given crystalline phase. A few much weaker bands also occur between 1.93 and 2.0  $\mu\text{m}$ .

[18] The spectrum of  $\text{H}_2\text{S}$  mixed in  $\text{SO}_2$  has also a clearly different shape with a series of blended bands strongly shifted (by more than 0.08  $\mu\text{m}$ ) relative to pure  $\text{H}_2\text{S}$ . Figure 4 shows the monomer and multimer absorption bands of  $\text{H}_2\text{S}$  at 110 K after the removal of the contribution of the  $\text{SO}_2$  matrix, which strongly absorb in that range (Figure 3). When  $\text{H}_2\text{S}$  is diluted at lower concentrations (i.e.,  $\ll 1\%$ ) only the two sharp monomer bands at 3.814 ( $\nu_3$  mode) and 3.831  $\mu\text{m}$  ( $\nu_1$  mode) remain, a result consistent with the measurements of Salama *et al.* [1990] at 85–100 K, but not with their mode attribution. All these spectral changes allow us to easily distinguish the different phases and to set temperature limits.

[19] The absorption coefficient of the disordered phase II  $\text{H}_2\text{S}$  at 107 K was obtained by assuming that the integrated absorption coefficient of the 3.906  $\mu\text{m}$  band is the same as for amorphous (15 K)  $\text{H}_2\text{S}$ . This assumption was necessary because we were not able to monitor the effective (and changing) thickness of the high temperature samples ( $>80$  K) in this dynamic experiment. The extraction protocol of the absorption coefficient of  $\text{H}_2\text{S}$  diluted in  $\text{SO}_2$  was about the same as for  $\text{Cl}_2\text{SO}_2$ .

### 3.3. Sublimation Rates

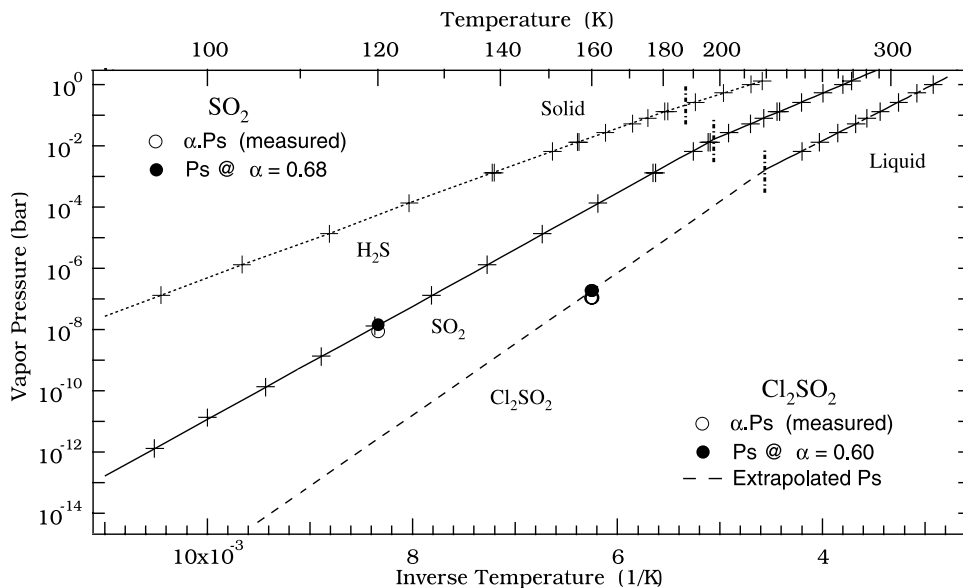
[20] Experiments were performed to measure the sublimation rate of pure solid  $\text{SO}_2$  and  $\text{Cl}_2\text{SO}_2$  at low temperature

in order to estimate their temperature dependent vapor pressure curves.

#### 3.3.1. $\text{SO}_2$ Sublimation

[21] For solid  $\text{SO}_2$  a sample about 80  $\mu\text{m}$  thick was slowly condensed at 110 K. Its deposition rate and thickness were monitored by He-Ne laser interferences and by recording several near-infrared spectra. After condensation a near-infrared spectrum was recorded before warmup to 120 K where the sample was allowed to sublimate. The temperature is stabilized within  $\pm 0.05$  K and its absolute value at the sample surface is known within  $\pm 0.2$  K. The residual  $\text{SO}_2$  pressure in the constantly pumped cell was about  $6 (\pm 2) \times 10^{-10}$  bar during the 14.5 hours necessary for complete sublimation of the sample. Spectra were recorded during sublimation. The thicknesses  $x$  were determined from the spectral interference fringes in the 3.0–3.7  $\mu\text{m}$  and 4.5–5.2  $\mu\text{m}$  “continuum” ranges ( $x = 1/(2n_\nu \Delta\nu)$  for normal incidence, where  $n_\nu$  is the refractive index at wavenumber  $\nu$  and  $\Delta\nu$  is the wavenumber period of the spectral interference). The occurrence of these spectral fringes demonstrates a high homogeneity of the sample thickness (better than 0.5%) within the measurement area. The refractive index of solid  $\text{SO}_2$  has been previously estimated from the Lorenz-Lorentz equation to be  $1.50 \pm 0.03$  at 0.633  $\mu\text{m}$  [Schmitt *et al.*, 1994]. Taking into account the dispersion of the refractive index (estimated from Kramers-Kronig relation [Trotta, 1996]), we obtain a value of  $n \approx 1.46 \pm 0.04$  in the 3–5  $\mu\text{m}$  range where the fringes have been measured.

[22] A sublimation rate of  $1.50 (\pm 0.04) \times 10^{-3} \mu\text{m s}^{-1}$  at  $120.0 \pm 0.2$  K was determined by this technique. This value is consistent to within 1% with the rate calculated using the initial thickness determined with the He-Ne laser interferences during deposition. On the other hand it is 5.5 times



**Figure 5.** Saturation vapor pressure of H<sub>2</sub>S, SO<sub>2</sub> and Cl<sub>2</sub>SO<sub>2</sub> as a function of temperature. Data for solid and liquid H<sub>2</sub>S and SO<sub>2</sub> (crosses) are from *Honig and Hook* [1960]. Our sublimation rate measurement of SO<sub>2</sub> ice at 120 K (circle) is consistent with the SO<sub>2</sub> curve with a condensation coefficient  $\alpha \approx 0.68 \pm 0.15$  (dot). Data for liquid Cl<sub>2</sub>SO<sub>2</sub> are from *Lide* [1990]. The vapor pressure curve of solid Cl<sub>2</sub>SO<sub>2</sub> (dashed line) is obtained by fitting a thermodynamic law to our data at 160 K (dot; assuming  $\alpha \approx 0.60$ ) and to the saturation pressure at the triple point.

larger than the nominal value calculated at 120 K from the sublimation equation of SO<sub>2</sub> derived by *Sandford and Allamandola* [1993].

[23] From statistical thermodynamics [see, e.g., *Haynes et al.*, 1992],

$$\frac{dx}{dt} = \frac{M}{\rho(T)} \frac{\alpha(T)(P_s(T) - P_g)}{\sqrt{2\pi MRT}} \quad [\text{in ms}^{-1}]$$

where  $M$  is the molar mass ( $\text{kg mol}^{-1}$ ),  $\rho(T)$  is the solid density ( $\text{kg m}^{-3}$ ),  $R$  is the perfect molar gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $\alpha(T)$  is the condensation coefficient,  $P_s(T)$  is the saturation vapor pressure at temperature  $T$  (K), and  $P_g$  is the residual gas pressure (Pa).

[24] Using the density of solid SO<sub>2</sub> ( $1.928 \text{ g cm}^{-3}$  at 77 K) measured by *Post et al.* [1952], this sublimation rate translates into a value of  $\alpha(P_s - P_g)$  of  $9.0 (\pm 0.25) \times 10^{-9}$  bar. *Honig and Hook* [1960] give a value of  $P_s$  of  $1.38 (\pm 0.25) \times 10^{-8}$  bar at 120 K (value derived from a thermodynamical curve fit (see section 3.3.2) of their tabulated data:  $P_s(\text{bar}) = 2.0 \times 10^6 \sqrt{T} e^{-4200/T}$ ). After correction of limited recondensation (about 4% of the sublimation rate) from the residual SO<sub>2</sub> pressure in our system this leads to a condensation coefficient  $\alpha \approx 0.68 \pm 0.15$ . This value is in good agreement with the one found for H<sub>2</sub>O ice at similar reduced temperature  $T/T_m$ , where  $T_m$  is the melting temperature [*Haynes et al.*, 1992]. This provides good confidence in the low temperature extrapolation ( $< 178$  K) of the vapor pressure curve of SO<sub>2</sub> ice given by *Honig and Hook* [1960] (Figure 5). On the other hand, the  $\alpha \cdot P_s$  curve derived from the sublimation rate equation of *Sandford and Allamandola* [1993] is not consistent with our data. It has a weaker slope than the

$P_s$  curve of *Honig and Hook* [1960] (Figure 5) implying condensation coefficients as low as 0.01 near the melting temperature and values larger than unity below 90 K. The frequently used vapor pressure curve of *Wagman* [1979] gives a value of  $P_s(\text{SO}_2)$  at 120 K lower by a factor of 2 compared to *Honig and Hook* [1960], but its simple exponential form ( $P_s(\text{bar}) = 1.516 \times 10^8 e^{-4510/T}$ ) and its too high value at the triple point (+12%) cast some doubt about the accuracy of this equation. We will therefore rely only on the *Honig and Hook* [1960] data in the following.

### 3.3.2. Cl<sub>2</sub>SO<sub>2</sub> Sublimation

[25] A  $14.5 \mu\text{m}$  thick sample of solid Cl<sub>2</sub>SO<sub>2</sub> was condensed at 120 K and sublimated at 160 K. In this experiment the laser interference fringes were clearly observed during sublimation, thus allowing us to directly measure the sublimation rate from the temporal interferences:

$$\frac{dx}{dt} = \frac{m}{2n\Delta t\nu_{\text{laser}}\sqrt{1 - \frac{\sin^2\Theta}{n^2}}}$$

where  $m$  is the number of interference fringes during the time interval  $\Delta t$ ,  $n$  is the refractive index at the He-Ne laser wavenumber  $\nu_{\text{laser}}$ , and  $\Theta$  is its incidence angle. The refractive index of solid Cl<sub>2</sub>SO<sub>2</sub> is unknown, as well as its density, but published values exist for liquid Cl<sub>2</sub>SO<sub>2</sub> [*Lide*, 1990]. We estimated its density by assuming a density ratio between the solid and liquid phases similar to that of SO<sub>2</sub> ( $\pm 15\%$ ) and derived the associated refractive index from the Lorenz-Lorentz equation. This gave  $2.36 \pm 0.35 \text{ g cm}^{-3}$  and  $1.675 \pm 0.12$ , respectively. A sublimation rate of  $1.75(\pm 0.15) \times 10^{-2} \mu\text{m s}^{-1}$  at  $160.0 \pm 0.2$  K was

determined by this technique giving a value of  $\alpha(P_s - P_g)$  of  $1.03(\pm 0.07) \times 10^{-7}$  bar. The residual Cl<sub>2</sub>SO<sub>2</sub> pressure  $P_g$  in the cell was about  $1.1(\pm 0.3) \times 10^{-8}$  bar during the measurement. If we assume (as found for SO<sub>2</sub>) that the condensation coefficient of H<sub>2</sub>O ice [Haynes *et al.*, 1992] can be applied to solid Cl<sub>2</sub>SO<sub>2</sub> at similar reduced temperature  $T/T_m$  ( $\alpha \approx 0.60 \pm 0.12$ ), we derive a saturation vapor pressure of Cl<sub>2</sub>SO<sub>2</sub> of  $1.85(\pm 0.5) \times 10^{-7}$  bar at  $160 \pm 0.2$  K.

[26] A thermodynamic vapor pressure curve of the form

$$P_s = \frac{A}{\alpha(T)} \sqrt{T} e^{-B/T}$$

has been adjusted between our data point at 160 K and the vapor pressure at the triple point (extrapolated from the vapor pressure curve of liquid Cl<sub>2</sub>SO<sub>2</sub>; [Lide, 1990]. With  $\alpha(T) = 0.60$  the fit gives  $A = 1.89 \times 10^9$  bar and  $B = 5280$  K for  $P_s$  expressed in bar (Figure 5). This law should provide an estimate of the vapor pressure of solid Cl<sub>2</sub>SO<sub>2</sub> from the triple point (219.05 K) down to about 100 K with an accuracy better than a factor 2. Most of the uncertainty comes from the assumption on the condensation coefficient  $\alpha(T)$  and its temperature dependence. For example, if a linear decrease law  $\alpha(T) = 1 - 0.0025 \times T$  (also giving  $\alpha(160 \text{ K}) = 0.60$ ) is used, the extrapolation of  $P_s$  at 100 K is 35% higher. On the other hand assuming  $\alpha(T) = 1$ , as implied for SO<sub>2</sub> if the Wagman [1979] equation is considered, leads to a  $P_s$  value 5 times lower.

## 4. Results and Interpretation

[27] In the following we select the candidate molecules relevant to Io's surface that satisfy the spectral criteria for identification of the 3.920  $\mu\text{m}$  band. We deduce their possible physical states and abundances and assess their probability of occurrence on Io in terms of thermodynamical stability and chemistry.

### 4.1. Band Identification

[28] An initial literature and database spectral search [Schinanouchi, 2000; J. Crovisier, Molecular Data Base (v 4.1), available at <http://www.usr.obspm.fr/~crovisie/basemole/>, 2001] (mainly gas phase or isolated molecules in matrix) among all possible molecules made of any combination of S, O, H and/or Cl atoms (>50) allowed us to select H<sub>2</sub>S ( $\nu_1$  and  $\nu_3$  modes), H<sub>2</sub>S<sub>2</sub> ( $\nu_1$  and  $\nu_5$ ), SO<sub>3</sub> ( $2\nu_3$ ), Cl<sub>2</sub>SO<sub>2</sub> ( $\nu_1 + \nu_6$ ) and ClSO<sub>2</sub> ( $2\nu_1$ ) as possible candidates for the 3.920  $\mu\text{m}$  band. The fundamental S-H stretching modes of the first two molecules and one first order combination of the S = O stretching modes of the last three have gas phase frequencies that may possibly shift close to the NIMS band position in some condensed state. Simple compounds of S, O, or Cl with Na, K, or Mg (NaO, Na<sub>2</sub>O, Na<sub>2</sub>S, NaCl, KCl, KO, K<sub>2</sub>S, MgO, MgS, ...) have been excluded despite the expected high abundance of some of them [Fegley and Zolotov, 2000] because only very weak third, or larger, order overtones/combinations occur below 4  $\mu\text{m}$ . Only the sulfate compounds (Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, ...) have first order combination modes (SO<sub>4</sub> vibrations) in the NIMS range but their bands are all situated above 4.2  $\mu\text{m}$  and have a wide and complex structure.

[29] Our laboratory measurements first allowed us to eliminate solid SO<sub>3</sub> as its suspected  $2\nu_3$  mode, surprisingly occurring at much lower wavelength (around 3.60  $\mu\text{m}$ ) than predicted, is far from the NIMS band and because it also displays three stronger bands between 4.03 and 4.10  $\mu\text{m}$  ( $\nu_1 + \nu_3$  modes) not observed in NIMS spectra.

#### 4.1.1. Cl<sub>2</sub>SO<sub>2</sub>

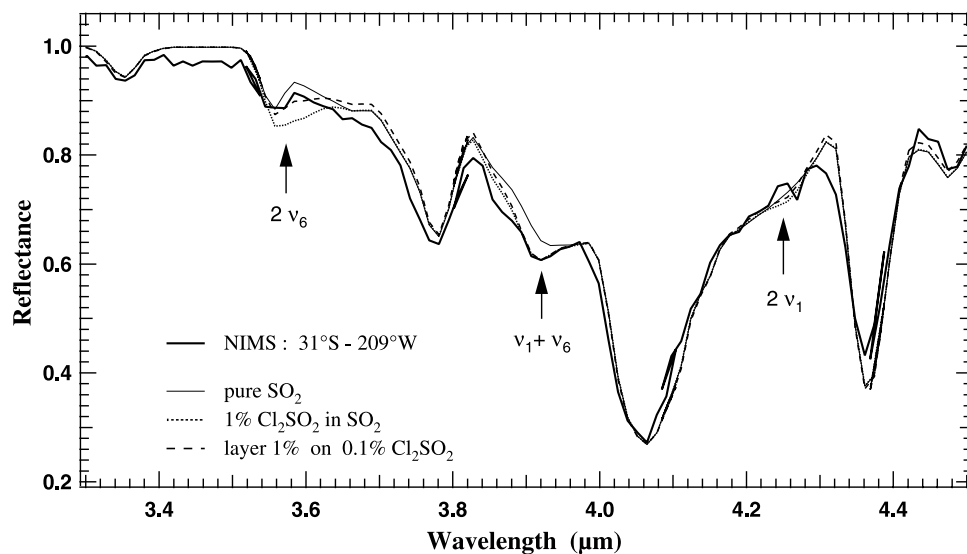
[30] Comparing our laboratory spectra of Cl<sub>2</sub>SO<sub>2</sub> with the NIMS band we observe that the  $\nu_1 + \nu_6$  band is slightly shifted in the pure solid state (3.902  $\mu\text{m}$  at 110 K) but this shift is reduced to 0.011  $\mu\text{m}$  (about 45% of the NIMS spectral resolution) when Cl<sub>2</sub>SO<sub>2</sub> is diluted at the molecular level in solid SO<sub>2</sub> around 110 K (3.909  $\mu\text{m}$ ), the mean SO<sub>2</sub> ice temperature on Io [Schmitt *et al.*, 1994, manuscript in preparation, 2003]. A lower temperature can further reduce this shift due to the high thermal sensitivity of this band in the diluted state (see section 3.1). On the other hand, 130 K is probably the maximum compatible temperature.

[31] A simulation of the NIMS spectrum has been performed between 1.5 and 4.7  $\mu\text{m}$  using our radiative transfer model in layered granular surfaces [Douté and Schmitt, 1998] and the optical constants of SO<sub>2</sub> ice at 110 K [Schmitt *et al.*, 1994, manuscript in preparation, 2003] and diluted Cl<sub>2</sub>SO<sub>2</sub> at 100 K (see experimental section). High resolution synthetic reflectance spectra generated by the model under the same bidirectional observation conditions than NIMS were then convoluted with the NIMS spectral instrument function (triangular with a FWHM of 0.0243  $\mu\text{m}$ ). The Io area corresponding to the spectrum (see Figure 2) was considered to consist of a geographic mosaic of patches of: 1) a Cl<sub>2</sub>SO<sub>2</sub>:SO<sub>2</sub> solid molecular mixture with uniform composition (both horizontally and with depth), and 2) a spectrally neutral material in the infrared ( $\sim$  impure sulfur). The parameters of the model are described in some detail by Douté *et al.* [2001] (see their Table II). We also used the value they derived for the anisotropic scattering parameter ( $g = -0.27$ ). The only additional parameter is the relative molar abundance of Cl<sub>2</sub>SO<sub>2</sub> and SO<sub>2</sub>.

[32] We obtained the best fit of the spectrum for SO<sub>2</sub> surface proportion ( $68 \pm 1\%$ ) and grain size ( $140 \pm 10 \mu\text{m}$ ) slightly different than the average of the values mapped by Douté *et al.* [2001] for this area of Io ( $64 \pm 2\%$ ,  $185 \pm 20 \mu\text{m}$ ), but they did not use the G2 orbit to derive their map (see their Figures 5 and 6). A quite good overall fit of the position (no residual shift), shape and strength of the 3.920  $\mu\text{m}$  band is obtained at NIMS spectral resolution for a relative Cl<sub>2</sub>SO<sub>2</sub>/SO<sub>2</sub> molar abundance of  $1 \pm 0.2\%$  (Figure 6). This error bar mainly comes from the uncertainty in the absolute calibration of the absorption coefficient extracted for diluted Cl<sub>2</sub>SO<sub>2</sub>. The derived Cl<sub>2</sub>SO<sub>2</sub> abundance is a mean value over the  $\sim 100,000 \text{ km}^2$  of the area depicted in Figure 2. Higher values ( $\sim 1.5\%$ ) are obtained for the central pixels of the area where the band is significantly stronger.

[33] Most of the SO<sub>2</sub> bands are well reproduced, although some moderate discrepancies remain in the intensity of the 1.98, 2.125, 3.78, and 4.36  $\mu\text{m}$  bands, possibly due to grain size or temperature distribution (horizontal or vertical) or sulfur contamination [see Douté *et al.*, 2001] or local noise perturbation. However, the main problem is the too strong and wide 3.57  $\mu\text{m}$  feature in our synthetic spectrum corresponding to a blending of the 3.56  $\mu\text{m}$  SO<sub>2</sub> band with the 3.58  $\mu\text{m}$  Cl<sub>2</sub>SO<sub>2</sub> band. Comparing this model with





**Figure 6.** Comparison (3.3–4.5  $\mu\text{m}$  range) between the local NIMS average spectrum (thick line) south of Marduk (31°S–209°W, G2 orbit) and synthetic reflectance spectra convolved to NIMS spectral resolution, involving 1) an optically thick molecular mixture of  $\text{Cl}_2\text{SO}_2$  and  $\text{SO}_2$  (dotted line) with relative molar abundance of 1%:99%; 2) a 1 mm thick layer (for 45% porosity) of the former mixture deposited on a similar mixture but with only 0.1%  $\text{Cl}_2\text{SO}_2$  (dashed line); and 3) pure  $\text{SO}_2$  frost (thin line). In all the above models the  $\text{SO}_2$  grain size and surface proportion are 140  $\mu\text{m}$  and 68% respectively. The vertical arrows show the positions of the three bands of diluted  $\text{Cl}_2\text{SO}_2$ . Note the respective contributions of  $\text{SO}_2$  and  $\text{Cl}_2\text{SO}_2$ .

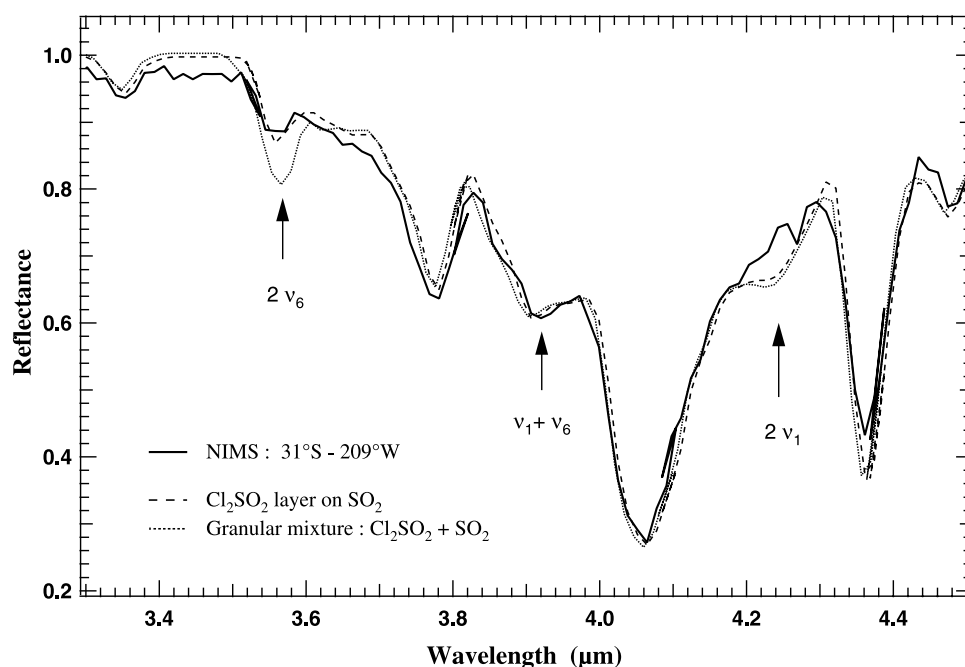
a simulation without  $\text{Cl}_2\text{SO}_2$  (with all  $\text{SO}_2$  parameters being the same) clearly emphasizes the chlorine molecule contribution to the synthetic spectrum around 3.58, 3.92, and 4.24  $\mu\text{m}$  (Figure 6). The last band is too weak (shoulder 1.5% deep) to be clearly discerned in the wing of the strong 4.07  $\mu\text{m}$   $\text{SO}_2$  band, but the 3.58  $\mu\text{m}$  band with a depth of 7% relative to a pure  $\text{SO}_2$  spectrum should emerge from the 3.56  $\mu\text{m}$   $\text{SO}_2$  band in the NIMS spectra. This is clearly not the case.

[34] Several factors may help to reduce the depth of the 3.58  $\mu\text{m}$  band of  $\text{Cl}_2\text{SO}_2$  without affecting the strength of the 3.920  $\mu\text{m}$  band: First, laboratory measurements showed that the relative peak intensity of the 3.58 and 3.91  $\mu\text{m}$  bands is reduced by a factor of about 8 upon dilution of  $\text{Cl}_2\text{SO}_2$  in  $\text{SO}_2$  ice (from pure to 2%  $\text{Cl}_2\text{SO}_2$ , Figure 4). At NIMS spectral resolution this decrease is still a factor of 2.3. A further reduction may occur for lower  $\text{Cl}_2\text{SO}_2$  concentrations, as those found near Marduk (i.e., 1%), but additional experiments need to be performed to assess this possibility. Second, sunlight at 3.58  $\mu\text{m}$  penetrates deeper below the surface, and thus probes more  $\text{Cl}_2\text{SO}_2$ , than at 3.92  $\mu\text{m}$  due to weaker absorption by  $\text{SO}_2$  at the former wavelength. The consequence is an enhancement by about an order of magnitude of the depth of the 3.58  $\mu\text{m}$  band relative to the 3.92  $\mu\text{m}$  band when compared to their respective peak absorption coefficients at NIMS resolution. This enhancement can be reduced if  $\text{Cl}_2\text{SO}_2$  is concentrated in the top layer of the surface. A simulation of such a stratification of the  $\text{Cl}_2\text{SO}_2$  abundance (using our layered reflectance model) shows that the 3.58  $\mu\text{m}$  band depth can indeed be reduced to a level compatible with the NIMS data by keeping the  $\text{Cl}_2\text{SO}_2$  abundance at 1% of in the top layer but decreasing its

value to less than 0.1% in the underlying layer (Figures 6 and 8). The maximum allowable thickness of the top layer ranges between 0.25 and 5 mm for porosities between 10 and 90%, respectively. For thicknesses smaller than about one quarter of these maximum values a  $\text{Cl}_2\text{SO}_2$  concentration larger than 1% is needed in the top layer to maintain the fit of the 3.92  $\mu\text{m}$  band. In all these simulations the depth of the 4.24  $\mu\text{m}$  shoulder is reduced to less than 1.5% making it virtually unobservable in the wing of the  $\text{SO}_2$  band. The average mass of  $\text{SO}_2$  contained in this top layer ranges between 50 and 450  $\text{g m}^{-2}$ .

[35] The only major remaining misfits in the 2.4–4.5  $\mu\text{m}$  range are on the one hand, the unidentified band around 4.62  $\mu\text{m}$  [Soderblom *et al.*, 1999] and, on the other hand an unidentified broad absorption around 3.15  $\mu\text{m}$  [Carlson *et al.*, 1997], apparently extending up to 3.5  $\mu\text{m}$  and eventually to 3.8  $\mu\text{m}$  if the misfit of the short wavelength wing of the 3.78  $\mu\text{m}$   $\text{SO}_2$  band is due to this same absorption (Figure 8). Preliminary modeling including pure  $\text{H}_2\text{O}$  ice (as a thin top layer or as a granular mixture with  $\text{SO}_2$ ) shows that ice could account only for part of the absorption wing below 3.13  $\mu\text{m}$ , not for the core of the feature. The analysis of these two bands are out of the scope of this paper.

[36] Although the band shift between pure and diluted  $\text{Cl}_2\text{SO}_2$  is small (8 nm at 110 K), simulations of the Marduk spectrum considering either a granular mixture of pure  $\text{Cl}_2\text{SO}_2$  and  $\text{SO}_2$  grains or a compact slab of pure  $\text{Cl}_2\text{SO}_2$  on top of pure  $\text{SO}_2$  frost display a noticeable short wavelength shift (about one NIMS spectral element,  $\sim 12$  nm) of the 3.92  $\mu\text{m}$  band at NIMS spectral resolution (Figure 7). However, the main arguments in disfavor of the presence of pure  $\text{Cl}_2\text{SO}_2$  are the intensities of the 3.58 and 4.24  $\mu\text{m}$  bands. In the granular case both bands are too strong ( $\sim 10\%$



**Figure 7.** Same as Figure 6 but for 1) a 10  $\mu\text{m}$  thick compact layer of pure  $\text{Cl}_2\text{SO}_2$  deposited on pure  $\text{SO}_2$  frost (dashed line) and 2) a granular mixture of pure  $\text{Cl}_2\text{SO}_2$  and pure  $\text{SO}_2$  grains (dotted line).

and 6% deep, respectively). In the stratified case, with the  $\text{Cl}_2\text{SO}_2$  layer thickness ( $\sim 10 \mu\text{m}$ ) constrained by the 3.92  $\mu\text{m}$  band depth, the contribution of the 3.58  $\mu\text{m}$  band is sufficiently reduced to allow to fit the 3.57  $\mu\text{m}$  NIMS absorption, but the 4.24  $\mu\text{m}$  band is still too strong ( $>4\%$ ) to be compatible with the observed NIMS spectrum near Marduk (Figure 7).

[37] Let us now consider the three other alternate candidates.

#### 4.1.2. $\text{ClSO}_2$

[38] Unfortunately no laboratory data exist on the combination modes of  $\text{ClSO}_2$  in the NIMS range. Only the fundamental modes have been measured in rare gas matrices [Bahou *et al.*, 2000]. We estimated these band positions by analogy with the measured behavior of the similar  $\nu_1$  and  $\nu_6$  S = O stretching fundamental and combination modes of  $\text{Cl}_2\text{SO}_2$  (matrix shifts and anharmonicity) (Rodriguez and Schmitt, submitted manuscript, 2003). The frequency of the fundamental  $\nu_1$  mode of  $\text{ClSO}_2$  diluted in rare gas matrix suggests a position of the first overtone of this mode ( $2\nu_1$ ) around 3.91  $\mu\text{m}$  when diluted in  $\text{SO}_2$ , making this molecule an additional good candidate for the 3.92  $\mu\text{m}$  Io band (Figure 8). In the same diluted state the estimated positions for the  $\nu_1 + \nu_2$  combination and  $2\nu_2$  overtone bands of  $\text{ClSO}_2$  are  $\sim 4.28 \mu\text{m}$  and  $\sim 4.63 \mu\text{m}$ , respectively. For pure  $\text{ClSO}_2$  the three band positions should differ by no more than 0.01  $\mu\text{m}$ .

[39] The position of the  $\nu_1 + \nu_2$  combination band fits quite well with the weak absorption band present at 4.27  $\mu\text{m}$  in the NIMS spectrum of Marduk's "red deposit" (Figure 8), but not in the "SO<sub>2</sub> reference" spectrum (Figure 1). In addition, the estimated  $2\nu_2$  overtone wavelength is also in rather good agreement with the  $\sim 4.62 \mu\text{m}$  band widely observed on Io by Soderblom *et al.* [1999], and also clearly seen in the Marduk spectrum. This good correlation of band positions for the three main combination bands of  $\text{ClSO}_2$

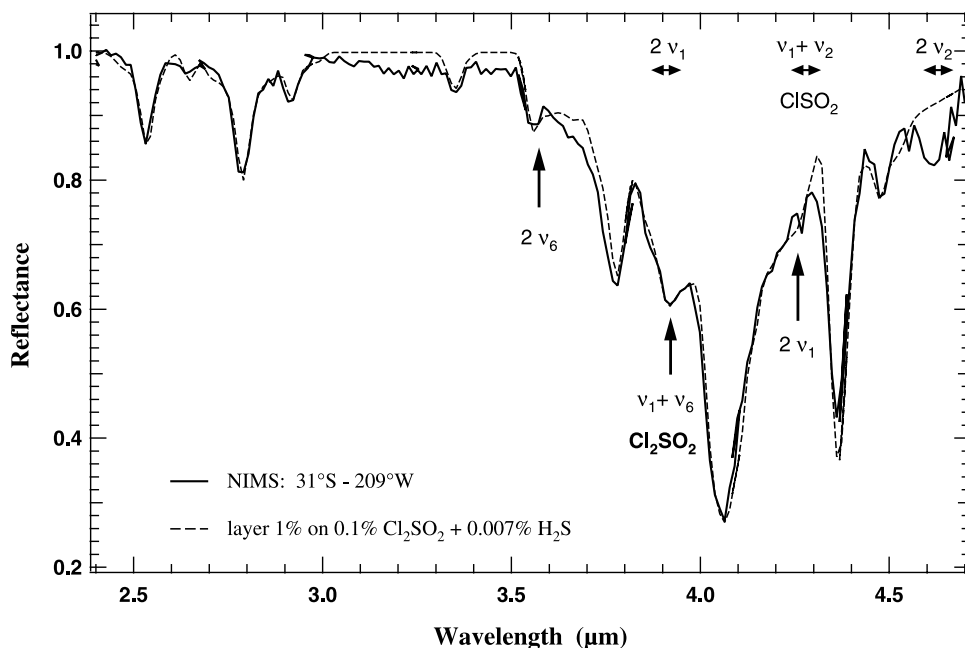
located in the NIMS range elects this molecule to the status of a highly interesting alternative (or competing) candidate. Unfortunately no confirmation of these band positions, no comparison of the band shapes and intensities with Marduk's spectrum, and no modeling of this spectrum can be achieved now to infer the abundance and state of this potential candidate molecule. Laboratory spectra of this poorly known molecule are needed before any confrontation with the "official" candidate  $\text{Cl}_2\text{SO}_2$  can be performed. However, if a similar band strength is assumed for the first overtone of the asymmetric  $\text{SO}_2$  stretching vibration of both molecules ( $2\nu_1$  mode for  $\text{ClSO}_2$ ,  $2\nu_6$  mode for  $\text{Cl}_2\text{SO}_2$ ) the required abundance of  $\text{ClSO}_2$  should be around 5%, more-or-less a factor of a few. Indeed the  $2\nu_6$  mode of  $\text{Cl}_2\text{SO}_2$  is about a factor of five weaker than its  $\nu_1 + \nu_6$  mode at 3.91  $\mu\text{m}$  (Figure 4).

#### 4.1.3. $\text{H}_2\text{S}_2$

[40] Although the  $\nu_1$  and  $\nu_5$  stretching modes of gas phase  $\text{H}_2\text{S}_2$  (3.908 and 3.913  $\mu\text{m}$ ; Schinanouchi, [2000]) fall within less than 0.012  $\mu\text{m}$  of the unidentified band, it is expected from comparison with  $\text{H}_2\text{S}$  that the band position of solid  $\text{H}_2\text{S}_2$  should be red-shifted by more than 0.05  $\mu\text{m}$ , as it is the case for liquid  $\text{H}_2\text{S}_2$  (3.986  $\mu\text{m}$ ; [Schinanouchi, 2000]). However,  $\text{H}_2\text{S}_2$  isolated in solid  $\text{SO}_2$  (or  $\text{S}_8$ ) may display a band (containing both modes) close to the gas phase position and thus may still be a potential candidate. Unfortunately no solid phase laboratory spectra of this molecule is available yet to conclude. Using the S-H stretch band strength of  $\text{H}_2\text{S}$  as a typical value for  $\text{H}_2\text{S}_2$  in our radiative transfer model, we estimate that its molar abundance in solid  $\text{SO}_2$  should be of the order of 0.01–0.1% to fit the NIMS band intensity.

#### 4.1.4. $\text{H}_2\text{S}$

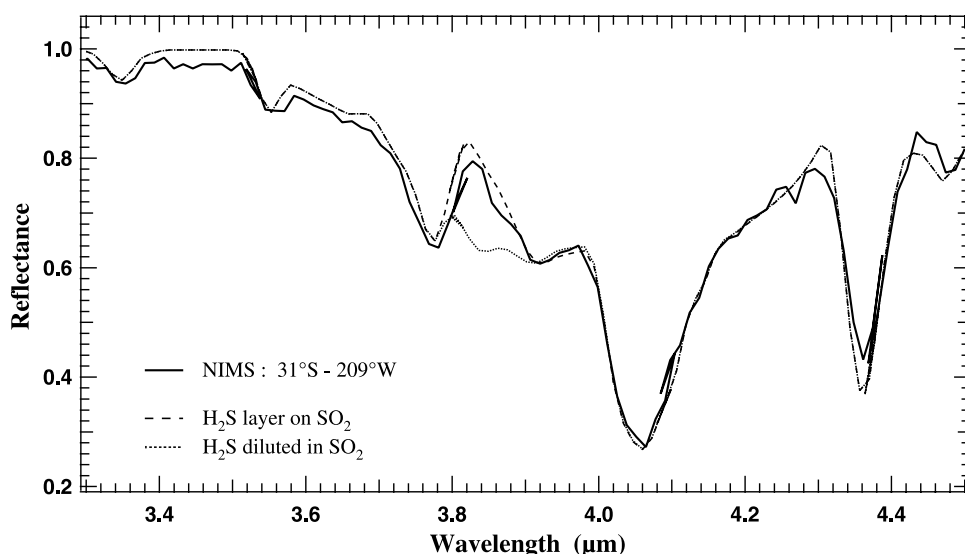
[41] Diluted  $\text{H}_2\text{S}$  can already be excluded as the absorber of the 3.92  $\mu\text{m}$  band on the basis of our laboratory data (Figures 3 and 4). A modeling shows that 0.08%  $\text{H}_2\text{S}$



**Figure 8.** Comparison (2.4–4.7  $\mu\text{m}$  range) of the average NIMS spectrum (thick line) with synthetic spectra involving: a 1 mm thick layer (for 45% porosity) of a molecular mixture of 1%  $\text{Cl}_2\text{SO}_2$  in  $\text{SO}_2$  deposited on 0.1%  $\text{Cl}_2\text{SO}_2$  diluted in  $\text{SO}_2$  with 0.007%  $\text{H}_2\text{S}$  added in both layers (dashed line).  $\text{SO}_2$  grain size: 150  $\mu\text{m}$ , surface proportion: 67%. The vertical arrows show the positions of the three bands of diluted  $\text{Cl}_2\text{SO}_2$ . The horizontal arrows depict probable ranges for the wavelength of the three combination bands of diluted  $\text{ClSO}_2$ .

diluted in  $\text{SO}_2$  partly fits the 3.92  $\mu\text{m}$  band but displays an additional strong component at 3.85  $\mu\text{m}$ , totally inconsistent with the NIMS spectrum (Figure 9). However, it should be noted that at this low concentration the 3.92  $\mu\text{m}$  component should disappear as it is due to aggregated  $\text{H}_2\text{S}$  molecules (multimers) that only exist at higher concentration (as in our laboratory sample, see section 3.2).

[42] On the other hand, the central band wavelength (3.906–3.910  $\mu\text{m}$ ) of the high temperature phases of pure  $\text{H}_2\text{S}$  (above 103.6 K) may barely fit the position of the NIMS band (Figure 4).  $\text{H}_2\text{S}$  should then be segregated from solid  $\text{SO}_2$ . It may be in the form of an extremely thin layer condensed on top of solid  $\text{SO}_2$  (or sulfur) or less probably dispersed as submicron-sized grains of pure  $\text{H}_2\text{S}$  within the



**Figure 9.** Same as Figure 6 but for 1) a molecular mixture of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  (dotted line) with a relative molar abundance of 0.08% and 2) a 0.3  $\mu\text{m}$  thick layer of pure  $\text{H}_2\text{S}$ -II particles (0.1  $\mu\text{m}$  in size) on top of  $\text{SO}_2$  ice (dashed line). This last model is equivalent to a compact  $\text{H}_2\text{S}$  layer 0.12  $\mu\text{m}$  thick. The  $\text{SO}_2$  grain size is 140  $\mu\text{m}$ .

$\text{SO}_2$  frost. The thickness of the  $\text{H}_2\text{S}$  layer condensed on  $\text{SO}_2$  frost (68% of the total area) should be  $0.12 \mu\text{m}$  to reproduce the strength and shape of the  $3.92 \mu\text{m}$  band, as calculated with the optical constants of pure phase II- $\text{H}_2\text{S}$  ice at 107 K and considering a thin compact  $\text{H}_2\text{S}$  slab (Figure 9). The weaker  $\text{H}_2\text{S}$  absorptions occurring at  $1.952$  and  $1.995 \mu\text{m}$  have synthetic depths of less than 0.1% and are hidden in the wings of the weak  $\text{SO}_2$  band at  $1.982 \mu\text{m}$  ( $\sim 1$ –1.5% deep). It should be noted that this last band is not seen in the NIMS spectrum of the Marduk area partly due to the noise level ( $1-\sigma \sim 0.4\%$ ).

[43] With our current “geometric optics” radiative transfer model [Douté and Schmitt, 1998] we cannot simulate scattering in an extremely thin layer composed of sub-micron grains. However, Mie calculations show that such a layer composed of spherical  $\text{H}_2\text{S}$  particles less than  $0.2 \mu\text{m}$  in diameter behaves like a purely absorbing medium (negligible scattering). We treated this layer independently (neglecting scattering) and coupled it to the reflectance model of the  $\text{SO}_2$  substrate. Three monolayers of  $0.1 \mu\text{m}$  particles (or correspondingly more layers for smaller particles) are required to fit the  $3.92 \mu\text{m}$  NIMS band depth implying a layer thickness in the range  $0.3$ – $4 \mu\text{m}$  for 30 to 95% porosity. The local thickness of this layer may be increased if we consider that only a fraction of the area covered by  $\text{SO}_2$  ice has condensed  $\text{H}_2\text{S}$  on top. However, for thicknesses larger than  $4 \mu\text{m}$  (for the minimum 30% porosity for a sphere layer) and fractional area lower than 8% the  $3.92 \mu\text{m}$  band starts to saturate, debasing the fit.

[44] It should be noted that crystalline phase III of solid  $\text{H}_2\text{S}$  is excluded because it should display a double band structure peaking around  $3.92$  and  $3.955 \mu\text{m}$  (see Figure 4) at NIMS spectral resolution, the second one being clearly incompatible with the observations. This sets a minimum temperature of 103.6 K for condensed  $\text{H}_2\text{S}$  on Io.

[45] Finally, though diluted  $\text{H}_2\text{S}$  is excluded as the main source of the  $3.92 \mu\text{m}$  absorption, adding a minor amount of  $\text{H}_2\text{S}$  ( $\sim 7 \times 10^{-5}$ ) in our stratified  $\text{Cl}_2\text{SO}_2$ : $\text{SO}_2$  models slightly improves the fit in the short wavelength wing of this band (Figure 8). Although not a tangible proof of the occurrence of diluted  $\text{H}_2\text{S}$ , it sets an upper limit of  $\sim 10^{-4}$  for its abundance in solid  $\text{SO}_2$ .

#### 4.1.5. Identification Summary

[46] To sum up, direct comparison between laboratory spectra and the average Marduk NIMS spectrum, coupled with radiative transfer modeling, allows us to propose as the surface material producing the  $3.92 \mu\text{m}$  absorption either (1) a (sub)micron thin layer of pure solid  $\text{H}_2\text{S}$  (phase II), either compact or made up of submicron particles, condensed at  $T \geq 103.6$  K on top of the  $\text{SO}_2$  ice, or (2) a millimeter thick layer of 1%  $\text{Cl}_2\text{SO}_2$  mixed at the molecular level within solid  $\text{SO}_2$  covering a similar mixture but strongly depleted in  $\text{Cl}_2\text{SO}_2$  ( $< 0.1\%$ ). There is no severe constraint on temperature, but it is probably lower than 130 K.

[47] Spectral constraints on the  $3.92 \mu\text{m}$  band alone, are not able to unambiguously distinguish between these two possible identifications. Unfortunately, both molecules do not possess other bands strong enough and far-off the  $\text{SO}_2$  bands to clearly appear in the NIMS data and thus to firmly confirm one of these candidates.  $\text{H}_2\text{S}$  has a few additional bands around  $1.98 \mu\text{m}$  but they are too weak to be observable in the NIMS Marduk spectrum. For diluted

$\text{Cl}_2\text{SO}_2$  we found that only a limited additional physical constraint (stratification) is necessary to hide its two weaker bands (at  $3.58$  and  $4.25 \mu\text{m}$ ) within the  $\text{SO}_2$  absorptions.

[48] Finally, in the absence of relevant laboratory spectra, theoretical considerations also led us to consider diluted  $\text{ClSO}_2$  (about 2–15% in solid  $\text{SO}_2$ ) and diluted  $\text{H}_2\text{S}_2$  (0.01–0.1%) as two additional potential candidates.  $\text{ClSO}_2$  is particularly attractive as it may fit, or contribute, to two other bands at  $4.27 \mu\text{m}$  (weak) and  $4.62 \mu\text{m}$  (strong and broad).

[49] The problem is now to find additional arguments in terms of chemistry and volatility that may help to discern between these four possible candidate molecules and to estimate their probability of occurrence in their respective physical states under Ionian conditions.

## 4.2. Chemistry and Volatility

[50] The molecules condensed at the surface of Io are expected to come mostly from volcanic eruptions or lava degassing [Zolotov and Fegley, 1998a, 1998b; Fegley and Zolotov, 2000] followed by photochemistry in the transient atmosphere [Summer and Strobel, 1996; Wong and Johnson, 1996a; Moses et al., 2002a, 2002b] and possible evolution by energetic particle bombardment at the surface [Moore, 1984; Wong and Johnson, 1996b; Johnson, 1997].  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{Cl}_2\text{SO}_2$  have been included in the equilibrium chemical model of the volcanic gases [Fegley and Zolotov, 2000] and in the photochemical model of Moses et al. [2002a, 2002b].  $\text{ClSO}_2$  and  $\text{H}_2\text{S}_2$  were not taken into account in the volcanic model. The results for  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}_2$  were not discussed in the Moses et al. [2002a, 2002b] papers due to the very low assumed elemental H abundance. The possible chemical reactions of the atmospheric gases with the surface materials and upon condensation have not yet been considered in models, but the possibility of heterogeneous reactions has been discussed by Moses et al. [2002a, 2002b].

[51] Besides the chemical considerations, the volatility of the candidate materials has to be taken into account in the elaboration of volcanic gas condensation scenarios able to produce the inferred physical states and molecular abundances at the surface. Extrapolations at low temperatures of the vapor pressure curves exist for solid  $\text{SO}_2$  and  $\text{H}_2\text{S}$  [Honig and Hook, 1960] but are restricted to the liquid phase above 225 K for  $\text{H}_2\text{S}_2$  and  $\text{Cl}_2\text{SO}_2$ . We derived this curve down to  $\sim 100$  K for solid  $\text{Cl}_2\text{SO}_2$  (see experimental part and Figure 5).

[52] In the following we will first compare, for each candidate molecule, the abundances we deduced in the solid phase with those expected for the volcanic gases from existing chemical models. Then we consider the volatility of these molecules to propose condensation scenarios and to assess the condensate stability at Io's surface under plausible temperature and pressure conditions. Finally, scenarios considering possible heterogeneous reactions are investigated.

### 4.2.1. $\text{Cl}_2\text{SO}_2$

[53] Within the range of volcanic conditions studied by Fegley and Zolotov [2000] their chemical model falls far short of producing enough  $\text{Cl}_2\text{SO}_2$  molecules to account for the intensity of the  $3.92 \mu\text{m}$  band. However, preliminary calculations by M. Zolotov (Washington University, personal



communication, 2000) show that the abundance of Cl<sub>2</sub>SO<sub>2</sub> may be increased by 2 to 4 orders of magnitude and reach a mole fraction relative to SO<sub>2</sub> of  $5 \times 10^{-7}$  to  $5 \times 10^{-5}$  under particular physical conditions in the vent ( $T = 1000$  K,  $P = 1$  to 100 bar) but with O and Cl atomic compositions (O/S = 2, Cl/S = 0.10 – 0.20) exceeding the upper limits of Io's torus. If directly applied to surface condensates, these Cl<sub>2</sub>SO<sub>2</sub> abundances are still too low by more than two orders of magnitude to account for the NIMS band intensity, but possible specific (though extreme) local vent conditions and chemical composition at Marduk may further increase the volcanic production of Cl<sub>2</sub>SO<sub>2</sub>. In particular, larger O/S and Cl/S atomic ratios and lower magma temperatures may favor Cl<sub>2</sub>SO<sub>2</sub> over the other, generally more abundant, nonoxidized Cl<sub>x</sub>S<sub>y</sub> chlorine compounds. On the other hand, atmospheric photochemistry seems unable to help significantly in that direction (*J. Moses*, Lunar and Planetary Institute, personal communication, 2001) because three-body reactions, inefficient in the low density Io atmosphere, are necessary to form ClSO<sub>2</sub>, the essential precursor of Cl<sub>2</sub>SO<sub>2</sub> [*Moses et al.*, 2002b].

[54] It is interesting to note at this point that, even if we directly apply the enhanced chlorine atmospheric abundances obtained by M. Zolotov (under the above volcanic conditions) to surface composition and combine them with molecular band strengths, the 3.91 μm band of diluted Cl<sub>2</sub>SO<sub>2</sub> may be already the “strongest” near-IR band of all 13 chlorine molecules included in the volcanic model. However, its depth would be only 0.03% for  $3 \times 10^{-5}$  Cl<sub>2</sub>SO<sub>2</sub> abundance! Although Cl<sub>2</sub>SO is generally slightly more abundant in the volcanic models, we found experimentally that its only near infrared band near 4.15 μm ( $2\nu_1$ ) is inactivated when diluted in solid SO<sub>2</sub> (Rodriguez and Schmitt, submitted manuscript, 2003). ClO and Cl<sub>2</sub>O have much too low abundances to have their second order overtone/combination bands observable in the NIMS range. Atomic Cl and the Cl<sub>2</sub> molecule are infrared-inactive. Even the most abundant chlorine-bearing molecules, NaCl, KCl, ClS, ClS<sub>2</sub>, Cl<sub>2</sub>S, and Cl<sub>2</sub>S<sub>2</sub>, have their fundamental bands at too low frequencies (>14 μm) to have observable overtone/combination modes (Rodriguez and Schmitt, submitted manuscript, 2003). Finally only the very strong bands of HCl around 3.5–3.6 μm may show up if its abundance exceeds about  $10^{-5}$ , that is for H/S atomic ratios larger than  $10^{-4}$  according to *Fegley and Zolotov* [2000]. But its very high volatility ( $2 \times 10^5$  times that of SO<sub>2</sub> at 110 K [*Honig and Hook*, 1960]) does not favor its condensation at Io surface temperatures.

[55] However, extreme volcanic conditions producing high Cl<sub>2</sub>SO<sub>2</sub> gas abundances are not requisite to reach 1% in the frost. Indeed, thermodynamical equilibrium between the atmospheric and condensate compositions should trigger a chemical differentiation that strongly enhances the concentration of the less volatile molecules, such as Cl<sub>2</sub>SO<sub>2</sub>, in solid SO<sub>2</sub>.

#### 4.2.1.1. Condensation Scenario

[56] From the extrapolation of the vapor pressure curves of solid SO<sub>2</sub> [*Honig and Hook*, 1960] and Cl<sub>2</sub>SO<sub>2</sub> (Figure 5) we determine a nominal saturation pressure ratio  $P_s(\text{SO}_2)/P_s(\text{Cl}_2\text{SO}_2)$  of about 12,000 at 110 K, but possible values may range between 6,000 and 30,000 depending on the assumed value for the condensation coefficient of

Cl<sub>2</sub>SO<sub>2</sub> (see experimental part). The upper limit of the ratio results from the assumption of unity condensation coefficient.

[57] If a SO<sub>2</sub>-rich (~65%) volcanic gas containing Cl<sub>2</sub>SO<sub>2</sub> condenses rapidly on cold surfaces surrounding the vent (i.e., when the SO<sub>2</sub> gas pressure over the surface is much larger than its saturation pressure at the surface temperature) then Cl<sub>2</sub>SO<sub>2</sub> should be dynamically trapped in SO<sub>2</sub> ice with a similar mole fraction than in the gas. However, if this condensation occurs in conditions close to thermodynamical equilibrium (i.e., with a small pressure ratio  $P(\text{SO}_2)/P_s(\text{SO}_2, T_{\text{surf}})$ ), a Cl<sub>2</sub>SO<sub>2</sub> mole fraction of only  $5 \times 10^{-7}$  is necessary to obtain a concentration of  $10^{-2}$  in solid SO<sub>2</sub> at 110 K, assuming ideal solid solution (i.e., following Raoult partial pressure law). The Cl<sub>2</sub>SO<sub>2</sub>:SO<sub>2</sub> mixture probably do not form an ideal solid solution, therefore the Cl<sub>2</sub>SO<sub>2</sub> equilibrium partial pressure may need to be larger than  $5 \times 10^{-7}$  by an unknown factor (the activity coefficient). The equilibrium concentration in the solid is also temperature dependent (decreasing with increasing surface temperature, as  $P_s(\text{SO}_2)/P_s(\text{Cl}_2\text{SO}_2)$ , see Figure 5) but SO<sub>2</sub> condensation should not occur above 140 K over large area if the plume pressure drops below  $10^{-6}$  bar a few kilometers away from the vent [*Zhang et al.*, 2003]. At 140 K, a Cl<sub>2</sub>SO<sub>2</sub> mole fraction of  $4 \times 10^{-6}$  is then needed to equilibrate  $10^{-2}$  in solid SO<sub>2</sub>. On the other hand, condensation of almost pure solid Cl<sub>2</sub>SO<sub>2</sub> requires a Cl<sub>2</sub>SO<sub>2</sub> mole fraction in the gas larger than  $10^{-3}$ , a highly improbable value.

[58] However, for this scenario to work most of the erupted SO<sub>2</sub> (99.99%) should not condense in the reddish area to maintain the 1% Cl<sub>2</sub>SO<sub>2</sub> abundance observed in the top frost layer. It can flow away but no sign of massive condensation outside the Marduk deposits is observed. If all this SO<sub>2</sub> (~ $10^{14}$  kg) is injected in the atmosphere, the implied global Io resurfacing rate is thousands of times the Pele rate [*Spencer et al.*, 1997]. Consequently this gas-solid differentiation scenario is difficult to support.

#### 4.2.1.2. Heterogeneous Formation Scenario

[59] Besides volcanic and atmospheric chemistries and condensation scenarios other chemical pathways may be considered to explain the high Cl<sub>2</sub>SO<sub>2</sub> abundance at the surface.

[60] Starting from our initial reports on the possible identification of large amounts of Cl<sub>2</sub>SO<sub>2</sub> near Marduk [*Schmitt and Rodriguez*, 2000, 2001] and from subsequent discussions on the possible chemical pathways toward Cl<sub>2</sub>SO<sub>2</sub>, an alternative possibility to form this molecule directly at the surface by heterogeneous reaction has been pinpointed by *Moses et al.* [2002b]. Laboratory investigations of the reactions occurring during UV irradiation (308 nm) of Cl<sub>2</sub> and SO<sub>2</sub> mixed in rare gas matrices [*Bahou et al.*, 2000] show that successive reactions of Cl atoms (formed by photo-dissociation of Cl<sub>2</sub>) with SO<sub>2</sub> first form ClSO<sub>2</sub>, then Cl<sub>2</sub>SO<sub>2</sub>.

[61] On Io a high atomic Cl abundance is directly produced in the volcanic magma when the elemental ratio Cl/(Na + K) exceeds unity [*Fegley and Zolotov*, 2000]. Most of the excess Cl is in atomic form. Its abundance is then slightly increased in the atmosphere (by about 0.2% for a typical 20 min plume flight time) by photolysis of NaCl and KCl [*Moses et al.*, 2002b]. On the other hand, condensed SO<sub>2</sub> is ubiquitous at

the surface of Io, even at short distances from active vents [Douté *et al.*, 2001, 2002], and also possibly forms in some volcanic plumes [Spencer *et al.*, 1997; Cataldo and Wilson, 1999]. It then appears that two necessary conditions for heterogeneous reaction of atmospheric Cl with condensed SO<sub>2</sub> are met. However, several major pieces of information are missing to quantify the production efficiency of Cl<sub>2</sub>SO<sub>2</sub> in the different scenarios that can be proposed.

[62] First, the single laboratory study available today [Bahou *et al.*, 2000] is only qualitative and thus did not allow us to infer the efficiency of the process, especially at Io's surface or plume conditions. In particular when Cl directly reacts on a solid SO<sub>2</sub> surface, the reaction may follow a different chemical pathway to Cl<sub>2</sub>SO<sub>2</sub> than in rare gas matrices. It should be also noted that Bahou *et al.* [2000] found that a small energy barrier should be overcome to form Cl<sub>2</sub>SO<sub>2</sub> from ClSO<sub>2</sub>. Thermal energy at Io's surface temperature might be sufficient to trigger this reaction. This barrier might also not exist for direct reaction with solid SO<sub>2</sub>. New experiments are urgently needed to solve these issues.

[63] The second major unknown is the chemical composition of the gases released during the eruption of Marduk. This volcano may be quite atypical on Io owing to its particular fan-shaped reddish deposit that is suspected to exhibit high pressure style eruption [McEwen *et al.*, 1998]. S<sub>3</sub> and S<sub>4</sub> radicals are suspected to produce this reddish color [Spencer *et al.*, 2000; McEwen *et al.*, 1998; and references therein], but as we will show later, Cl<sub>2</sub>S might be an alternative, or competing, source for this coloration. However, the discrimination and quantification of these molecules are not yet possible due to a lack of laboratory data, and no other compositional information is available to constrain the chlorine content in the plume and near the surface.

[64] Another key question is: do the heterogeneous reactions leading to Cl<sub>2</sub>SO<sub>2</sub> occur on SO<sub>2</sub> particles condensing in the volcanic plume, or directly at the surface on condensing SO<sub>2</sub> frost or, as suggested by Moses *et al.* [2002b], on adsorbed SO<sub>2</sub>? Indeed, it is not yet completely clear what is the effective process of SO<sub>2</sub> "frost" formation in the annular or irregularly shaped "deposits" around volcanos. Models of SO<sub>2</sub> condensation in the plume [Cataldo and Wilson, 1999] as well as direct (ballistic) SO<sub>2</sub> deposition on the surface [Glaze and Baloga, 2000] have been recently proposed.

[65] The situation certainly depends on the volcano and of the type of eruption. Using the plume particle sizes and masses derived by Spencer *et al.* [1997] for Pele and Loki we can compare the condensation time constants of SO<sub>2</sub> and Cl on the plume particles with the typical flight time of the plume and infer if significant SO<sub>2</sub> condensation and Cl reaction may occur on the plume particles.

[66] Assuming the SO<sub>2</sub> gas is greatly supersaturated in the plumes and that the particles are smaller than the mean free path of the gas (true for Io's plumes), the condensation time constant  $\tau_c$  (derived from gas kinetic laws) of the gas on particles of radius  $r_p$  and number density  $n_p$  is

$$\tau_c = \frac{1}{\langle c \rangle \alpha n_p \pi r_p^2} \quad \text{with} \quad \langle c \rangle = \sqrt{\frac{8RT}{\pi M}}$$

where  $\langle c \rangle$  is the mean speed of the condensible molecules and  $M$  is their molar mass.

[67] In the case of Pele we consider the two extreme particle radii and associated total masses of the plume ( $2.8 \times 10^9$  g for 0.05  $\mu\text{m}$  particles,  $1.15 \times 10^9$  g for 0.08  $\mu\text{m}$ ) derived by Spencer *et al.* [1997] from their modeling of the wavelength dependent optical depth of the plume. Assuming an homogeneous hemispheric plume with radius 420 km we derive particle number densities of  $1.7 \times 10^7$  partic.  $\text{m}^{-3}$  (0.05  $\mu\text{m}$ ) and  $1.7 \times 10^6$  partic.  $\text{m}^{-3}$  (0.08  $\mu\text{m}$ ). With these parameters we obtain time constants of 15 h and 60 h for SO<sub>2</sub> (with  $\alpha = 0.68$ ) and Cl (with assumed  $\alpha = 0.5$ ) for the 0.05  $\mu\text{m}$  and 0.08  $\mu\text{m}$  particle cases, respectively. These values are much larger than the typical plume time of flight ( $\sim 20$  min). However, for Loki (with 200 km plume radius) the figure dramatically changes. For the assumed 0.01  $\mu\text{m}$  particle radius and the plume mass of  $9.3 \times 10^{10}$  g calculated by Spencer *et al.* [1997] we obtain a particle number density of  $6.6 \times 10^{11}$  partic.  $\text{m}^{-3}$  and condensation time constants of only 30 s for SO<sub>2</sub> and Cl. This value is almost two orders of magnitude lower than the time of flight, thus strongly favoring SO<sub>2</sub> condensation and possible reactions of Cl on the plume particles. The heterogeneous reactions of Cl atoms with SO<sub>2</sub> condensing on very fine particles ( $\sim 0.1$ – $0.01$   $\mu\text{m}$ ) are also favored by the large surface area available in the volcanic plume. For Loki the total area of the particles is 10–100 times larger than the plume deposit area.

[68] There is not yet published plume optical depth analysis at Marduk, but a "visible plume" (measured at 0.42  $\mu\text{m}$ ) is quoted in the SSI images during the G8, E11, and possibly E6, C9 and C10 Galileo orbits by McEwen *et al.* [1998]. As Marduk has a "prometeus-type plume" (larger optical depth than Pele) and is suspected to have "overpressured eruptions", we can suspect rather favorable pressure and particle density conditions for SO<sub>2</sub> to condense efficiently in the plume and for atomic Cl to meet SO<sub>2</sub> and react with it on the particles. Given the very short expected condensation time scale the full condensation-reaction process may well mostly occur in the very first minute(s) of the plume flight. During that time continuous SO<sub>2</sub> condensation in the plume allows to progressively incorporate in the particles the Cl<sub>2</sub>SO<sub>2</sub> molecules freshly formed at their surfaces. This also renews the SO<sub>2</sub> surface for further reactions. Given the much lower evaporation rate of Cl<sub>2</sub>SO<sub>2</sub> compared to SO<sub>2</sub>, the trapping process should be very efficient. Even if the particle composition constantly equilibrates with the gas phase during all this process, the loss of Cl<sub>2</sub>SO<sub>2</sub> to the gas should be negligible as a gaseous mole fraction of only  $\sim 10^{-6}$  Cl<sub>2</sub>SO<sub>2</sub> is needed to stabilize 1% in solid SO<sub>2</sub>. This scenario is compatible with the deduced physical state of Cl<sub>2</sub>SO<sub>2</sub>, i.e., diluted at the molecular level within the SO<sub>2</sub> grains.

[69] In this process a minimum Cl/SO<sub>2</sub> ratio of 2% is needed to produce 1% Cl<sub>2</sub>SO<sub>2</sub> in solid SO<sub>2</sub> if we assume 1) similar sticking coefficients for Cl and SO<sub>2</sub> on a SO<sub>2</sub> particle, 2) complete conversion of adsorbed Cl to Cl<sub>2</sub>SO<sub>2</sub>, 3) no chemical or thermal desorption of Cl, ClSO<sub>2</sub>, Cl<sub>2</sub>SO<sub>2</sub> or SO<sub>2</sub>, and 4) all the available SO<sub>2</sub> condenses on the particles. In fact the sticking coefficient of Cl on SO<sub>2</sub> ice is probably lower than the condensation coefficient of SO<sub>2</sub>, but on the other hand the thermal desorption rate of SO<sub>2</sub>

may be a significant fraction of its condensation rate, depending on particle temperature and plume conditions. Part of the Cl atoms may also desorb before reaction or react with other molecules or radicals condensed with  $\text{SO}_2$  and a fraction may be locked in  $\text{ClSO}_2$  isolated in solid  $\text{SO}_2$  before being able to react with another Cl atom. Finally a significant part of the volcanic  $\text{SO}_2$  may not condense on the particles and escape from the plume thus contributing to the background Io atmosphere. Favorable conditions for effective heterogeneous formation of  $\text{Cl}_2\text{SO}_2$  on plume particles are then met only for Cl-rich volcanic eruptions (i.e.,  $[\text{Cl} - (\text{Na} + \text{K})]/\text{S} > 0.015$ ) and when the particle density in the plume is high enough to allow efficient  $\text{SO}_2$  condensation and Cl sticking. For a global efficiency of the  $\text{Cl}_2\text{SO}_2$  formation process of about 50%, and for  $(\text{Na} + \text{K})/\text{S} = 0.02$  the formation of 1%  $\text{Cl}_2\text{SO}_2$  relative to  $\text{SO}_2$  may require a Cl/S ratio of 0.05.

[70] If  $\text{SO}_2$  condensation did not occur in the plume, fresh  $\text{SO}_2$  frost should directly develop at the surface and the chlorine atoms should then react with the  $\text{SO}_2$  molecules condensing on the frost crystal surfaces (i.e., with the top molecular layer, considered as “adsorbed  $\text{SO}_2$ ” by *Moses et al.* [2002b]) in a way similar to that on plume particles. So the formation of  $\text{Cl}_2\text{SO}_2$  should only occur where and when the  $\text{SO}_2$  molecules condense. On the other hand it is difficult to imagine a scenario in which Cl efficiently reacts with  $\text{SO}_2$  grains previously condensed or deposited at the surface. Indeed, the poorly volatile  $\text{Cl}_2\text{SO}_2$  molecules accumulating as a monolayer at the surface of the grains (typically larger than 10–50  $\mu\text{m}$  [*Douté et al.*, 2001]) probably hinder further reaction between Cl and  $\text{SO}_2$ .

[71] We were also not able to imagine a simple scenario, consistent with our observations, in which Cl reacts with  $\text{SO}_2$  adsorbed in “warm” area, as proposed by *Moses et al.* [2002b]. Indeed, only part of the volcanic  $\text{SO}_2$  will adsorb in these warm area, but most of the available Cl should adsorb and react with this  $\text{SO}_2$  and form  $\text{Cl}_2\text{SO}_2$ , otherwise extreme Cl/S ratios are needed. This weakly volatile molecule should then efficiently desorb to go back and mix in the ballistic plume and then cocondense with the bulk of  $\text{SO}_2$  to form the observed millimeter thick intimately mixed  $\text{Cl}_2\text{SO}_2:\text{SO}_2$  solid deposit. We rather think that the  $\text{Cl}_2\text{SO}_2$  molecules possibly formed in this way will be predominantly segregated in the “warm” area where they formed.

[72] Once deposited or formed at the surface, the frost composition should be stable as the millimeter thick  $\text{Cl}_2\text{SO}_2$ -rich layer contains more than  $10^7$  times the  $\text{Cl}_2\text{SO}_2$  amount required to maintain its equilibrium partial pressure in the whole atmospheric column above the deposits.

[73] At the surface  $\text{Cl}_2\text{SO}_2$  is destroyed by UV radiation with a time constant of about 3 years ( $\lambda < 360 \text{ nm}$ ,  $J \approx 10^{-8} \text{ s}^{-1}$  [*Moses et al.*, 2002b]). The  $\text{SO}_2$  ice matrix adds some UV protection as a thickness of only a tenth of a millimeter completely absorbs all solar radiations below 320 nm and a decreasing fraction of the wavelengths up to 370 nm [see, e.g., *Nash et al.*, 1980]. Adding a small amount of sulfur molecules (0.5%–3%  $\text{S}_8$ ) in  $\text{SO}_2$  strongly decreases the UV penetration depth below 400 nm [see *Douté et al.*, 2001]. In this case an almost complete shielding of  $\text{Cl}_2\text{SO}_2$  from UV photolysis is achieved.

[74] In addition any Cl atom formed by photolysis of  $\text{Cl}_2\text{SO}_2$  will react immediately with the surrounding  $\text{SO}_2$

matrix molecules to form  $\text{ClSO}_2$ , the precursor of  $\text{Cl}_2\text{SO}_2$ . This may explain why  $\text{Cl}_2\text{SO}_2$  was still present in similar amount in the Marduk deposits at the time of the E14 encounter (March 1998), 1.5 years after the G2 observation. The  $\text{Cl}_2\text{SO}_2$  molecules will be exposed to UV radiation only when the  $\text{SO}_2$  matrix will slowly sublimate through the day-night cycles, i.e., after the plume supply will stop. A progressive segregation of  $\text{Cl}_2\text{SO}_2$  (as a pure solid or mixed with sulfur) from  $\text{SO}_2$  may then occur, depending on the local conditions.

[75] The thickness of the  $\text{Cl}_2\text{SO}_2$ -rich layer (0.2–0.5 mm with unit compacity) may reflect the amount of gas condensed during the last eruption(s) of Marduk (post Voyager): of the order of  $5 \times 10^9$ – $5 \times 10^{10} \text{ kg}$  of  $\text{SO}_2$  frost over the whole reddish area. Marduk was probably active at the time of the G2 observations (September 1996) as plumes were still visible above the volcano during at least the next 8 months (orbits E6, G8 [see *McEwen et al.*, 1998]).

[76] The lower concentration deduced for the underlying layer may be due either to different volcanic conditions (lower  $[\text{Cl} - (\text{Na} + \text{K})]/\text{S}$  abundance ratio, for example) during the previous eruption or to the burial of  $\text{Cl}_2\text{SO}_2$  below a layer of “pure”  $\text{SO}_2$  ice before being overlaid by the frost coming from the last eruption. Indeed, the day-night sublimation-condensation cycle may segregate the less volatile  $\text{Cl}_2\text{SO}_2$  molecules and accumulate a couple of millimeters of pure  $\text{SO}_2$  frost on top, enough to hide the overlaid  $\text{Cl}_2\text{SO}_2$  from the solar infrared photons. Only  $\text{Cl}_2\text{SO}_2$  deposited in the top layers by the last eruption is then being probed. On the other hand, as demonstrated before, the complete depletion by UV photo-destruction of  $\text{Cl}_2\text{SO}_2$  in the  $\text{SO}_2$  layer takes more than a decade.

#### 4.2.2. $\text{ClSO}_2$

[77] The heterogeneous formation mechanism of  $\text{Cl}_2\text{SO}_2$  observed by *Bahou et al.* [2000] requires the intermediate formation of  $\text{ClSO}_2$ , as in the gas phase. Although only a minor atmospheric product on Io [*Moses et al.*, 2002b] this molecule may be formed on  $\text{SO}_2$  ice and trapped in appreciable quantity, especially if its reaction with another Cl atom and subsequent conversion to  $\text{Cl}_2\text{SO}_2$  is hindered by some energy barrier, as suggested by *Bahou et al.* [2000]. A high condensation rate of volcanic  $\text{SO}_2$  on plume particles or on surface grains, eventually coupled with a low atomic Cl abundance, may also isolate this first reaction product into solid  $\text{SO}_2$  before another Cl atom may react with it. On the other hand  $\text{ClSO}_2$  is a quite unstable molecule and easily decomposes under reaction with most atoms and molecules [see *Moses et al.*, 2002b]. Some condition dependent partition or steady-state balance between production and destruction of these two molecules may occur. Both molecules are then likely to be simultaneously present but in a unknown ratio. Preliminary results from recent experiments on the heterogeneous formation of  $\text{Cl}_2\text{SO}_2$  seem to show that, contrary to the results of *Bahou et al.* [2000],  $\text{ClSO}_2$  may be only a minor product (L. Schriver and A. Schriver, Université P. & M. Curie, personal communication, 2002).

[78] We should also note here that only half the amount of Cl required to form  $\text{Cl}_2\text{SO}_2$  is necessary for the formation of  $\text{ClSO}_2$ . But on the other hand, a larger amount (2–15% in  $\text{SO}_2$ ) may be required to fit the 3.92  $\mu\text{m}$  band strength if the intrinsic strength of the  $2\nu_1$   $\text{ClSO}_2$  band is effectively



weaker (see section 4.1.2). This may further increase the constraint on the abundance of atomic Cl (in excess of Na + K) in the atmosphere of Io if this molecule is effectively the main absorber at 3.92  $\mu\text{m}$  in the Marduk spectrum.

#### 4.2.3. H<sub>2</sub>S

[79] The H<sub>2</sub>S gas abundance may be inferred from the number of H<sub>2</sub>S molecules segregated in the candidate submicron top layer only if the differentiation process and scenario that led to it are assumed. The thermodynamical properties of solid H<sub>2</sub>S and SO<sub>2</sub> should be taken into account to assess if such a differentiation is realistic on Io.

[80] The very high volatility of H<sub>2</sub>S ice (vapor pressure 10<sup>4</sup> times that of SO<sub>2</sub> around 110 K [Honig and Hook, 1960]) (Figure 5) makes it very unstable even at temperatures as low as 103.6 K, the minimum temperature of occurrence of the crystalline phase II of solid H<sub>2</sub>S compatible with the observation. At this temperature a partial pressure of  $1.5 \times 10^{-6}$  bar is necessary to stabilize a layer of pure solid H<sub>2</sub>S. Even if we consider a H<sub>2</sub>S mole fraction in the gas as large as 10<sup>-4</sup>, a total pressure above 0.01 bar is then needed. Such a high pressure on Io may possibly occur locally near erupting vents but then SO<sub>2</sub> should condense very rapidly and dynamically trap H<sub>2</sub>S at the low gas concentration. If condensation occurs under thermodynamical equilibrium with the above gas composition, then the concentration of H<sub>2</sub>S in solid SO<sub>2</sub> will be about 10<sup>-7</sup>–10<sup>-8</sup> depending on condensation temperature. Both scenarios lead to diluted H<sub>2</sub>S and thus are unable to fit the NIMS 3.92  $\mu\text{m}$  band position and shape. Diluted H<sub>2</sub>S, if present, may however marginally contribute to the NIMS spectrum (in the wing around 3.85  $\mu\text{m}$ ) for concentrations ranging from a few 10<sup>-5</sup> to a maximum of 10<sup>-4</sup> (Figures 8 and 9). For surface temperatures around 110 K these concentrations imply local H<sub>2</sub>S equilibrium pressures in the range  $5 \times 10^{-11}$ – $1 \times 10^{-9}$  bar, i.e., just above the upper limit found for the global H<sub>2</sub>S background atmosphere [Lellouch *et al.*, 1990].

[81] As the gas expands away from the vent source the pressure drops and SO<sub>2</sub> condenses on progressively colder plume particles or surfaces. If this occurs sufficiently slowly (i.e., close to equilibrium) the SO<sub>2</sub> ice should trap most of the less volatile plume molecules but only a minor fraction of H<sub>2</sub>S. The H<sub>2</sub>S mole fraction in the gas will progressively increase due to preferential SO<sub>2</sub> condensation. At some point, when most of the SO<sub>2</sub> will have condensed, the remaining gas may be dominated by the more volatile H<sub>2</sub>S, with possibly some HCl and Cl<sub>2</sub>. Phase II H<sub>2</sub>S-rich ice may then condense on cold area if its partial pressure has not dropped below  $1.5 \times 10^{-6}$  bar. Considering a maximum gas pressure at the vent output of 10 bar and a minimum gas expansion factor of 10<sup>3</sup> at the condensation zone [Zhang *et al.*, 2003], a minimum initial H<sub>2</sub>S abundance in the gas of 10<sup>-4</sup> is necessary to maintain such a high partial pressure as far as 100 km from the vent (the typical extent of the material producing the 3.92  $\mu\text{m}$  band). However, if the H<sub>2</sub>S pressure drops below 10<sup>-6</sup> bar the time to completely sublimate a micron-thick layer of solid H<sub>2</sub>S will be less than one minute at 104 K. So any thin deposit of solid H<sub>2</sub>S-II should be very unstable and ephemeral. This is in complete contradiction with the persistence of the 3.92  $\mu\text{m}$  band on Io over at least 1.5 years. Sublimation time scales

of that order imply temperatures as low as 70 K, and thus solid phase III H<sub>2</sub>S.

[82] Now, considering the chemical aspects of H<sub>2</sub>S, the volcanic model may produce enough of this molecule to account for the band strength. However, 10 times more H<sub>2</sub>O is formed with H<sub>2</sub>S (with O/S = 1), independently of the hydrogen abundance [Fegley and Zolotov, 2000]. This ratio is certainly higher for larger O/S atomic ratios. There is no sign in the NIMS spectra of the presence of the strong band of diluted H<sub>2</sub>O around 2.7  $\mu\text{m}$  (Figure 1) but H<sub>2</sub>O is probably segregated from the SO<sub>2</sub> frost owing to their very different volatilities. If we consider that pure H<sub>2</sub>O ice contributes to the wing of the unidentified 3.15  $\mu\text{m}$  NIMS absorption (Figure 8), an upper limit of 0.04 is deduced for the H<sub>2</sub>O/H<sub>2</sub>S abundance ratio. This value is smaller by more than 2 orders of magnitude than the predicted abundance ratio but specific chemical conditions (O/S  $\ll$  1, ...) may possibly release the H<sub>2</sub>O constraint on the local H<sub>2</sub>S abundances. The expected strong differential H<sub>2</sub>O and H<sub>2</sub>S segregation from SO<sub>2</sub> frost may also have hidden H<sub>2</sub>O (below a few millimeters of SO<sub>2</sub> frost, for example) in area where H<sub>2</sub>S condensed on top of the frost. So the nonobservation of H<sub>2</sub>O does not allow us to strictly exclude the presence of an observable amount of H<sub>2</sub>S.

[83] In addition to the water molecule, HCl and NaOH are produced with abundances around 10<sup>-4</sup> when H<sub>2</sub>S is formed in the 10<sup>-4</sup>–10<sup>-2</sup> range in the nominal volcanic conditions considered by Fegley and Zolotov [2000]. The fundamental HCl band falls within the 3.56  $\mu\text{m}$  SO<sub>2</sub> band but should be detectable above 10<sup>-5</sup> mole fraction. However, owing to its 30 times higher volatility than H<sub>2</sub>S, its nonobservation on the surface cannot strongly constrain the H<sub>2</sub>S abundance. On the other hand NaOH, with a very low volatility, sets similar constraints than H<sub>2</sub>O.

[84] A high H<sub>2</sub>S abundance ( $>10^{-4}$ ) also implies a volcanic H/S atomic ratio larger than 10<sup>-3</sup> [Fegley and Zolotov, 2000]. With the upper limit of H atom number density of  $1.1 \times 10^4 \text{ cm}^{-3}$  above the surface and the average SO<sub>2</sub> pressure of 0.2–0.35 nbar implied by the Lyman alpha HST observations [Strobel and Wolven, 2001], a H/S atomic ratio of less than 10<sup>-6</sup> is deduced near the surface. This is perhaps the most severe constraint on H/S, but on the one hand it is a global value that takes into account only atomic H, not the hydrogenated molecules like H<sub>2</sub>S, and on the other hand there are now converging evidences that the Io plasma torus, and not the surface, may supply most of the atmospheric H [Roesler *et al.*, 1999; Strobel and Wolven, 2001]. We should also note that H<sub>2</sub>S<sup>+</sup> has been inferred from a peak observed by Galileo in a single spectrum of ion cyclotron waves at a few Io radii from the surface [Russell and Kivelson, 2001]. However, this identification is only tentative and we suspect a possible contribution from <sup>34</sup>S<sup>+</sup> (a smaller unidentified peak is also observed at the position of <sup>33</sup>S<sup>+</sup>).

[85] To sum up, the chemical constraints did not favor the constant supply of the high volcanic H<sub>2</sub>S abundance ( $>10^{-4}$ ) required to eventually stabilize over months, or years, an ultra-thin H<sub>2</sub>S frost layer covering the Marduk deposits.

#### 4.2.4. H<sub>2</sub>S<sub>2</sub>

[86] Although H<sub>2</sub>S<sub>2</sub> is not currently included in the volcanic model of Fegley and Zolotov [2000], it is probably



formed with an abundance much lower than HS and should follow a similar trend as a function of the H/S ratio (same reduction state). The vapor pressure of  $\text{H}_2\text{S}_2$  is unknown in the solid state but from thermodynamical extrapolation of the liquid curve [Lide, 1990] we derive a saturation pressure  $10^4$ – $10^5$  times smaller than  $\text{SO}_2$  at 110 K. Consequently the concentration of  $\text{H}_2\text{S}_2$  diluted in  $\text{SO}_2$  ( $10^{-4}$ – $10^{-3}$ ) estimated to produce the NIMS absorption band needs an equilibrium abundance of about  $10^{-9}$ – $10^{-7}$  in the gas. However, as for  $\text{Cl}_2\text{SO}_2$ , such a large differentiation creates the unsolvable problem of the destiny of the superfluous  $\text{SO}_2$ . If no, or only a limited, differentiation occurs (i.e.,  $\text{H}_2\text{S}_2$  is mostly dynamically trapped by  $\text{SO}_2$  condensing on plume particles or at the surface) a H/S atomic ratio larger than  $10^{-2}$  is implied even if we assume that  $\text{H}_2\text{S}_2$  is formed in the volcanic vent at an abundance just a few times lower than HS [Fegley and Zolotov, 2000]. Such an unexpectedly high H/S ratio is clearly in conflict with the much smaller global atmospheric value obtained by Strobel and Wolven [2001]. In addition,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  should form in exceedingly large amounts ( $>10^{-3}$  and  $>10^{-2}$ , respectively), facing even more critically with the problem of their nondetection in the atmosphere and/or at the surface of Io (see section 4.2.3).

[87] Therefore these strong chemical constraints did not allow us to continue to consider  $\text{H}_2\text{S}_2$  as a possible contributor to the 3.92  $\mu\text{m}$  band in the Marduk spectrum.

#### 4.3. Reddish Material

[88] An intriguing point is the good correlation we found between the area displaying the 3.92  $\mu\text{m}$  absorption band in the NIMS data and the low albedo reddish deposit south of the Marduk volcanic center, as seen in the SSI images (Figure 2). This deposit is linked with recent (post Voyager) plumes still active after the G2 observation [McEwen et al., 1998]. The red coloration is assumed by several authors to be mainly due to  $\text{S}_4$  radicals (with some contribution from the yellow-green  $\text{S}_3$  radical) emitted by the volcano [Zolotov and Fegley, 1998b] or formed either by atmospheric photochemistry or by surface reaction of abundant  $\text{S}_2$  [Moses et al., 2002a; Spencer et al., 2000; McEwen et al., 1998]. The fan-tail shape of the deposit indicates that the plume was probably overpressured, a condition that favors the formation of  $\text{S}_n$  radicals ( $n \geq 3$ ), but also of several chlorine molecules, including  $\text{ClS}_2$ ,  $\text{Cl}_2\text{S}$ ,  $\text{Cl}_2\text{SO}$  and  $\text{Cl}_2\text{SO}_2$  [Fegley and Zolotov, 2000; M. Zolotov, Washington University, personal communication, 2001]. In particular,  $\text{Cl}_2\text{S}$  (sulfur dichloride), one of the most abundant chlorine molecules at high pressure (0.1%–1% when Cl dominates over Na + K), is known to be dark red in the liquid phase. Although we have not yet succeeded in measuring its visible spectrum in the solid state, this coloration is clearly retained in the solid phase. This leads us to suggest that the presence of this molecule, probably also trapped within the  $\text{SO}_2$  frost, may be an alternative (or competing) explanation for the reddish coloration of some volcanic deposits. Unfortunately this molecule did not have bands strong enough in the NIMS range to be detectable (Rodriguez and Schmitt, submitted manuscript, 2003). Laboratory visible spectra of solid  $\text{Cl}_2\text{S}$ ,  $\text{S}_3$ , and  $\text{S}_4$ , pure and diluted in  $\text{SO}_2$  ice and solid  $\text{S}_8$ , are clearly needed to compare with the band shape of Io's "red" absorption feature and to assess the absolute and relative abundances of these molecules.

[89]  $\text{Cl}_2\text{S}$  exposed to solar radiation has a photolysis rate constant of only 3.5 hours at Io's surface ( $\lambda < 465$  nm,  $J \approx 8 \times 10^{-5}$  s $^{-1}$ ). This value is already 2–3 orders of magnitude larger than for  $\text{S}_4$  (2.6 min) and  $\text{S}_3$  (24 s) [Moses et al., 2002a, 2002b] but not large enough to account for the "years to decades" fading time of the red material [McEwen et al., 1998]. The  $\text{SO}_2$  ice matrix cannot efficiently protect  $\text{Cl}_2\text{S}$  against photolysis. However, it is highly probable that a significant amount of sulfur is mixed with  $\text{SO}_2$  ( $\text{S}_8/\text{SO}_2 \approx 3$ –10% for O/S = 1–1.5 assuming most  $\text{S}_2$  is converted to octosulfur at the surface [Zolotov and Fegley, 1998b]). The photons up to 400–420 nm are then almost completely absorbed by  $\text{S}_8$  but progressively less efficiently at higher wavelengths [Douté et al., 2001]. We ran a simple modeling, assuming that all solar photons not absorbed by sulfur mixed with  $\text{SO}_2$  can dissociate  $\text{Cl}_2\text{S}$  with an efficiency of 1 below 400 nm, decreasing linearly to 0 at 465 nm. This model gives an average photolysis rate of diluted  $\text{Cl}_2\text{S}$  reduced by about a factor of 50–100 compared to unshielded molecules. In addition sulfur reduces the penetration depth of the "destructive photons" compared to the photons that induce the red color (absorbed between  $\sim 500$  and 650 nm [Geissler et al., 1999]). So the  $\text{Cl}_2\text{S}$  molecules trapped below some depth ( $\sim 0.1$  mm) in the  $\text{S}_8:\text{SO}_2$  deposit might be well protected against photolysis (dissociation rate possibly divided by 1,000–10,000) while they are still able to contribute to the visible absorption producing the red color.

[90] In comparison  $\text{S}_3$  radicals, although similarly protected by sulfur, are 500 times more sensitive to dissociation ( $J \approx 4 \times 10^{-2}$  s $^{-1}$ , 350 nm  $< \lambda < 455$  nm).  $\text{S}_4$  radicals trapped in a mixture of  $\text{SO}_2$  and  $\text{S}_8$  (or in pure solid sulfur) are also much more sensitive to photolysis as their photo-dissociation rate ( $J \approx 6.4 \times 10^{-3}$  s $^{-1}$ , 425 nm  $< \lambda < 575$  nm) is 80 times larger than  $\text{Cl}_2\text{S}$  and their photolysis range is at much higher wavelength. Between 500 and 575 nm  $\text{S}_8$  did not shield  $\text{S}_4$  efficiently. A reduction by only a factor of 2 is found for their photolysis rate. In addition, the depth of  $\text{S}_4$  photolysis is about the same as the absorption depth of the photons inducing the red color (same photons!). So even if the  $\text{S}_4$  radicals can easily reform from their photolysis products ( $\text{S}$ ,  $\text{S}_2$ , and  $\text{S}_3$ ), every radical should do this more than  $10^5$  to  $10^6$  times to survive over a few years! On the other hand, the  $\text{Cl}_2\text{S}$  molecules protected in the under-layer need to reform at most a few times (but not necessary if the protection factor is  $>5000$ ) to produce a time scale of red color fading compatible with observations. In addition to the direct recombination of the dissociation products of  $\text{Cl}_2\text{S}$  ( $\text{SCl}$  and  $\text{Cl}$ ) [Moses et al., 2002b, reaction R357] other recombination cycles of  $\text{Cl}_2\text{S}$  exist which use only a single ubiquitous  $\text{SO}_2$  molecule (reactions R340 + R443) or less probably one  $\text{S}$  (R228 + R440) or  $\text{S}_2$  radical (R277 + R347 + R294) trapped near the photolysis products. But there are also a number of ways to lose Cl and  $\text{SCl}$  by reaction with other trapped atoms or molecules [Moses et al., 2002b].

[91] In conclusion,  $\text{Cl}_2\text{S}$  has the required properties to provide a strongly challenging explanation (over  $\text{S}_4$  and  $\text{S}_3$ ) for the reddish color of the Marduk deposits (and possibly others) and its progressive fading with time [McEwen et al., 1998]. The very high dissociation rates of  $\text{S}_3$  and  $\text{S}_4$  are

crucial issues to be solved if these radicals are indeed at the origin of some red deposits.

## 5. Summary

[92] On the basis of purely spectroscopic arguments, four molecules ( $\text{Cl}_2\text{SO}_2$ ,  $\text{ClSO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}_2$ ) have been selected as the only potential candidates to explain the  $3.92\ \mu\text{m}$  absorption band observed in the reddish area south of the Marduk volcanic center. Their abundances and physical states have been inferred from the NIMS observation using radiative transfer modeling. Formation, condensation and destruction scenarios, taking into account the existing volcanic and atmospheric chemical models completed with some chemical and thermodynamical data, have been proposed for each of these molecules in order to link their state at the surface with volcanic plume physical conditions and abundances. Their analysis allowed us to accept or reject the various proposed scenarios.

[93] The major conclusions reached in this study are summarized in the following:

[94] 1.  $\text{Cl}_2\text{SO}_2$  is our favorite candidate. An excellent fit of the  $3.92\ \mu\text{m}$  band is obtained for a millimeter thick layer of 1%  $\text{Cl}_2\text{SO}_2$  diluted in solid  $\text{SO}_2$  and covering a similar mixture but strongly depleted in  $\text{Cl}_2\text{SO}_2$  ( $<0.1\%$ ). Although the  $\text{Cl}_2\text{SO}_2$  gas mole fraction ( $\sim 10^{-6}$ ) necessary to condense this enriched layer may be compatible with volcanic abundances under special but still plausible vent conditions, the issue of the destiny of the major part of  $\text{SO}_2$  did not allow us to further support this differentiation scenario. We rather strongly favor a formation process of this molecule by direct reaction of abundant atmospheric Cl atoms on condensing  $\text{SO}_2$  ice. This heterogeneous reaction may occur either on growing  $\text{SO}_2$  plume particles or on condensing  $\text{SO}_2$  frost at Io's surface, depending on the effective process of  $\text{SO}_2$  condensation at Marduk. Favorable conditions for abundant  $\text{Cl}_2\text{SO}_2$  formation are met only for Cl-rich volcanic eruptions (i.e., for  $[\text{Cl} - (\text{Na} + \text{K})]/\text{S} > 0.015$ ). This was probably the case at Marduk. Once at the surface  $\text{Cl}_2\text{SO}_2$  should be efficiently protected from UV destruction by a small amount of  $\text{S}_8$  mixed with  $\text{SO}_2$  ice. Detailed laboratory experiments to demonstrate and quantify the formation of  $\text{Cl}_2\text{SO}_2$  by direct reaction of Cl atoms on cold  $\text{SO}_2$  surfaces are necessary to validate this scenario.

[95] 2.  $\text{ClSO}_2$  is a potential alternative candidate as its three main combination bands might fit three bands (including the  $3.92\ \mu\text{m}$  one) observed in Marduk's NIMS spectrum. However, the lack of laboratory data did not allow us to resolve this question.  $\text{ClSO}_2$  may be easier to produce in substantial amounts by heterogeneous reaction as it appears to be the intermediate product toward the eventual formation of  $\text{Cl}_2\text{SO}_2$ , but recent unpublished experiments seem to be at variance with this fact. On the other hand  $\text{ClSO}_2$  is much less stable and might need a larger abundance ( $\sim 2 - 15\%$ ), and thus a large volcanic Cl/S ratio, to fit the NIMS band strength. Some condition dependent equilibrium between the abundances of  $\text{Cl}_2\text{SO}_2$  and  $\text{ClSO}_2$  may possibly occur but at the present stage in this study we distinctly favor  $\text{Cl}_2\text{SO}_2$  over  $\text{ClSO}_2$ . Spectral and chemical studies of these molecules are urgently needed.

[96] 3.  $\text{H}_2\text{S}$  in the form of a submicron thin layer of pure ice (phase II) condensed on top of  $\text{SO}_2$  ice also well fits the observed NIMS band. However, even at the lowest allowed temperature (103.6 K), the persistence of such a thin layer over months at Io's surface is highly improbable. Therefore  $\text{H}_2\text{S}$  can be safely discarded from being the  $3.92\ \mu\text{m}$  absorber. However,  $\text{H}_2\text{S}$  diluted in  $\text{SO}_2$  ice might be present at a maximum concentration of 0.01% and marginally contribute to the spectrum around  $3.85\ \mu\text{m}$ . But no positive proof exists.

[97] 4.  $\text{H}_2\text{S}_2$  diluted at low concentration (0.01% – 0.1%) in  $\text{SO}_2$  ice might possibly fit the band position, but the lack of laboratory data did not allow any spectral conclusion to be made. As for  $\text{Cl}_2\text{SO}_2$ , no strong differentiation can occur otherwise unsolvable problems arise with  $\text{SO}_2$ . The very strong H/S ratio ( $>10^{-2}$ ) and the unlikely abundances of the other hydrogenated molecules implied by the  $\text{H}_2\text{S}_2$  abundance allows us to exclude this molecule as a possible contributor to the  $3.92\ \mu\text{m}$  band.

## 6. Conclusion

[98] Two major questions raised by the local identification of  $\text{Cl}_2\text{SO}_2$  (with maybe some  $\text{ClSO}_2$ ) near Marduk, and possibly at a few other local spots, are: Why are these molecules not observed in all the volcanic deposits? What determines their formation and their abundance?

[99] First, the heterogeneous formation of these chlorine molecules should be efficient only on condensing  $\text{SO}_2$ . If during an eruption  $\text{SO}_2$  did not condense on the plume particles, the reaction can only occur on condensing frost at the surface. In addition, their destruction by UV or their burial by  $\text{SO}_2$  frost is effective where the diurnal sublimation-recondensation cycle segregates these molecules. All this restricts their observability to fresh volcanic deposits.

[100] Second, the atmospheric abundance of atomic Cl mainly and strongly depends on the relative elemental abundances of Cl compared to Na and K. Typical abundances of Cl atoms relative to  $\text{SO}_2$  vary from 0.001% to 13% for  $[\text{Cl} - (\text{Na} + \text{K})]/\text{S}$  ratios varying from  $-0.1$  to  $0.1$  [Moses *et al.*, 2002b]. An excess of a few hundredth of the elemental ratio Cl/S over  $(\text{Na} + \text{K})/\text{S}$  is then enough to obtain abundant atomic Cl in the atmosphere. But this is probably a rather uncommon volcanic composition that may occur only at some places on Io.

[101] Finally, the  $3\text{-}\sigma$  detection limit for  $\text{Cl}_2\text{SO}_2$  diluted in solid  $\text{SO}_2$  (with the  $3.92\ \mu\text{m}$  band) is of the order of 0.2%, just a factor of 5 below the abundance derived near Marduk. So  $\text{Cl}_2\text{SO}_2$  would be difficult to observe in other regions of Io if it were just a few times less abundant than at Marduk. At concentrations below 0.2% none of the few IR-active chlorine molecules ( $\text{Cl}_2\text{SO}_2$ ,  $\text{ClSO}_2$ ,  $\text{Cl}_2\text{SO}$ ,  $\text{ClO}$ ,  $\text{Cl}_2\text{O}$ , ...) in the solar spectrum might be observable by NIMS. Only spectroscopic observations in the thermal IR (emission features) might reveal the presence of some of the most abundant Cl-bearing volcanic molecules such as NaCl, KCl,  $\text{ClS}_2$  or  $\text{Cl}_2\text{S}$ . NaCl has very recently been observed in the atmosphere of Io and a mean volcanic flux in the range 0.3–1.3% relative to  $\text{SO}_2$  has been inferred [Lellouch *et al.*, 2003]. NaCl having a very low vapor pressure it might differentiate from  $\text{SO}_2$  and then be locally present at much higher concentrations at the surface.

[102] In order to solve all the issues raised by the identification of Cl<sub>2</sub>SO<sub>2</sub> (and possibly ClSO<sub>2</sub>), additional laboratory experiments on the spectroscopic properties of several molecules (ClSO<sub>2</sub>, Cl<sub>2</sub>S, S<sub>n</sub>, . . .) and on the heterogeneous formation of Cl<sub>n</sub>SO<sub>2</sub> ( $n = 1, 2$ ) are needed. A series of experiments have already been initiated at LPMA (L. Schriver and A. Schriver, Université P. & M. Curie, Paris, 2002). New chemical models including more realistic condensation and transport processes in volcanic plume conditions are also needed to incorporate the heterogeneous reactions occurring on plume particles. Finally, the search of new areas unambiguously displaying the 3.92 μm band, with possibly some associated bands, should help to determine the possible presence of ClSO<sub>2</sub> and its contribution to the bands.

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