TENTATIVE IDENTIFICATION OF LOCAL DEPOSITS OF Cl_2SO_2 AT IO'S SURFACE. B. Schmitt[1] and S. Rodriguez[1,2] and the NIMS Team. [1] Laboratoire de Planétologie de Grenoble, Bâtiment D de Physique, B.P. 53, 38041 Grenoble Cedex 9, France, email: Bernard.Schmitt@obs.ujf-grenoble.fr, [2] Observatoire de Bordeaux, 2 rue de l'Observatoire, B.P. 89, 33270 Floirac, France, email: rodriguez@observ.u-bordeaux.fr

Introduction: Since 1979 SO_2 is the only molecule firmly identified at the surface of Io although several forms of allotropic sulfur are strongly suspected to explain some spectral features of Io's visible spectra. SO_2 and S8 could also explain two emission features of the mid-infrared spectra recorded by IRIS (Voyager 1). Detailed Galileo data analysis showed that these species are two dominant compounds of the chemical composition over most of the satellite surface [1,2]. A few other molecules have been suggested to explain some of the remaining absorption and emission bands seen on Io's spectra: SO_3, H_2O, H_2S and CO_2 but Schmitt et al. [3,4] showed that solid SO_2 could fully explain most of the bands attributed to the last 3 molecules. The presence of sodium and potassium, discovered in Io’s torus, at the surface in the form of Na_2S, NaHS, K_2S, Na_2SO_3 and Na_2SO_4 been also studied but none has been yet formally identified.

The recent discovery of abundant chlorine ions in Io's plasma torus [5] leaded us to consider Cl-bearing molecules as a new family of compounds to explain some of the unidentified or controversial features of Io's surface spectra. Lava degassing and high temperature volcanic chemistry predict a large number of molecules in Io's atmosphere [6], 15 of them containing chlorine. Some of these species are expected to condense at the surface of the satellite.

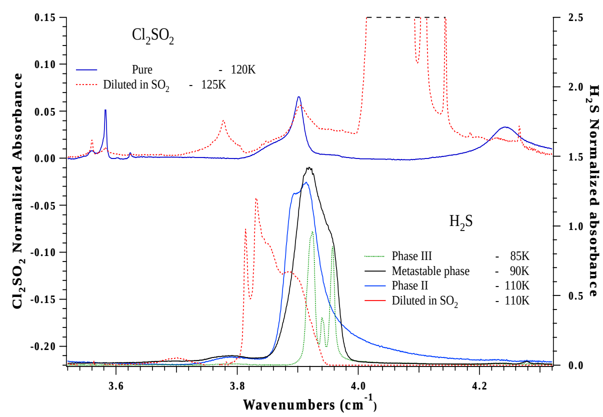
We started our study with the 4 IR-active and commercially available molecules containing at least one Cl and one S atom: Cl_2S, Cl_2S_2 Cl_2SO, and Cl_2SO_2. Laboratory experiments on two “classical” candidates: H_2S and SO_2 have been also performed.

This presentation focuses on the analysis of one new infrared absorption band at 3.915 µm we recently discovered locally in NIMS/Galileo spectro-images of Io.

Observations: During a systematic spectral search on the NIMS data of the initial Galileo mission an absorption feature at 3.915 µm appeared to be locally present on some pixels of the G2 and C3 observation periods and retained our attention. After a careful check in the raw data for possible energetic particle spikes, the occurrence of this band was confirmed in at least one area south of Marduk (30S, 212W) (Figure 2). Possible confirmation in other areas is under progress.

Laboratory measurements: Cl_2S, Cl_2S_2 Cl_2SO, Cl_2SO_2, SO_3 and H_2S solid samples were synthesized in the vacuum optical cell by direct gas deposition on a CsI window at 100-120K. We performed experiments on pure solid samples as well as for these molecules diluted (typically 2%) in solid SO_2. Transmission spectra were recorded in the mid-infrared (2-25 µm) at 1 cm^{-1} resolution for several sample thicknesses and for a series of temperatures (typically from 100K to sublimation temperature). We give below some details for Cl_2SO_2 and H_2S, the 2 candidates of the 3.915 µm NIMS band.

Cl_2SO_2. About 15 absorption bands of various intensities have been attributed to fundamental, combination and isotopic vibration modes. Weak to medium frequency shifts (±20 cm^{-1}) between pure solid-state and diluted state band positions have been measured. In particular the $\upsilon_1+\upsilon_6$ combination mode at 3.901 µm (pure) shifts to 3.908 µm upon dilution in SO_2 (at 120 K). The position of this band is strongly temperature sensitive in diluted state (+0.2 nm/K) but not for pure Cl_2SO_2. Notable changes occurs in the relative band intensities: The three combination modes ($2\upsilon_1$, $\upsilon_1+\upsilon_6$, $2\upsilon_6$) of similar intensity for pure Cl_2SO_2 change to a predominant $\upsilon_1+\upsilon_6$ and unobservable $2\upsilon_1$ bands when diluted (Figure 1). The Cl_2SO_2 absorption band positions and intensities are then relevant indicators of the physical



state (temperature and dilution) of this molecule.

Figure 1: Infrared spectra of Cl_2SO_2 and H_2S pure and diluted in solid SO_2.

H_2S. The H_2S spectrum strongly changes with temperature due to the occurrence of at least 3 crystalline phases in the 85-120K range. Phase III has 3 sharp bands around 3.94 µm while phase II and the intermediate metastable phase have one broad structured band around 3.91 µm (Figure 1). The spectrum of H_2S diluted in SO_2 has also a clearly different shape with several peaks and

is strongly shifted (by more than 0.08µm) allowing to easily recognize between these phases.

Results and Interpretation: A comparison of the band positions of the 6 molecules measured with the 3.915 µm NIMS band shows that the $\upsilon_1+\upsilon_6$ band of Cl_2SO_2 at 3.910 µm provides a rather good fit when diluted in SO_2 (Figure 2). In addition, in this state only this band is strong and the two others near 3.34 and 4.25 µm are virtually unobservable at the resolution of the NIMS observations. Detailed models of the spectra are not yet completed but we can already estimate that an abundance of the percent order is necessary to reproduce the band intensity relative to SO_2.

It should be noted that the $\upsilon_1+\upsilon_3$ band of SO_2 (4.07 µm) has a wide shoulder with small bumps in that ranges, easily observed in full disk spectra. It is these bumps that have been formerly attributed to H_2S diluted in SO_2. Our laboratory data excludes diluted H_2S as the absorber of the 3.915 µm band but the high temperature phases of pure H_2S (above 90 K) may fit the position of that band. H_2S should then be in the form of a very thin layer (1-10 µm) condensed on top of solid SO_2.

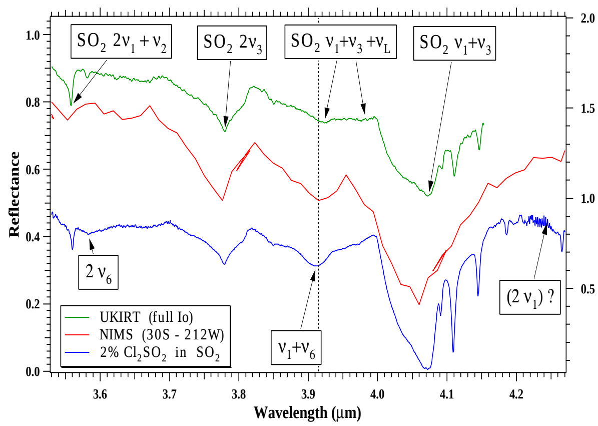


Figure 2: Comparison between full disk observation of Io (UKIRT), local NIMS observation south of Marduk and a laboratory spectrum of a Cl_2SO_2/SO_2 mixture at 100K.

The problem is now to found other arguments to separate between these two possible identifications.

Volatility. The lowest volatility of Cl_2SO_2 compared to SO_2 and much lowest compared to H_2S strongly favor the chlorine molecule at the surface of Io. Differential sublimation should enhance the concentration of Cl_2SO_2 in SO_2 but should rapidly remove any layer of condensed H_2S, very unstable even at temperatures as low as 100K.

Chemistry. The main problem with Cl_2SO_2 is that the standard chemical models of the volcanic gases [6] did not produce enough molecules to account for the intensity of the 3.915 µm band. However, preliminary calculations by Zolotov [pers. com.] show that the abundance of Cl_2SO_2 may be increased by almost 4 orders of magnitude and reach a mole fraction relative to SO_2 of almost 5 10^{-5} under particular, but still torus-compatible conditions (O/S=2, Cl/S=0.11). When calculated abundances are combined with band strengths we found that the 3.910 µm band of Cl_2SO_2 is the strongest near-IR band of all the possible chlorine molecules. On the other hand The chemical model [6] produces an appreciable amount of H_2S (i.e. > 10^{-4}) only for high H/S atomic ratios (> 10^{-3}). Furthermore 10 times more H_2O is formed (with O/S=1). H_2O being present at a concentration much lower than 0.1%,[7,4], being much less volatile than H_2S and having stronger bands, it seems difficult to be able to see H_2S without H_2O.

Galileo Images: Finally the area where the 3.915 µm band is identified in the NIMS data is well correlated with a large red irregular deposit south of the Marduk volcanic center. This deposit is linked with recent overpressured plumes [8]. Cl_2S, a dark red molecule, being emitted in larger amounts than Cl_2SO_2 in volcanic gases [6], we suggest that this molecule may be an alternative (or complimentary) to sulfur allotropes for the red coloration of some volcanic deposits.

The paper presenting these results will be submitted to Astronomy & Astrophysics.

References: [1] Geissler P. et al. (1999) *Icarus*, *140*, 265-282. [2] Douté S. et al. (2001) *Icarus*, *149*, 107-132. [3] Schmitt B. et al. (1994) *Icarus*, *111*, 79–105. [4] Schmitt B. et al. (2001) *Icarus*, *in prep.* [5] Kueppers M. and Schneider N. (2000) *GRL*, *27*, 513-516. [6] Zolotov M. and Fegley B. (2000) *Icarus*, *148*, -. [7] Dahmani R.and Khanna R. (1996) Astr. Sp. Sci. 236, 125-133. [8] Mc Ewen A. et al. (1998) *Icarus*, *135*, 181-219.

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