

Sulfur chemistry in the Venus mesosphere from SO₂ and SO microwave spectra

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ABSTRACT

First measurements of SO₂ and SO in the Venus mesosphere (70–100 km) are reported. This altitude range is distinctly above the ~60–70 km range to which nadir-sounding IR and UV investigations are sensitive. Since July 2004, use of ground-based sub-mm spectroscopy has yielded multiple discoveries. Abundance of each molecule varies strongly on many timescales over the entire sub-Earth Venus hemisphere. Diurnal behavior is evident, with more SO₂, and less SO, at night than during the day. Non-diurnal variability is also present, with measured SO₂ and SO abundances each changing by up to 2× or more between observations conducted on different dates, but at fixed phase, hence identical sub-Earth Venus local times. Change as large and rapid as a 5σ doubling of SO on a one-week timescale is seen. The sum of SO₂ and SO abundances varies by an order of magnitude or more, indicating at least one additional sulfur reservoir must be present, and that it must function as both a sink and source for these molecules. The ratio SO₂/SO varies by nearly two orders of magnitude, with both diurnal and non-diurnal components. In contrast to the strong time dependence of molecular abundances, their altitude distributions are temporally invariant, with far more SO₂ and SO at 85–100 km than at 70–85 km. The observed increase of SO₂ mixing ratio with altitude requires that the primary SO₂ source be upper mesospheric photochemistry, contrary to atmospheric models which assert upward transport as the only source of above-cloud SO₂. Abundance of upper mesospheric aerosol, with assumption that it is composed primarily of sulfuric acid, is at least sufficient to provide the maximum gas phase (SO + SO₂) sulfur reported in this study. Sulfate aerosol is thus a plausible source of upper mesospheric SO₂.

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1. Introduction

Sulfur compounds play a critical, albeit poorly understood role in the Venus atmosphere. The global, dense (opaque at most wavelengths) 45–60 km cloud layer is composed of sulfuric acid. SO and SO₂ react with water in formation of that sulfuric acid aerosol, thereby removing H₂O from the gas phase, limiting the above-cloud water content, and limiting the amount of water available for photodissociation in, and hydrogen escape from, the upper atmosphere.

Above the clouds, the primary sulfur containing molecules are believed to be SO, SO₂, and H₂SO₄ (sulfuric acid). Allotropes of elemental sulfur (S_n) are also believed to be present, but with small abundances that decrease very rapidly above the clouds (Toon et al., 1982; Esposito et al., 1997). H₂SO₄ exists in aerosol form, such that the primary gaseous carriers of sulfur are SO and SO₂ (referred to collectively as SO_x). Cloud-top (~60 km) SO₂ has been measured by nadir-looking UV (Barker, 1979; Na et al., 1990;

McClintock et al., 1994; Esposito et al., 1997) and IR (Moroz et al., 1986) spectroscopy, and remarkable long term (10 year) SO₂ nadir-looking UV instruments variability is evident (Esposito et al., 1988, 1997; Na, 1992). Cloud-top (~60 km) SO has also been observed (Na et al., 1990, 1994). Limb-viewing IR observations of SO₂ from cloud-top to 75 km (Belyaev et al., 2008) have been conducted from Venus orbit with the Solar Occultation in the InfraRed (SOIR) instrument on the European Space Agency's (ESA's) Venus Express (VEX) probe. Measurements of lower thermospheric (90–110 km) SO₂ are reported by Bertaux et al. (2008), based upon VEX observations with the SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Venus (SPICAV) instrument.

In the present work, we describe the first measurements of SO and SO₂ in the Venus mesosphere (70–100 km). UV and IR methods are fundamentally sensitive to column abundance along the line of sight. For that reason, nadir-looking UV and IR measurements (e.g. Esposito et al., 1988, 1997; Na et al., 1990, 1992, 1994) are strongly weighted by the mixing ratio just above the clouds (~60–70 km), as this is the densest part of the above-cloud atmosphere that UV and IR methods observe. In contrast, microwave spectroscopy

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is primarily sensitive to mixing ratio at 70–100 km (sometimes higher), such that it is uniquely capable of providing geophysical in this altitude range.

Photochemical modeling of the above-cloud atmosphere of Venus has long been hampered by a paucity of observational data. The thorough, early models of (e.g.) Yung and DeMore (1982) and Krasnopolsky and Parshev (1983) are still relevant today, in part because the amount of middle atmospheric empirical data collected in the 20 years following those publications is relatively small. The pace of new discoveries, and of increasingly precise measurements began to increase in the first years of this century, owing to improvements in technology of ground-based (e.g. Sandor and Clancy, 2005) and Earth-orbiting (e.g. Gurwell et al., 2007) observatories. Beginning with its 2006 orbital insertion, ESA's Venus Express (VEX) mission accelerated this pace both directly with orbiter instrumentation (e.g. Vandaele et al., 2008) and indirectly by motivating intensive ground-based observations (e.g. Lellouch and Witasse (2008), and accompanying papers in that special issue journal). New photochemical models (e.g. Mills and Allen, 2007; Mills et al., 2007) incorporate the expanding empirical data, and are under intense development.

Temporal variability of CO and temperature in Venus' lower thermosphere (above ~ 100 km) (Clancy and Muhleman, 1985a; Clancy et al., 1991, 2003, 2008) is qualitatively well explained by variation of atmospheric dynamics (Clancy and Muhleman, 1985b; Lellouch et al., 1997), details of which are an ongoing research area. Long-term (10 year) variation of cloud-top (~ 60 km) SO₂ (Esposito et al., 1988, 1997; Na, 1992), has also been suggested to be dynamically driven (Clancy and Muhleman, 1991). Large variations of mesospheric water vapor (Sandor and Clancy, 2005; Gurwell et al., 2007) are documented, with no compelling mechanism yet proposed. Temporal variations of mesospheric SO_x (Sandor et al., 2007, 2008) are addressed in this paper. As for water vapor, the physical/chemical drivers of SO_x variation are unknown. It is probable that photochemical reactions between SO_x and water vapor or aerosols, in association with sulfate aerosol formation, are at least partially responsible for SO_x temporal variation. Such SO_x/water interactions are less clearly relatable to observed variations of mesospheric water vapor, due to the much larger water abundance (up to 1000's of parts per billion, versus <100 ppb SO_x). There may also be a link between temporal variations of SO_x and CO. CO is produced by photolysis of CO₂ in Venus' dayside upper atmosphere, such that CO-rich air parcels are also rich in atomic oxygen. Areas of enhanced CO in the nightside lower thermosphere correspond to areas of downwelling air, hence transport of atomic oxygen into the mesosphere, where it may significantly affect sulfur chemistry. Beyond the intrinsic interest of Venus photochemistry, investigation of SO_x variability is important for understanding time-variation of other atmospheric constituents. In this respect, SO_x studies contribute to understanding the basic photochemical/dynamical properties of Venus' atmosphere.

2. Observations

Beginning in July 2004 (first mesospheric SO₂ detection), and continuing through the present, spectrally resolved observations of Venus SO₂ (346.65217 GHz) and SO (346.52848 GHz) were obtained with the James Clerk Maxwell Telescope (JCMT), located on Mauna Kea, Hawaii (Matthews, 2003). The 346.652 GHz SO₂ absorption line corresponds to the $N = 16$, $K_{-1} = 3 \rightarrow 4$, $K_{+1} = 13 \rightarrow 12$ transition (Pickett et al., 1996; Poynter and Pickett, 1985). The 346.528 GHz SO absorption results from the $N = 7 \rightarrow 8$, $J = 8 \rightarrow 9$ transition.

These SO and SO₂ lines are separated by only 123.7 MHz, such that the two line positions are always observed simultaneously

within the same bandpass. Observations in the period 2004–2006 were conducted with spectrometer bandwidth 250 MHz, and frequency resolution 313 KHz. Following a major hardware upgrade at the JCMT, data from 2007 to present are obtained with spectrometer bandwidths 250 MHz (most commonly), 500 MHz, or 1000 MHz, corresponding to frequency resolutions of 30.5 KHz, 61.0 KHz, and 488 KHz, respectively. The upgraded hardware provides significantly improved sensitivity, such that SO_x data quality and quantity are increased beginning January, 2007.

Pressure broadening of each microwave line sets the lower limit (70 km) on the altitudes that can be measured with spectrometers employed in this study. The upper altitude limit is set by weakening of signal strength as measured specie density declines. When mixing ratios are approximately constant (e.g. HDO (Sandor and Clancy, 2005)), or linearly increasing with altitude, the upper altitude limit is 100 km. When mixing ratios increase exponentially with altitude (e.g. CO Clancy and Muhleman, 1985a; Clancy et al., 1991, 2003, 2008; Lellouch et al., 1994), sensitivity of microwave spectroscopy extends as high as 115 km. Microwave detections require a temperature contrast between the measured altitude and the deeper layers where the atmosphere becomes optically thick across the bandpass to form a continuum level of microwave emission. In the case of Venus' mesosphere, optically thin SO and SO₂ in the (colder) 70–100 km range absorb blackbody emission from the (warmer), optically thick altitudes below 60 km. The 70–100 km absorption features are pressure broadened to a range of spectral widths ≤ 0.1 MHz (>95 km altitudes) to 10's of MHz (<75 km altitudes). Emission from the (warmer) region below 60 km is pressure broadened to more than 1000 MHz, such that the $z < 60$ km emission is spectrally flat across our receiver's bandwidth, and closely approximates a featureless black body. Altitude dependence of pressure broadening over 70–100 km determines the shape of each microwave line, such that 10–15 km altitude resolution is obtained within the 70–100 km range we probe with ground-based sub-mm spectroscopy. Sensitivity of microwave absorption to temperature is linear, hence relatively unimportant for analysis of optically thin absorption lines.

Results of SO_x measurements are listed in Table 1, beginning with our July 2004 first detection of SO₂, and continuing through 2008. Measured SO values are listed beginning with the January 2007 date of our first detection. Data quality and variability for SO₂ and SO are illustrated in Figs. 1 and 2, respectively. Fig. 3 presents the observed bandwidth containing both SO and SO₂ features from April and August, 2007. Fig. 3 also indicates the presence of a second (346.52388 GHz; $N = 18 \rightarrow 19$, $K_{-1} = 0 \rightarrow 1$, $K_{+1} = 18 \rightarrow 19$) SO₂ line, 44% weaker than the primary (346.652 GHz) SO₂ line described above, located only 4.6 MHz from our target SO line. When significant SO and SO₂ absorptions are both present, we derive the measured SO₂ abundance profile from the stronger SO₂ line, calculate a synthetic spectrum for the weaker SO₂ line, and subtract this synthetic spectrum from the data. In this manner, SO is cleanly separated from SO₂, such that SO and SO₂ measurements do not interfere with one another. Implicit in this correction is the accurate RT fitting to both SO₂ line absorptions for a single SO₂ mixing profile solution.

The JCMT employs a 15 m primary mirror, which for SO_x at 346.6 GHz provides a gaussian shaped beam with full width half power (FWHP) beam footprint of 13". The Venus angular diameter varies between 9.6" and 60" at superior and inferior conjunctions, respectively. Meaningful spatial resolution at horizontal scales smaller than the observed Venus hemisphere is possible for angular diameters larger than 22", corresponding to Venus phase less than 0.57, and to the Venus apparent disk exceeding the FWHP beam size by a factor of 1.7. For Venus diameter $<22''$, all observations are made with the telescope beam placed at the sub-Earth position on the Venus disk, for hemispheric mean determinations.

Table 1Measured abundance and altitude dependence of SO₂ and SO in the Venus mesosphere.

Date	Phase	<i>D</i>	SO ₂ min(<i>z</i>), km	SO ₂ , vmr ppb	SO min(<i>z</i>), km	SO, vmr ppb	SO ₂ /SO, vmr ratio	SO ₂ + SO, vmr ppb
12 June 2004	0.005	57"	84	25 ± 9			–	
31 October 2005	0.513	24"	84	18 ± 6			–	
4 November 2005	0.493	25"	84	11 ± 3			–	
14 January 2006	0.004	63"	86 ± 4	14 ± 3			–	
15 January 2006	0.005	63"	86 ± 10	7 ± 4			–	
14 January 2007	0.948	11"	84	11 ± 6	84	3 ± 2	3.7(+7.6; –2.5)	14 ± 6
20 January 2007	0.941	11"	84	7 ± 5	88 ± 4	12 ± 3	0.6 ± 0.4	19 ± 6
21 January 2007	0.939	11"	84	19 ± 7	86 ± 8	5 ± 3	3.8(+5.9; –2.0)	24 ± 8
21 April 2007	0.721	15"	86 ± 4	35 ± 10	84 ± 2	13 ± 2	2.7 ± 0.9	48 ± 10
22 April 2007	0.718	15"	84 ± 2	30 ± 5	82 ± 2	10 ± 1	3.0 ± 0.6	40 ± 5
29 April 2007	0.691	16"	86 ± 2	27 ± 4	84 ± 2	15 ± 1	1.8 ± 0.3	42 ± 4
2 June 2007 nite	0.536	22"	84	9 ± 4	84	0.6 ± 0.4	15(+31; –9)	10 ± 4
2 June 2007 day	0.536	22"	84	4 ± 2	84	2.3 ± 0.5	1.7 ± 0.9	6 ± 2
9 June 2007 nite	0.498	24"	84	0 ± 2	84	1.0 ± 0.3	<2.0	1.0(+2.0; –0.3)
9 June 2007 day	0.498	24"	84	0 ± 3	84	2.1 ± 0.5	<1.4	2.1(+3.0; –0.5)
11 August 2007 W	0.000	56"	84 ± 2	76 ± 9	84	1.7 ± 1.3	45(+140; –20)	78 ± 9
11 August 2007 N	0.000	56"	84 ± 4	50 ± 11	84	1.0 ± 0.7	50(+120; –23)	51 ± 11
11 August 2007 S	0.000	56"	84 ± 2	67 ± 6	84	0.0 ± 0.7	>96	67 ± 6
23 March 2008	0.940	11"	84	7 ± 4	84 ± 4	9 ± 3	0.8 ± 0.5	16 ± 5
8 August 2008	0.958	10"	84 ± 8	26 ± 13	84 ± 2	15 ± 3	1.7 ± 0.9	41 ± 13
17 August 2008	0.945	10"	86 ± 6	38 ± 16	86 ± 2	31 ± 4	1.2 ± 0.5	69 ± 16
Mean			84 ± 2		84 ± 2			

D is the angular diameter of Venus (arcsec). Measured volume mixing ratios and their 1σ *s/n* uncertainties have units of parts per billion (ppb). Measurements are sensitive to abundances at 70–100 km. For sufficient *s/n*, finer altitude resolution within this 30 km range is possible. In all such cases, best-fit altitude distributions determine that SO_x is observed only above a cutoff altitude, variable between 84 and 88 km, specified here by min(*z*). Entries which include the 1σ uncertainty for min(*z*) are best fits to the altitude distributions. Entries for which *s/n* is not sufficient to fit the altitude distribution use an assumed min(*z*), equal to the mean of the measured min(*z*) values, and are listed in this table with no specified uncertainty. Measurements in August 2007 were at positions West, North, and South of disc center, all on Venus nightside. June 2007 observations were at points East and West of center, corresponding to nightside and dayside respectively. Measurements on dates outside of June and August 2007 are of disc average values.

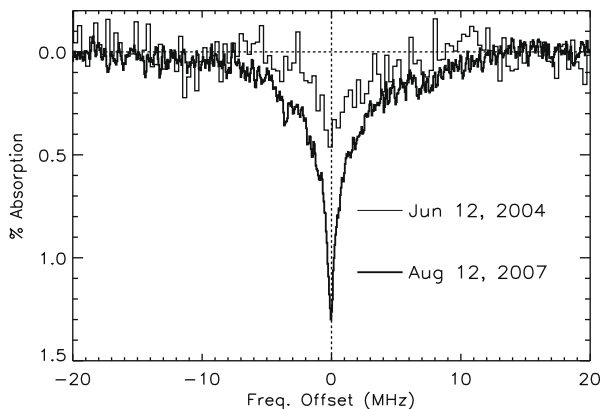


Fig. 1. Observed SO₂ spectra: temporal variation. SO₂ spectra observed at inferior conjunctions of June 12, 2004 (thin line) and August 12, 2007 (thick line), such that the measurements are at identical phase (zero), with Venus local midnight on its sub-Earth meridian. The June 2004 spectrum is best fit with 25 ± 9 ppb SO₂ above 84 km. Retrieval from the August 2007 data identifies 57 ± 8 ppb SO₂ above 82 ± 2 km. Best interpretation of this result is that SO₂ abundance above 84 km was larger in August 2007 than in June 2004 by a factor of 57/25 = 2.28, and that SO₂ extended 2 km lower in altitude in August 2007 than June 2004. Relative importance of altitude distribution versus SO₂ abundance is illustrated by an alternate retrieval in which we constrained altitude distributions to be identical (SO₂ present only above 84 km for each spectrum). In this case, August 2007 abundance would be greater than that of June 2004 by a factor of 62/25 = 2.48.

For larger diameters, 22–60", offsetting the telescope beam from disc center provides both spatially resolved data (by analysis of individual beam positions), and hemispheric mean determinations (by analysis of data averaged over the individual beam positions). Optimal spatial resolution is possible at inferior conjunction, when the telescope beam footprint corresponds to 4000 km diameter regions on Venus. This paper emphasizes disk-average measurements, which constitute the bulk of our observations to date. Mapping measurements for multiple positions on the disk exist

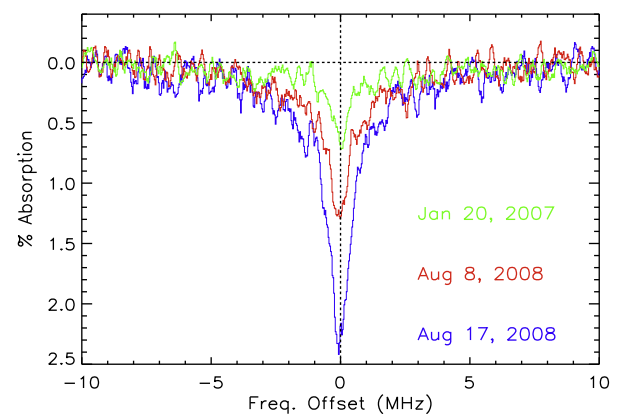


Fig. 2. Observed SO₂ spectra: temporal variation. SO spectra observed January 20, 2007 (green), August 8, 2008 (red), and August 17, 2008 (red), at nearly identical phase values (0.941, 0.958, and 0.945, respectively). Best fits to the three spectra are 12 ± 3 ppb SO above 88 ± 4 km, 15 ± 3 ppb SO above 84 ± 2 km, and 31 ± 4 ppb SO above 86 ± 2 km, respectively. Mean hemispheric SO abundance in August 2008 underwent a 5σ doubling above 86 km, from 15 ± 3 to 31 ± 4 ppb, in 9 days.

for increasing proportions of our Venus measurements since 2005, and are the topic of a future paper.

Observations are conducted in beam-switch mode, wherein the telescope pointing rapidly alternates between positions on the planet, and positions 30–90" off the planet. Both the on- and off-position spectra include signal from sources other than Venus (primarily Earth's atmosphere), but only the on-position spectrum contains signal from Venus. Subtraction of off-position from on-position data is performed by JCMT software, such that we are provided with the differenced signal, i.e. Venus spectra from which background sources have been removed. SO and SO₂ lines appear as absorption features, corresponding to absorption by SO_x in the cold mesosphere from continuum blackbody radiation emitted

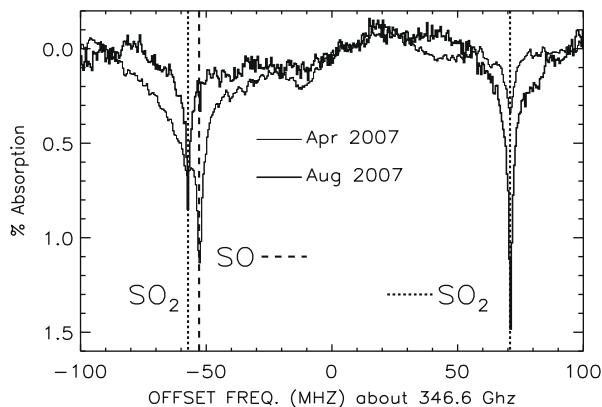


Fig. 3. SO_x anti-correlated time variation. SO_x spectra obtained in April (thin line) and August (thick line) 2007, respectively, using 250 MHz spectrometer bandwidth. The SO_2 absorption was far deeper, and the SO absorption much less deep, in August than in April. This can only be explained as a temporal change, a simultaneous increase of SO_2 and decrease of SO in August relative to April. Any spectrometer calibration error, or change in a background property of the atmosphere (e.g. temperature) would cause absorptions to change in the same direction, contrary to the changes in these data. SO_2 and SO sometimes change in opposite directions, as in this figure, sometimes in the same direction. Over the full set of observations (Table 1), they are neither positively nor negatively correlated. Total SO_x ($\text{SO}_2 + \text{SO}$) is not conserved.

from the warmer, lower atmosphere. Spherical geometry of the Venus atmosphere is incorporated in analysis of each observation, allowing for absorption contributions from various slant paths across the face of the disk, as well as for limb emission (Clancy and Muhleman, 1991). All data are interpreted in terms of fractional absorption from the continuum, wherein depth of absorption is divided by the continuum signal. This method for calibrating the spectral absorption depends on accurate modeling of the continuum emission, for which we compare observed signal level far from line center to observations and models of the sub-millimeter continuum emission of the Venus atmosphere below ~ 70 km (e.g. Muhleman et al., 1973). Uncertainty in the observed continuum signal level caused by irregularities in the measured spectral baseline is negligible, typically $\pm 0.03\%$. Uncertainty in the observed depth of absorption from continuum is dominated by a 1% uncertainty in the receiver's rejection of the image sideband, corresponding to 1% uncertainty in the measured SO_x abundance. Modeling of the continuum emission is used to construct synthetic spectra for comparison with the data. Continuum modeling includes spherical geometry of Venus convolved with the telescope beam shape, a temperature profile of the atmosphere below 70 km, and radiative transfer calculations to determine the altitude range from which our observations measure the continuum (Muhleman et al., 1973). Uncertainties in modeling the continuum emission introduce 5–10% uncertainty in the derived SO_x . Uncertainties from observed (1%) and model (5–10%) continuum levels add in quadrature, such that all sources of uncertainty in the continuum level collectively contribute 5–10% uncertainty to retrieved SO_x abundance. Continuum-associated uncertainties contribute primarily systematic errors, with minimal effect on precision among measurements. Uncertainties in the telescope beam size ($\pm 1''$) and pointing ($\leq 5''$) (Matthews, 2003) contribute negligible effect on derived SO_x abundance or basic interpretation of the source location on Venus.

Integration time for each measurement is determined by signal to noise (s/n) constraints. Spectral noise is defined as random channel-to-channel variations in brightness temperature of the observed absorption spectrum. Noise is decreased (s/n is improved) by increased observation time (such that the average of the random variations becomes small relative to the SO_x absorption sig-

nal), and by excellent observing conditions (very low water abundance in the sky above the telescope). For long integration times, random noise is sufficiently reduced that limits of the spectrometer channel-to-channel gain calibration become significant, setting a spectrometer-dependent lower limit to detectable absorption strength, and reducing precision of stronger, 1–2% absorptions (e.g. Fig. 1). We reduce the gain-associated uncertainties through substantial increases in the time devoted to gain calibration (2 min versus 5 s). Detailed description of this issue is provided in Clancy et al. (2004).

Spectrometer baselines include artifacts, primarily low-amplitude waves manifesting as sinusoidal variations in continuum level as a function of frequency. Features in Fig. 3 data near zero frequency offset are illustrative. These artifacts vary among observations, and during each individual integration. Their sources (partly contributed by standing waves between the primary and secondary elements) are not quantitatively determined, such that there is no a priori basis to remove them from the receiver output. They are generally removed during analysis, by fitting sinusoidal waves to baseline regions apart from the absorption lines. Remaining, unremoved baseline irregularities contribute to retrieval uncertainties, and can be significant when the channel-to-channel noise level is small. Our calculated s/n uncertainties include effects of both true noise (random, channel-to-channel variation of the signal level), and these baseline artifacts. With 2-min calibrations, gain-associated uncertainties (random, channel-to-channel variation associated with the calibration source) contribute negligibly to calculated s/n .

When the SO absorption is negligible relative to that of SO_2 , the SO_2 abundance can be retrieved from either of the two SO_2 lines. The stronger (346.652 GHz) SO_2 line is generally preferred. However, for some cases in which baseline imperfections are significant, and are less significant at the frequency of the weaker line (346.524 GHz), our measured SO_2 is based upon that weaker line. Sample test retrievals from simultaneous observations of the two SO_2 lines give consistent results.

3. Data analysis

RT analysis of the SO_x sub-millimeter measurements follows procedures described previously for CO (Clancy et al., 2003, 2008) and HDO (Sandor and Clancy, 2005) spectral line observations. Forward model radiative transfer calculations of synthetic spectra are performed over the 65–155 km altitude region of the Venus atmosphere (Clancy and Muhleman, 1991). Contributions from multiple slant paths across the face of the disk, and from limb emission, are included, such that SO_x is determined as a function of pressure, which is then related to altitude based upon hydrostatic equilibrium calculations. A primary focus of this paper is our preliminary characterization and interpretation of SO_x variability, subject to continuing observations and follow-on analysis of spatial variabilities across the observed Venus disk. This is a work in progress. The other primary focus of this paper is the vertical distribution of SO_x . The intrinsic shape of each absorption line is a Voigt profile, determined by temperature and pressure (collisional) broadening. Pressure broadening is important below 100 km, and dominant below 90 km, such that depth of absorption at any given offset ($v - v_0$) from line center (v_0) is determined by SO_x mixing ratio at and above a given pressure, $P \geq P(v - v_0)$ (at and below a given altitude, $z \leq z(v - v_0)$). SO_x mixing ratio varies as much as 3000%, while temperature varies $<10\%$ below 90 km (based upon submm data (Clancy et al., 2008) and Venus Express data (Bertaux et al., 2007)). Venus SO_x absorption lines are therefore a measure of species abundance, not temperature. Temperature variation is a

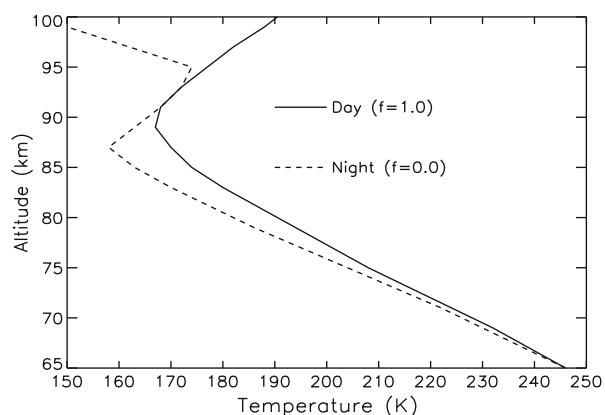


Fig. 4. Temperature profiles. Temperatures used in retrieval of SO_x abundances and altitude distributions are based upon the Clancy et al. (2003) diurnal study. Fig. 4 profiles indicate the Clancy et al. (2003) nightside ($f=0.0$) and dayside ($f=1.0$) temperatures. The temperature profile used for each SO_x retrieval is interpolated between these $f=0.0$ and $f=1.0$ temperatures, to the value of f applicable to the date and geometry of that SO_x observation.

source of uncertainty which we calculate explicitly by perturbing temperature inputs to our synthetic absorption line calculation.

Temperatures used in SO_x retrievals are based upon the dayside (phase $f=1.0$) and nightside ($f=0.0$) temperature profiles measured by Clancy et al. (2003). The temperature profile used for each SO_x retrieval is interpolated between the Clancy et al. (2003) day and night profiles to the f value appropriate for each observation. For disc-average observations, temperatures are interpolated to the Venus phase. Temperatures applied to the April 2007 SO_x disc-average data, for example, are interpolated to the Venus phase, $f=0.7$, corresponding to the telescope beam enclosing an atmosphere that is 70% dayside and 30% nightside. In June 2007, Venus phase was 0.5, but the telescope beam was placed alternately on the day and night limbs, not on the disc-center terminator. Therefore, the June 2007 dayside and nightside SO_x measurements were retrieved using dayside ($f=1.0$) and nightside ($f=0.0$) temperature profiles, respectively. Dayside and nightside temperature profiles are presented in Fig. 4.

Diurnal variability is small below the mesopause, and large above it. The simple mean of day minus night temperatures over 80–96 km (at and below the mesopause) is 6 K, while the simple day minus night mean over 80–100 km (extending above the mesopause) is 10 K. Altitude ranges discussed here have a lower bound of 80 km, because this is the lowest altitude at which we detect SO_x . Specifically, SO on April 22, 2007 is measured to be present only above 82 ± 2 km. We discuss 100 km as an upper bound, because it is the highest altitude at which we have sensitivity to SO_x abundances of 10s of ppbv. The mesopause transition is sharp, with day minus night differences of 0, 3, 20, and 30 K at altitudes 94, 96, 98, and 100 km, respectively. While the simple mean of diurnal temperature variation over 80–100 km is 10 K, weighting of our measurement sensitivity decreases rapidly at the top of this range. Relative weighting of measurement sensitivity at 98–100 is (at most) only 20% of the weighting of any 2-km altitude bin (e.g. 80–82 km; 86–88 km) between 80 and 90 km. Thus, the effect of diurnal temperature variation, determined as its weighted mean, is closer to 6 K than to 10 K. However, we make the very conservative estimate that the effect of diurnal temperature variation on our measurements can be approximated with a 10 K day minus night variation over the full altitude range we measure. This would correspond to a temperature uncertainty of ± 5 K if we used the same (day, night average) temperature profile for all our retrievals. However, that is not what we do – we determine the temperature

Table 2

Uncertainties in retrieved SO_x abundances from microwave observations.

Error source	δSO_2	δSO
Collisional width	6%	20%
Spectral line strength	<1%	<1%
Continuum level	5–10%	5–10%
Temperature	7%	11%
Spectral noise	2–10 ppbv	0.3–3.0 ppbv
Telescope beam size	<1%	<1%
Telescope pointing	<1%	<1%

Errors associated with collisional width, spectral line strength, and telescope beam size are systematic. They do not contribute to uncertainty of temporal variation.

profile as a function of phase, as discussed in the previous paragraph. Temperature uncertainty at a specific must be significantly smaller than the diurnal variation – if this were not the case, and given the modest number of temperature profiles used in the Clancy et al. (2003) analysis, then the diurnal variation would be obscured by, and undetectable because of, temperature variation at constant phase. Because we use a phase-dependent temperature profile in our retrievals, the effect of uncertainty on our retrievals would be better approximated with a ± 2.5 K, rather than ± 5 K temperature uncertainty. However, we make a second very conservative estimate by using a ± 5 K temperature uncertainty to estimate the effect of temperature uncertainty on retrieved abundance. Perturbing the temperature profile by 5 K during retrieval results in changes to SO_2 and SO abundances of 7% and 11%, respectively (see Table 2).

Spectroscopic line parameters, obtained from the JPL microwave spectroscopy database (Pickett et al., 1996; Poynter and Pickett, 1985), are employed for radiative transfer (RT) analysis of the SO_x sub-millimeter line observations. These include line frequencies and intensities. Line-width parameters are derived from the HITRAN 2004 spectroscopic database (Rothman et al., 2005), with modifications as described below. Pressure-broadened line width varies exponentially with altitude, such that line shape is a sensitive measure of altitude distribution, allowing us to obtain altitude resolution from our nadir-looking observation geometry. The pressure broadening coefficients (V_{pres}) of 346.65217 and 346.52388 GHz lines of SO_2 are estimated as 4.6 MHz/hPa, which is 1.4 times the HITRAN 2004 spectroscopic database (Rothman et al., 2005) values for broadening of these SO_2 lines by air (terrestrial mix of N_2 and O_2). The air-broadened coefficient is increased by a factor of 1.4 for application to Venus, based upon the measured air-to- CO_2 increases in collisional broadening coefficients for millimeter transitions of H_2O and CO (Varanasi, 1971, 1975). Adopting $\pm 10\%$ as the $V_{\text{pres}}(\text{SO}_2)$ uncertainty implies $\pm 6\%$ uncertainty in retrieved SO_2 abundance. The pressure broadening coefficient for SO is not included in HITRAN. We estimate $V_{\text{pres}}(\text{SO})$ at 346 GHz as identical to $V_{\text{pres}}(\text{CO})$ at 345 GHz, 2.8 MHz/hPa in a CO_2 atmosphere. Adopting $\pm 30\%$ as the $V_{\text{pres}}(\text{SO})$ uncertainty implies $\pm 20\%$ uncertainty in the measured SO mixing ratio. Pressure broadening uncertainties are systematic. They imply uncertainties in absolute abundances, but have no impact on measured variations of SO_x among multiple observing dates.

Table 2 lists sources of error and the sensitivity of retrieved SO_x mixing ratios to those error sources. SO_x abundances and altitude distributions are determined by iterative comparison between data and synthetic absorption spectra. Each best-fit solution corresponds to the minimum rms difference between observed and synthetic absorption lines. 1σ s/n uncertainties in both SO_x abundance and altitude distribution are determined as perturbations from each best-fit solution such that the rms difference between perturbed and best-fit solutions matches the rms difference between data and best-fit spectra.

4. Results

As a preface to the following presentation of measured SO_x abundances, we note that the retrieved variabilities of SO_2 and SO are extreme, unanticipated in prior modeling work (e.g. Yung and DeMore, 1982), and unexplained with current models of photochemistry (Mills, 1998; Mills and Allen, 2007). Additionally, retrieved altitude abundance profiles for SO and SO_2 indicate volume mixing ratios that increase with altitude over 70–100 km, contrary to theoretical predictions of altitude decreasing mixing ratios (Yung and DeMore, 1982; Mills, 1998; Mills and Allen, 2007). The crux of this data/model disagreement relates to the fact that models supply SO_x to the mesosphere only by transport of SO_2 from the underlying sulfate cloud region. No in situ source of SO_x is provided for the Venus mesosphere. In contrast, the extreme temporal variations and vertically increasing mixing ratios for mesospheric SO_x determined from the submm data require existence of an in situ photochemical SO_x source in the upper mesosphere.

The large variability among, and relatively small number of our SO_x abundance measurements mandates that average values of the data be interpreted cautiously. The mean values of our measured abundances are approximations to mean abundances in the Venus atmosphere, approximations which will improve as more data are obtained. While this statement is true of all empirical data, it is most important in cases with high variability. As an example, the simple average of our six dayside SO abundances for the period January 2007 to July 2008 is 5.6 ppbv. Including one additional month in this time period leads to an 80% larger simple average of 9.9 ppbv SO for the eight dayside observations obtained January 2007 to August 2008.

s/n related uncertainties of individual SO_x abundance measurements are dominated by absolute error when abundances are small, and by relative error when abundances are large. Therefore, neither absolute nor relative weightings are rigorously correct for use in calculation of a weighted mean. Absolute, relative, and unit weightings can lead (and do lead in the case of dayside SO) to significantly different weighted-mean abundance values. In contrast, uncertainties of the abundance sample means, determined from uncertainties of the individual measurements, are much smaller than rms scatter among those measurements, independent of the weighting algorithm. In the case of daytime SO , the eight measurements have a simple mean of 9.9 ppbv, with only ± 0.3 ppbv uncertainty of the sample mean, based upon uncertainties of the individual measurements. However, the rms scatter among those data is ± 9.1 ppbv, such that this dominates uncertainty of the parent population mean (SO in the dayside atmosphere). Consequently, observed abundance variabilities (dayside SO in this example) indicate real geophysical variations, far outside the measurement uncertainties.

Table 1 lists 21 measurements of SO_2 , and 16 measurements of SO . Of these, 10 SO_2 , and 8 SO spectral observations have sufficient s/n to retrieve altitude distribution as well as mixing ratio. These measurements are identified in Table 1 by uncertainties associated with their indicated lower altitude boundary (e.g. 84 ± 2 km). For both SO_2 and SO , the average lower altitude boundary is 84 ± 2 km, where uncertainty of the mean (± 2 km) includes effects of both the uncertainties of the individual measurements, and rms scatter among them. Lower altitude boundaries that are listed without uncertainties (e.g. 84 km), are assumed values (applied to data with low s/n), set equal to the mean boundary (84 ± 2 km) determined from high s/n data. Each molecular abundance measurement in Table 1 indicates the mixing ratio above the specified low-altitude boundary. For example, the January 14, 2006 SO_2 measurement is of 14 ± 3 ppb above 86 ± 4 km, and negligible SO_2 between 70 and 86 ± 4 km.

In the following discussion, SO_x abundances are quoted for the altitudes listed in Table 1. Generically, mixing ratios are discussed for altitudes above 84 ± 2 km. When mixing ratios on two dates are compared, the comparison applies to the altitudes at which abundances were measured on each date. For example, SO abundances on August 8 and August 17, 2008 were 15 ± 3 ppb above 84 ± 2 km, and 31 ± 4 ppb above 86 ± 2 km, respectively. In this case, SO abundance doubled (from 15 ± 3 to 31 ± 4 ppb) at altitudes above 86 ± 2 km, and the altitude distribution shifted 2 km (1σ) upward. The altitude boundary between negligible SO_x (below), and significant SO_x (above) is precisely determined (often to ± 2 km) in part because the 84 km boundary is near the altitude of maximum measurement sensitivity, at the center of the 70–100 km measurement range.

4.1. Temporal variability

Spectra corresponding to mesospheric SO_2 in June 2004 (first detection) and in August 2007 are shown in Fig. 1. These nightside, inferior conjunction observations indicate a factor of 2.4 increase in measured SO_2 , from $25. \pm 9$ ppbv in June 2004, to $60. \pm 9$ ppbv in August 2007.

SO spectra in Fig. 2 illustrate variability on long (19 month) and short (9 day) timescales. Venus–Earth–Sun geometry in January 2007 and August 2008 were identical, such that local time on Venus' sub-Earth meridian was 13:35–13:50 for each Fig. 2 spectrum. The apparent Venus diameter was $10.5''$ in each case, smaller than the telescope beam footprint, such that each observation corresponds to a hemispheric mean measurement. Spectra of August 8 and August 17, 2008 are of particular interest in that they were obtained only 9 days apart from one another. In that 9-day period, SO abundance exhibited a 5σ change, doubling from 15 ± 3 to 31 ± 4 ppbv.

Fig. 3 compares disc-average SO_x spectra observed in April and August 2007, respectively. In this case, SO_2 and SO change dramatically, and oppositely. Clearly, uncertainties in calibration and background atmospheric parameters (e.g. temperature) are minor effects in the interpretation of such variations in SO and SO_2 line absorptions. Diurnal variation is suggested between the full nightside (August) and 70% dayside (April) 2007 measurements presented in Fig. 3, and photolysis is expected to be important for both species.

However, it is also apparent that SO_x variability is not a purely diurnal phenomenon: local Venus time is midnight for each of the two SO_2 spectra presented in Fig. 1, and 13:40 for each of the three SO spectra presented in Fig. 2.

Comparison of data from the sunlit (day) and dark (night) atmosphere provides the basis for a diurnal analysis. SO_x abundances are plotted (Fig. 5) as a function of local Venus time (LVT) at the center of the telescope beam position. LVT for disc center measurements corresponds to LVT at the sub-Earth meridian, which varies through 24 h versus the Venus 19 month (as observed from Earth) orbital cycle. When the apparent Venus disk is large, observations at multiple local times may be obtained on a single date. For the purpose of this diurnal analysis, observations which have contributions of more than 93% from the illuminated atmosphere, or 93% from the dark atmosphere, are considered dayside and nightside, respectively, and indicated in Fig. 5 by solid error bars. Dotted error bars in Fig. 5 indicate measurements with significant contributions from both day and night local times.

SO , which is more abundant in daytime versus nighttime, exhibits the strongest diurnal signature in Fig. 5. The largest of five SO night time abundances is 1.7 ppbv, while the seven daytime SO measurements vary from 2.1 to 31 ppbv. Low SO abundances occur during day and night local times, whereas high SO abundances

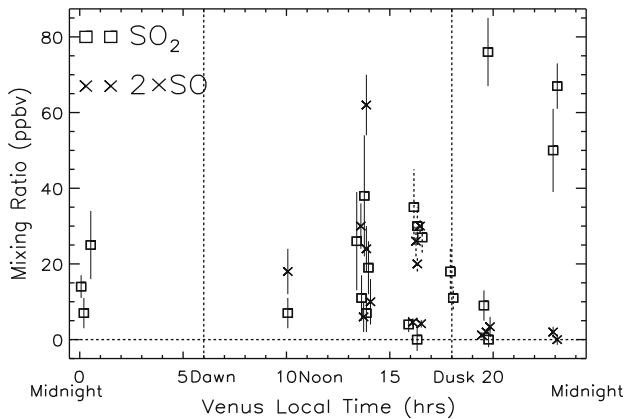


Fig. 5. SO_x versus Venus local time. Abundances of SO_2 (squares) and SO (X's) as a function of local Venus time (LVT). For improved readability, SO abundances (and uncertainties) are plotted at $2\times$ their measured values. Error bars indicate the 1σ s/n uncertainties. For clarity, values are plotted with small horizontal offsets when necessary to prevent error bars of two points from overlapping. Solid error bars indicate measurements that are either day or night. (i.e. The telescope beam footprint is filled with either $>93\%$ sunlit, or $>93\%$ dark areas.) Dotted error bars indicate observations for which both day and night conditions make significant contributions to the observed spectra. Plotted abundances correspond to mixing ratios listed in Table 1. Note that altitude distributions (Table 1) of these abundances are similar, but not identical.

have been observed only in daytime. SO_2 abundances present large variability for both day and night local times, although the largest measured SO_2 abundances are obtained for nightside local times. The large intrinsic variability of Venus mesospheric SO_x precludes quantitative definition of diurnal variations, but they are clearly significant. Additional observations are required to characterize SO_x variability, as illustrated by the SO determination of August 17, 2008 (31 ± 4 ppb), which is more than twice any of the previous 15 measurements obtained over the preceding 19 months.

In summary, hemispheric mean SO_2 and SO abundances vary temporally by more than $30\times$. SO_2 increased from <1.7 to 66 ± 5 ppb from June 9 to August 11, 2007. SO increased from 0.7 ± 0.5 to 31 ± 4 ppb from August 11, 2007 to August 17, 2008. Between two observation dates, SO_2 and SO may vary oppositely (e.g. between April and August 2007, Fig. 3), or similarly (e.g. between March and August 2008, Table 1). Over the full set of measurements, SO and SO_2 exhibit anti-correlation associated with opposite diurnal variations (more SO during day than night, more SO_2 during night than day), although this anti-correlation is diminished by the extreme temporal variations of both species over non-diurnal timescales. Total SO_x ($\text{SO}_2 + \text{SO}$) is clearly not conserved among the observed variations, as detailed in the following section.

4.2. Altitude variability

The altitude distributions of SO and SO_2 are constrained by the shapes of their observed absorption lines. The altitude dependence of atmospheric pressure, which affects the collisionally broadened linewidth of spectral absorption provides vertical profiling capability. The particular vertical distribution of the observed species determines the vertical range and resolution that may be retrieved from sub-millimeter absorption spectra. In the case of Venus mesospheric SO and SO_2 observations, very little (if any) absorption is contributed below ~ 85 km, such that a simple two-layer model of SO_x altitude distribution, in which SO_x is present only in the upper layer, provides a good fit to all observed spectra. When s/n is sufficiently high, we determine both the upper layer SO_x abundance, and altitude of the boundary between the two layers from the data. Precision of the altitude boundary can be as good as ± 2 km, in part

because greatest sensitivity of sub-mm absorption spectra (on a per unit mixing ratio basis) at 80 km, very close to the ~ 85 km SO_x boundary. At lower s/n , only the SO_x abundance in the upper layer is retrieved, and the altitude of the layer boundary is assumed to be the mean of boundary altitudes measured from the higher s/n spectra. Sub-mm absorption spectra are sensitive to altitudes 70–100 km and have peak sensitivity at 80 km, such that the data are actually more sensitive to SO_x below the ~ 85 km boundary than above it. Hence the finding of far less SO_x below than above the ~ 85 km boundary is a robust result from this measurement system.

Retrieved values (Table 1) are SO_x abundance of the upper layer, and the altitude boundary between the upper and lower layers. To test the robustness of this approach, an alternative retrieval was run for two of our highest s/n spectra (South and West positions observed August 11, 2007), in which we explicitly fit abundances for both the upper and lower layers. In these cases we solve for X and R , where X is the upper layer mixing ratio (ppbv), and $R \times X$ is the lower layer mixing ratio (ppbv). i.e. R is the ratio of lower layer to upper layer SO_2 abundances. Best-fit values of R are 0.0 ± 0.19 and 0.0 ± 0.28 for the South and West position spectra, respectively. Each spectrum is best fit with zero SO_2 in the lower layer. Residuals increase with increasing R , reaching the 1σ level at 0.19 and 0.28, respectively. Averaging these two results determines an upper limit of 0.16 ($R = 0.0 \pm 0.16$), supporting use of a 2-layer altitude structure to fit the data.

Despite the large variability in observed SO_x absorption depths, minimal variation in lineshape is exhibited. Consequently the vertical profile dependence of mesospheric SO and SO_2 is observed to be time invariant within the measurement uncertainties. The mean boundary altitude for both SO_2 and SO is 84 ± 2 km. Every observation with sufficient s/n for vertical resolution reveals SO_x mixing ratios are much larger at 85–100 km than at 70–85 km. While the details of this vertical dependence are not clearly defined, the existing observations firmly establish that SO and SO_2 are vertically increasing by large factors (100s of percent) within the Venus mesosphere (70–100 km).

Fig. 6a presents an SO_2 spectrum observed August 11, 2007. Overlain are synthetic absorption spectra corresponding to the best-fit altitude distribution and mixing ratio, and to best-fit mixing ratios with altitude distributions constrained to be other than best fit (Fig. 6b). Best fit (blue) to the data (black) is with 67 ppb SO_2 above 84 km, and zero SO_2 at lower altitudes (blue profile of Fig. 6b). If SO_2 is assumed to be uniformly mixed above the cloud tops (green) or restricted to altitudes above 100 km (red), poor model-data fits result. Best-fit mixing ratios for the alternate altitude distributions, 28 and 485 ppb, respectively, do not provide agreement with the observed line shape.

Observed sub-mm SO_2 spectra appear incompatible with the very large lower thermospheric SO_2 abundances reported by Bertaux et al. (2008; pers. comm., 2009), based on Venus Express SPICAV measurements. Bertaux et al. (2008) find SO_2 abundances of 300–400 ppb at 100 km, increasing with altitude to 800–1200 ppb near 110 km. Synthetic microwave spectra corresponding to the Venus Express thermospheric SO_2 values measured during Venus Express orbit 434 (J.L. Bertaux, pers. comm., 2009) are narrow, Doppler (temperature)-broadened absorptions of 1.2–1.6% at line center. These lines have shape identical to that of the Fig. 6 thermospheric profile (red; 485 ppb at 100–120 km), and are 1.5–2.0 $\times$ deeper. Low optical depth absorptions such as these display linear behavior, such that an SO_2 altitude profile with 67 ppb in the upper mesosphere, together with 500 ppb in the lower thermosphere, would create a submm spectrum with line-center absorption 2–3 $\times$ deeper than the deepest we observe. Further, the SO_2 determinations of June 9, 2007 correspond to absorption upper limits less than 0.05%. This conflicts with absorp-

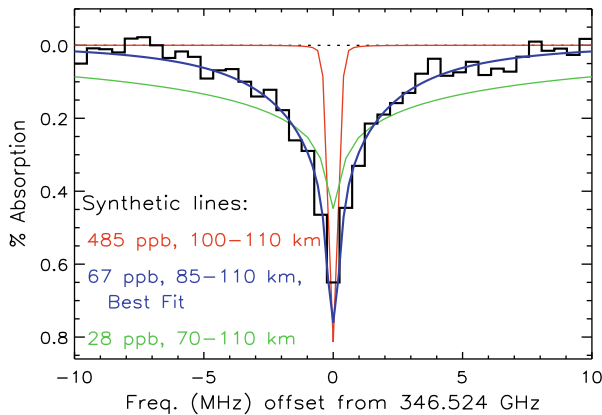


Fig. 6a. SO₂ data: altitude sensitivity. Sensitivity of submm SO_x spectra to altitude distribution is based upon shape of the pressure broadened lines. Absorptions at low altitudes (high pressures) are broader than absorptions at high altitudes (low pressures). This August 2007 SO₂ spectrum (black histogram) is best fit with a synthetic spectrum corresponding to 67 ppbv SO₂ at 85–110 km (blue). When the altitude distribution is forced a priori to be a uniform mixing ratio at 100–110 km (red), or 70–110 km (green), best fit abundances obtained for those constrained distributions are 485 ppb, and 28 ppb, respectively. It is clear that no acceptable fit is possible for those alternative distributions. SO₂ confined above 90 km (red) corresponds to absorption lines far more narrow than that observed, while SO₂ uniformly distributed through the mesosphere (green) corresponds to an absorption line that is far too broad.

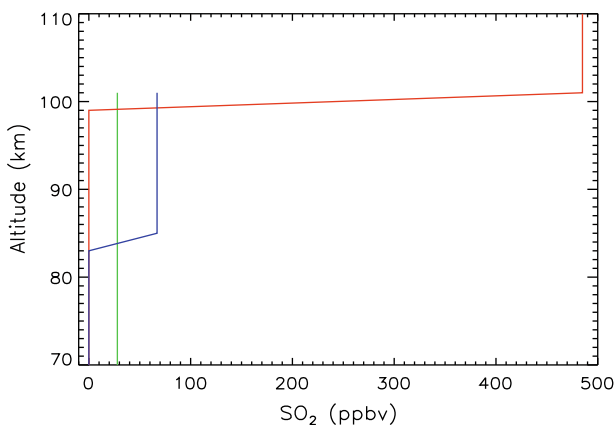


Fig. 6b. SO₂ abundance profiles. SO₂ altitude profiles corresponding to absorption lines in Fig. 6a. The best-fit (blue) and uniform 70–110 km altitude profiles are not shown above 100 km. This is to emphasize that SO₂ spectral observations are not sensitive to abundances of only 67 ppb above 100 km. This would correspond to a 0.1% absorption in a single (center) spectrometer channel, that could not be separated from the 70–100 km signal. We would be sensitive to much larger, e.g. 485 ppb (red) at 100–110 km, as illustrated by the 0.8% absorption (red) in Fig. 6a. While we are not sensitive to 67 ppb above 100 km, we would be sensitive to (and do not find) the much larger 100–110 SO₂ mixing ratios indicated from Venus Express SPICAV data (Bertaux et al., 2008).

tions >1.2% that Bertaux et al. (2008; pers. comm., 2009) thermospheric abundances would generate. On the other hand, such lower thermospheric abundances may be present at finer (unresolved) spatial scales not adequately sampled with the JCMT beam resolution.

Yung and DeMore (1982) present three model studies (designated A, B, and C), which are calculated for different assumptions about the underlying chemistry. All three Yung and DeMore (1982) models predict SO₂ mixing ratios that decrease monotonically with altitude above 70 km, contrary to the observed increase of SO₂ mixing ratio with altitude. Disagreement between observed model and model altitude profiles is determined based upon shapes of their respective pressure-broadened sub-mm SO₂

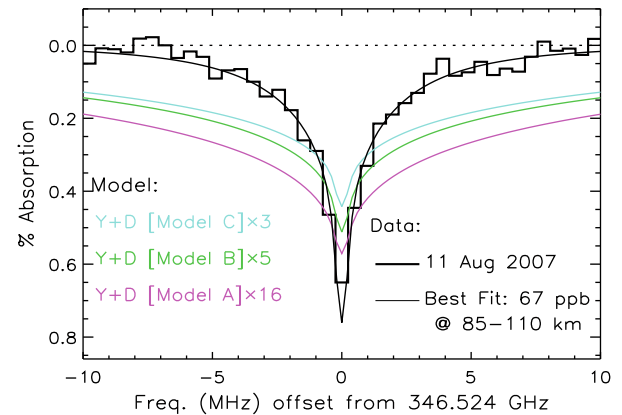


Fig. 7a. SO₂ data and PCE model. SO₂ observed (thick black) August, 11, 2007, and best-fit (thin black) synthetic spectra are compared with synthetic spectra corresponding to the photochemical equilibrium (PCE) model SO₂ abundances of Yung and DeMore (1982). PCE abundances corresponding to Yung and DeMore (1982) models C (cyan, chlorine-dominated chemistry), B (green, nitrogen-dominated chemistry) and A (purple, hydrogen-dominated chemistry) are increased here by factors of 3, 5, and 17, respectively, to provide synthetic spectra with amplitudes comparable to the observation (black). This facilitates comparison of line shapes. All Yung and DeMore (1982) model spectra are far too broad to be consistent with the observation.

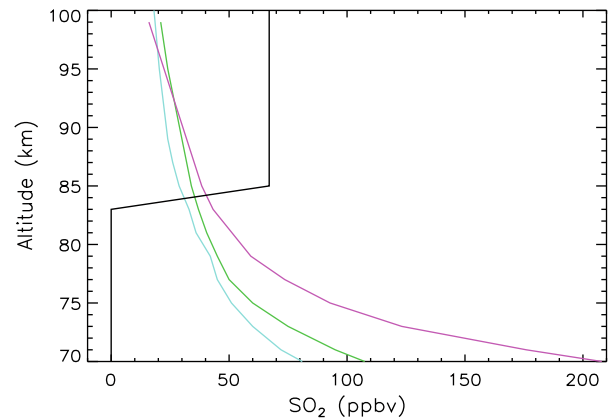


Fig. 7b. SO₂ abundance profiles. Sensitivity of submm SO_x spectra to altitude distribution is based upon shape of the pressure broadened lines. Absorptions at low altitudes (high pressures) are broader than absorptions at high altitudes (low pressures). Correspondingly to their spectral line shapes (Fig. 7a) the best-fit SO₂ altitude profile (thin black) requires SO₂ abundance increase with altitude, contrary to the strong decrease with altitude of all Yung and DeMore (1982) PCE model SO₂ abundances (cyan, green, purple).

absorption lines. Fig. 7a presents data and best-fit synthetic spectra, together with synthetic spectra generated with the Yung and DeMore (1982) (models C, B, A) SO₂ profile abundances presented in Fig. 7b. Yung and DeMore (1982) photochemical equilibrium (PCE) model spectra are far too broad to be consistent the observation, indicating PCE model SO₂ abundances are too large below 85 km.

The altitude distribution of SO is observed to be similar to that for SO₂ (Table 1). SO absorption spectra are well fit by a two-layer altitude distribution in which SO is present only above 85 km. Observed and best-fit spectra from August 17, 2008 are presented in Fig. 8, together with synthetic spectra corresponding to Yung and DeMore (1982) models A, B, and C abundance profiles for SO. Comparisons of line shapes between the models and data are facilitated by synthetic lines based upon Yung and DeMore (1982) abundances that are increased by factors of 17, 5, and 2, respectively

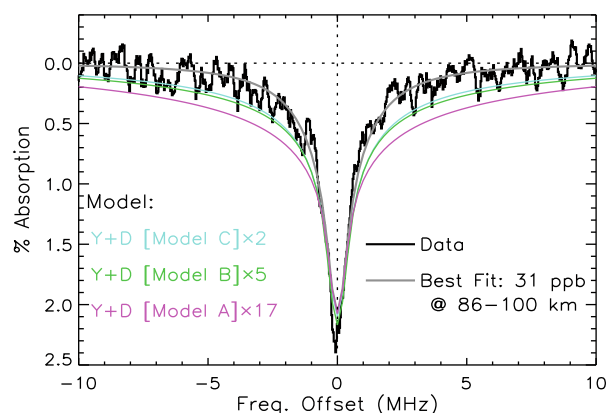


Fig. 8a. SO₂ data and PCE model. Similar to Fig. 7a, but for SO₂ rather than SO₂. This August 17, 2008 SO₂ data spectrum (thick black) is best fit with a synthetic spectrum corresponding to 31 ppbv SO at 86–100 km (thin black). The three Yung and DeMore (1982) PCE model SO abundance profiles correspond to synthetic spectra (cyan, green, purple) which are too broad to fit the data. Disagreement between the observed and Yung and DeMore (1982) model SO spectral shapes is smaller than that for SO₂ (Fig. 7), because the difference between best fit and model SO altitude profiles (Fig. 8b) is less extreme than that of SO₂ (Fig. 7). The PCE model SO profiles do increase with altitude, but too slowly to be consistent with observations.

(Figs. 7a and 7b; purple, green, and cyan lines, respectively). While Yung and DeMore (1982) SO mixing ratios do increase with altitude, all corresponding synthetic lines are too broad, indicating all three Yung and DeMore (1982) models predict too much SO in the lower (relative to upper) mesosphere.

4.3. SO_x budget

Data on hand give important clues about the SO_x budget, i.e. the distribution of sulfur atoms among all atmospheric species. It is clear that sulfur atoms are not conserved by SO₂ and SO alone (Table 1). Total SO_x (SO₂ + SO) varies more than 20× June 9 to August 11, 2007. At least one additional sulfur reservoir is required. The dramatic 9-day SO_x increase in August 2008 (Fig. 2; Table 1) requires the additional sulfur reservoir must be a source as well as a sink for SO_x.

The balance between SO₂ and SO, expressed as their ratio [SO₂]/[SO], also varies strongly, from 0.6 ± 0.5 (January 20, 2007), to values exceeding 40 at all three measured positions on August 11, 2007, including a lower limit of $[SO_2]/[SO] > 96$, at the South position. The $[SO_2]/[SO]$ ratio is plotted as a function of local Venus time in Fig. 9, where each of the 16 ratios was determined from simultaneous measurements of SO₂ and SO. Note that the (Fig. 9) ratios are presented on a log scale, in contrast to the linear scale on which diurnal behavior of the individual molecules (Fig. 5) are plotted. This reflects that, over the full diurnal cycle, the $[SO_2]/[SO]$ ratio varies more strongly than does either SO₂ or SO alone. Further, uncertainty of each ratio is dominated by the larger of the SO₂, SO relative uncertainties, such that error bars for the $[SO_2]/[SO]$ ratios are generally larger than those of the individual molecules.

The 13 ratios that are either dayside or nightside are presented with solid error bars (Fig. 9), while dotted error bars indicate the three observations in which the field of view includes both night and day conditions. Four of the five nightside ratios are much larger than all eight dayside (and all three mixed-phase) ratios, consistent with the uniformly small nightside abundances of SO. Large uncertainties of the night time ratios follow from the large relative uncertainties of weak night time SO absorptions. The three ratios with smallest uncertainty are the three ratios which include

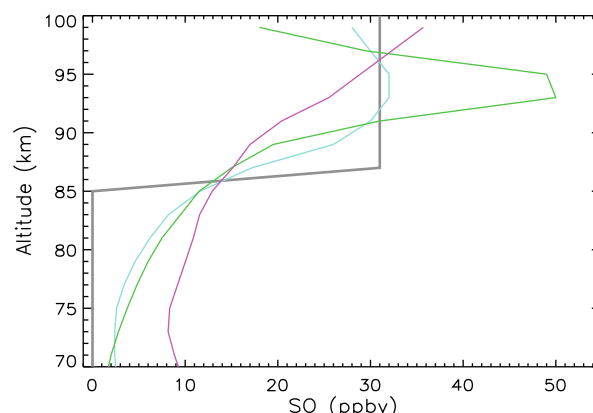


Fig. 8b. SO abundance profiles. SO altitude profiles corresponding to absorption lines in Fig. 7a.

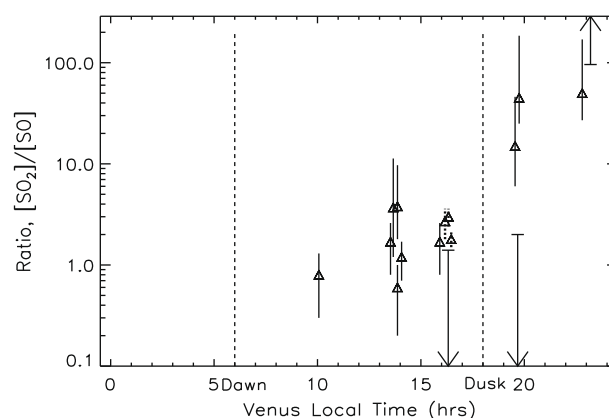


Fig. 9. $[SO_2]/[SO]$ versus Venus local time. SO_2/SO ratios determined from simultaneous measurements of SO₂ and SO, plotted as a function of local Venus time (LVT). Error bars indicate the 1σ s/n uncertainties. For clarity, values are plotted with small horizontal offsets when necessary to prevent error bars of two points from overlapping. Solid error bars indicate measurements that are either day or night. (i.e. The telescope beam footprint is filled with either >93% sunlit, or >93% dark areas.) Dotted error bars indicate observations for which both day and night conditions make significant contributions to the observed spectra. Plotted ratios apply to altitudes at which both species are present. e.g. April 22, 2007 data identify 30 ± 5 ppbv SO₂ above 84 ± 2 km, and 10 ± 1 ppbv SO above 82 ± 2 km. The ratio for this date, $SO_2/SO = 30/10 = 3$, applies to altitudes above 84 km.

data from both the day and night side atmosphere. While not conclusive, it may be that the spectra determining those mixed-phase ratios include SO and SO₂ signals that are predominantly from the day and night atmospheres, respectively. If this is the case, then those three values would indicate ratios of [nightside SO₂] to [day-side SO] at spatially distinct locations, not the ratio of molecules coexisting within a single air parcel.

Mean values of the dayside and nightside $[SO_2]/[SO]$ ratios are 1.9 ± 1.2 , and 37 ± 15 , respectively, where upper and lower limit determinations are excluded from the calculation. Uncertainties ± 1.2 and ± 15 are derived from scatter among the included seven dayside and three nightside values, respectively. In contrast, uncertainty of the daytime sample mean (associated with uncertainty of the individual measurements) is ± 0.24 , i.e. much smaller than the scatter-based uncertainty ± 1.2 , indicating that variability of the daytime ratio is real. It is not a result of measurement uncertainty. The corresponding night side uncertainties (± 15 for the sample mean, versus ± 15 rms scatter) are equal, such that observed variation among these three night side ratios is within the measurement noise, and does not demonstrate the variation is real. Note however, that the other two night time ratios (upper limit of 2.0,

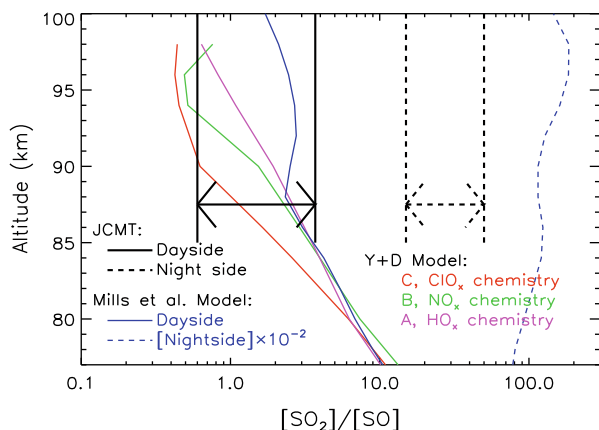


Fig. 10. $[SO_2]/[SO]$ ratios. Comparison of $[SO_2]/[SO]$ ratios determined from submm data (this study), the Yung and DeMore (1982) models, and recent modeling by Mills et al. (in preparation). Measured ratios are not defined below 85 km because zero abundance provides the best fit to both SO_2 and SO in the lower mesosphere. Plotted daytime (solid black) and night time (dotted black) values indicate the range from smallest to largest measured ratios in each diurnal phase. Upper limit and lower limit ratio determinations are not considered here. The Yung and DeMore (1982) model results are global average calculations. The Mills et al. model day and night results are based on approximate analytic day (solid blue) and night (dashed blue) equilibrium relations for $[SO_2]/[SO]$ but assume $[O]$, $[ClO]/[O]$, $[ClCO_3]/[O]$, and $[OH]/[O]$ do not change from day to night. The basic chemistry in the Mills et al. model is similar to Yung and DeMore (1982) model C.

and lower limit of 96.) do indicate that Venus' $[SO_2]/[SO]$ ratio at night also varies outside the measurement uncertainties.

Measured $[SO_2]/[SO]$ ratios are compared with Yung and DeMore (1982) and Mills et al. (in preparation) models in Fig. 10. Vertical, 85–100 km lines indicate the ranges of measured day (solid black, 0.6–3.7) and night (dashed black, 15–50) ratios, respectively. Measured ratios are not defined in the lower mesosphere, because best-fit SO_2 and SO profiles are characterized by zero (i.e. undetectable) abundances below 85 km altitudes. Above 85 km, observed daytime $[SO_2]/[SO]$ values are consistent with all three Yung and DeMore (1982) global average models and the Mills et al. day side approximate model, while the observed night time ratios are larger than the Yung and DeMore (1982) global average models and smaller than the Mills et al. night side approximate model. (Note that upper and lower limit determinations are not considered in Fig. 10. The June 9, 2007 nightside upper limit is in fact compatible with Yung and DeMore (1982) model ratios.)

5. Summary and discussion

This study presents the first observations of SO_2 and SO (collectively, SO_x) in the Venus mesosphere (70–100 km altitudes). Altitude distributions of SO_2 and SO , based upon shape of their pressure-broadened absorption lines, indicate that abundances for SO_2 and SO increase dramatically (100s of percent) with altitude in the mesosphere. Best fits to observed spectra are obtained with negligible SO_x abundances over 70–85 km (upper limit 16% of abundances over 85–100 km), versus well-determined, but highly variable SO_x abundances at 85–100 km altitudes (<1.7 to 66 ± 5 ppb SO_2 ; and 0.7 ± 0.5 to 31 ± 4 ppb SO) solely responsible for the observed absorption lines. Averaged over all measurements, the mean lower altitude boundary for both SO_2 and SO detectable abundances is 84 ± 2 km.

SO_2 and SO abundances undergo extreme temporal variability, whereas their altitude-increasing distributions remain a feature of all the observations. SO_2 abundances over 85–100 km altitudes range from <1.7 to 66 ± 5 ppb, while measured SO varies between 0.7 ± 0.5 and 31 ± 4 ppb. Lower thermospheric SO_2 abundances of

400–1200 ppb, reported by Bertaux et al. (2008), are larger than allowed in any of our observations. However, we cannot rule out such large values within much finer spatial scales than sampled by the JCMT beam resolution (e.g. >1000 km).

A diurnal pattern is seen in the full data set, wherein there is more SO , and less SO_2 during day versus night local times. Large temporal (non-diurnal) variation of both molecules is superimposed on this diurnal behavior, without clear evidence for correlation (or anti-correlation) between these temporal SO and SO_2 variations. Abundances at constant phase (constant local Venus time) can vary by more than $2\times$ for both SO_2 (Fig. 1) and SO (Fig. 2). In the case of SO (Fig. 2), a 5σ doubling in 85–100 km abundance occurred over the entire sub-Earth hemisphere in only nine days.

Model SO_x (Yung and DeMore, 1982) abundances above 85 km are a factor of 2–20 smaller than the largest observed SO_2 and SO values, such that model mixing ratios are well within the range of the measurements. However, the observed increase of the SO_2 mixing ratio with altitude strongly disagrees with the Yung and DeMore (1982) photochemical modeling results, all of which predict altitude-decreasing SO_2 abundances. The retrieved altitude increase of SO is also substantially greater than presented in the Yung and DeMore (1982) model of SO . The ratio SO_2/SO is observed to vary more strongly than either SO_2 or SO alone, with the greatest differences between night (larger) and day (smaller) ratios. The mean measured daytime ratio $[SO_2]/[SO]$ is 1.9 ± 1.2 , where the 1σ rms scatter among data points (± 1.2) is much larger than the 1σ uncertainty of the sample mean (± 0.24). This indicates that variation of the daytime SO_2/SO ratio is a real physical phenomenon, well outside the measurement uncertainties. The range of daytime SO_2/SO ratios (above 85 km) includes photochemical model predictions from the Mills et al. (in preparation) dayside model, and from all three of the Yung and DeMore (1982) global mean model cases, such that dayside observations do not discriminate among the models (Fig. 10). Measured night time ratios are ~ 50 times larger than the Yung and DeMore (1982) global mean model, and ~ 500 times smaller than the Mills et al. nightside model.

The observations of rapidly increasing SO_x (SO_2 and SO) abundance with altitude in Venus' upper mesospheric present a sharp conflict with model (Yung and DeMore, 1982) predictions. Temporal variability, which was not considered in the models of Yung and DeMore (1982) or of Mills et al. (in preparation), is observed to be extreme. Both altitude and temporal variabilities indicate non-conservation of SO_x within the Venus mesosphere such that an additional source for SO_x production in the upper mesosphere/lower thermosphere must be present. This source must also be quite large relative to background SO and SO_2 abundances in that it drives many 100's of percent variations in these species (vertically and temporally). We do not clearly identify the source, but point out that aerosols (possibly sulfate) are observed with significant extinction ratios and temporal variabilities in the Venus mesosphere (Wilquet et al., 2009).

In each of the Yung and DeMore (1982) models, H_2SO_4 (sulfuric acid) is a stable end-product of mesospheric photochemistry, formed as a solid aerosol which precipitates and gravitationally settles to altitudes below the clouds. Model thermochemistry in turn destroys H_2SO_4 in the lower atmosphere, producing SO_2 as a stable (lower atmospheric) end-product. Upward transport of SO_2 along its abundance gradient returns sulfur to the mesosphere, closing the sulfur cycle. The Yung and DeMore (1982) model photochemistries include exchange between SO and SO_2 (collectively SO_x), and destruction of SO_x to form H_2SO_4 , which forms aerosols that are gravitationally lost from the mesosphere. However, there is no in situ mechanism for mesospheric production of SO_x associated with these same aerosols. Because transport of SO_2 from the lower atmosphere is the only mechanism supplying SO_x to their

model atmosphere Yung and DeMore (1982) models produce monotonic decreases in SO_x with altitude.

The three Yung and DeMore (1982) model cases (A, B, and C) consider catalytic control of sulfur chemistry by active hydrogen (HO_x), nitrogen (NO_x), and chlorine (ClO_x), respectively. While none of these models are expected to correctly predict total SO_x (see preceding paragraph), one or more of these catalysis cycles could plausibly control the relative abundances of SO_2 and SO, expressed here as their ratio SO_2/SO . However, measured daytime ratios are consistent with all three catalysis schemes (Fig. 10), and do not distinguish among them. Further, the 1σ rms scatter among observed ratios encompasses the predicted ratios of all three models, such that it is unlikely the ratio SO_2/SO is controlled solely by any of the three catalytic cycles. Much larger SO_2/SO ratios at night are consistent with Yung and DeMore (1982) chemistry, in that SO_2 photolysis is their model's only means of SO production. What is missing in model photochemistry is an additional source of upper mesospheric/lower thermospheric SO_x , perhaps associated with the time variable, substantial haze of sulfate aerosols apparent in limb observations of the Venus upper atmosphere (e.g. Wilquet et al., 2009).

At mesospheric temperatures, sulfuric acid produced photochemically from SO_x would exist in aerosol form, either as a solid composed of pure H_2SO_4 , or as a solid or liquid solution of H_2SO_4 in water. Upper mesospheric aerosol observations with the SPICAV and SOIR solar occultation instruments on Venus Express (Wilquet et al., 2009) indicate a bimodal particle size distribution, with radii of 0.1–0.3 and 0.4–1.0 μm for modes one and two, respectively. Wilquet et al. (2009) observe particle number densities to be temporally variable. Representative values (their Fig. 9) at 90 km are $\sim 7\text{ cm}^{-3}$ for mode 1 particles, and $0.2\text{--}5\text{ cm}^{-3}$ for mode 2 particles. At 90 km, the maximum SO_x mixing ratio (80 ppb, Table 1) observed with the JCMT corresponds to a sulfur atom number density of $6.7 \times 10^8\text{ cm}^{-3}$. If all these atoms were moved from the SO_x gas reservoir to an H_2SO_4 solid reservoir of aerosol particles with radii 0.1–1.0 μm , the resultant aerosol particle density would be $14\text{--}0.014\text{ cm}^{-3}$, comparable to the aerosol density and size distribution reported by Wilquet et al. (2009). Hence, the aerosol abundance is sufficient that conversion of that aerosol (assuming it is H_2SO_4) to gas-phase SO_x would explain the full range of observed SO_x abundances. The mechanism for conversion of aerosol H_2SO_4 to gaseous SO_x is not known. Yung and DeMore (1982) include no such mechanism in their model calculations, but its existence is plausible. Photolysis of H_2SO_4 directly from the solid to gas-phase SO_x is one plausible mechanism.

Gurwell et al. (2007) suggested formation and destruction of sulfuric acid (in water solution) aerosol as a possible explanation for observations (Gurwell et al., 2007; Sandor and Clancy, 2005) of rapid, large variations of water vapor abundance. Gurwell et al. (2007) explicitly suggest this may entail "... variation in the fractional content of sulfuric acid within the aerosols and variability in distribution of aerosols ...". Implicitly, the Gurwell et al. (2007) suggestion regarding water variability allows that there may be variation of (gas phase) SO_x correlated with water variation. An ongoing objective of our Venus research is to measure water variability (as described in Sandor and Clancy (2005) for the period 1998–2004) simultaneously with SO_x variability (as reported in this study for 2004–2008). Our observations 2004 to March 2008 find the Venus mesosphere to be very dry, with water abundances that are undetectable, or barely detectable, such that no determination of water variability associated with the SO_x variability described in the present work is possible. Preliminary analysis indicates significantly more water in the Venus mesosphere in August 2008, and in January 2009, than in any of the 2004 to March 2008 measurements. If water abundance of this magnitude continues to be present, our future observations will provide simulta-

neous characterizations of water and SO_x temporal variabilities, and determination of any correlation in their behaviors.

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