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Climatology of SO₂ and UV absorber at Venus' cloud top from SPICAV-UV nadir dataset.

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Abstract

Following our previous work (Marcq *et al.*, 2011, 2013), we have updated our forward radiative transfer code and processed the whole SPICAV-UV/Venus Express nadir dataset (2006-2014) in order to retrieve SO₂ abundance at cloud top – assuming a SO₂ decreasing scale height of 3 km and a ratio SO/SO₂ tied to 10% – as well as the imaginary index of scattering mode 1 particles, representative of the remaining UV absorption, since the OSSO vertical profile found by Frandsen *et al.* (2016) cannot account for our observations. Our main results mostly confirm and extend the validity of those discussed by Marcq *et al.* (2013), namely: (i) long-term variations of low latitude SO₂ at 70 km between ~ 100 ppbv (2007, 2009) and less than 10 ppbv (2014); (ii) in average, decreasing SO₂ with increasing latitude and depletion near the sub-solar point, consistent with a competition between advection and

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photo-chemical destruction; (iii) secular increase of mode 1 imaginary index at 250 nm, from 10^{-2} to $5 \cdot 10^{-2}$ between 2006 and 2010; (iv) if not related instead to long-term variability, a possible localized enrichment of SO₂ and UV brightness increase above the western slopes of Aphrodite Terra, consistent with Bertaux *et al.* (2016) supply mechanism through orographic gravity waves. This spatial and temporal variability underlines the need for a long term monitoring of Venus SO₂ and cloud top from ground-based facilities until the next generation of Venusian orbiters is operational.

Keywords:

Venus, atmosphere, Ultraviolet, observations, Atmospheres, composition

1 1. Introduction

Sulphur dioxide is arguably the most variable species in Venus' cloud top 2 atmosphere, on a large range of temporal and spatial time scales. The first 3 attempt to detect it in UV only yielded a 0.1 ppmv upper limit (Jenkins *et al.*, 4 1969). Yet, a decade later, Barker (1979) found between 0.1 and 0.5 ppmv of 5 SO_2 using the same UV spectral range. The most extensive data set before 6 Venus Express was acquired with UVIS onboard Pioneer Venus (Esposito 7 et al., 1979; Esposito, 1984; Esposito et al., 1988), and revealed an important 8 short term variability, as well as a long term decrease between 1978 and 1988. 9 These long-term variations were interpreted as possible evidence for active 10 volcanism, which would alter the thermal buoyancy of the lower atmosphere 11 and allow for an intermittent resupply of SO_2 above Venus' clouds, where it 12 is photochemically destroyed. Meanwhile, IR measurements from Venera 15 13 (Zasova et al., 1993) and UV measurements from rockets (Na et al., 1994) 14

¹⁵ also evidenced a latitudinal gradient, with SO₂ increasing with increasing
¹⁶ latitude, consistent with a photochemical control of SO₂ since photolysis is
¹⁷ less effective at higher latitudes.

After a blank decade (1995-2005), Venus exploration (including cloud top 18 SO_2 monitoring) resumed with ESA Venus Express. Occultation measure-19 ments from SOIR (Belyaev *et al.*, 2008) allowed for a retrieval of SO_2 scale 20 height above the clouds, confirmed that SO_2 had returned to the relatively 21 high values of the early 1980s, and evidenced a reversal in the latitudinal gra-22 dient of SO₂. These features were confirmed by our first SPICAV-UV nadir 23 measurements (Marcq et al., 2011, 2013), along with a long-term decrease 24 of low latitude SO_2 similar to the one observed by *Pioneer Venus*. In par-25 allel, high spectral resolution measurements in the thermal IR using NASA 26 IRTF (Encrenaz et al., 2012, 2016, 2019), or in the UV using STIS/HST (Jes-27 $\sup et al., 2015$) have confirmed and supported this trend, with two possible 28 SO_2 regimes above the clouds: a high abundance regime more prevalent in 29 the early 1980s or late 2000s, with a large number of SO_2 plumes located 30 at lower latitudes and a negative latitudinal gradient, and a low abundance 31 regime with little to no SO_2 convective plumes, and a reversed latitudinal 32 gradient more typical of the early 1990s or mid-2010s. The transition be-33 tween these regimes can occur within a few Earth days (Jessup *et al.*, 2015), 34 and accounts for the large short-term dispersion of the measurements. The 35 long-term change in the relative prevalence of these two regimes explain the 36 long-term change in the average SO_2 latitudinal gradient that we observed 37 in our previous study (Marcq et al., 2013, Fig. 2). Nevertheless, the physical 38 processes ruling both these regimes are still poorly known. Convective mix-39

ing with the lower atmosphere where SO₂ is always abundant – more than
100 ppmv near 30-40 km (Bézard *et al.*, 1993; Marcq *et al.*, 2008; Arney *et al.*,
2014) is most certainly involved, but the reasons behind these variations of
the convective mixing intensity are still debated, including possible episodic
volcanism or other atmospheric processes.

Following the recent progress in our knowledge of Venus clouds and 45 hazes (Luginin et al., 2016), as well as in our processing of SPICAV-UV 46 nadir spectra, we have completely rewritten our analysis pipeline and pro-47 cessed the whole of SPICAV-UV archive in order to complete and update 48 our SO_2 climatology, as well as other derived observable parameters such as 49 the mean UV brightness of the clouds. A short description of our data set 50 in given in $\S2$, and of our forward radiative transfer model in $\S3$, since both 51 were already extensively described in a previous paper (Marcq et al., 2019). 52 Our results about SO_2 and UV absorber variability is detailed in §4 and 53 their scientific implications further commented in §5, before we summarize 54 and conclude in $\S6$. 55

⁵⁶ 2. Observations

⁵⁷ Our data set and processing is detailed in our previous paper (Marcq ⁵⁸ *et al.*, 2019). For the convenience of the reader, we summarize the main ⁵⁹ points below.

60 2.1. Data set

⁶¹ Our data set consists in the whole archive of SPICAV-UV (Bertaux *et al.*, ⁶² 2007) nadir or near-nadir spectra, from 170 to 320 nm at a spectral resolution

of 1 nm. There are 1508 such observations, from 2006-06-01 up to 2014-11-63 20. Coverage in local time and latitude is extensive except for the south 64 polar region (Marcq et al., 2019, their Fig. 1), with southern hemisphere ob-65 servations dominated by near nadir *tracking pointing mode* observations over 66 single spots spot targets (implying continuously changing emission and phase 67 angles along the orbit), whereas northern hemisphere observations consisted 68 mainly in nadir latitudinal scans (where emission angle is essentially zero 69 along the orbbital track). 70

71 2.2. Processing

The first steps of data processing are unchanged since Marcq *et al.* (2011), 72 namely cosmic ray hit removal, dark subtraction, correction of electronic 73 readout artifact, flat-fielding, wavelength assignment. Most recent progress 74 come from a better knowledge of the instrument **PSF**Point Spread Function 75 (PSF), especially at large distances from the center (far wings). Richardson-76 Lucy deconvolution is now performed in order to clean the far wing con-77 tribution, which enables the scientific use of spectra from 200 nm instead of 78 215 nm in our first analyses, which in turn enables to retrieve more observable 79 parameters relative to Venus' clouds and SO_2 . 80

Photometric calibration of the spectral radiance spectra was performed from the CALSPEC catalog of bright UV stars observed in-flight (Bohlin *et al.*, 2014). From these calibrated spectral radiances, we computed the corresponding radiance factors $\beta(\lambda) = \frac{I(\lambda) \times \pi \operatorname{sr}}{F_{\odot}(\lambda)}$ where $I(\lambda)$ is the spectral radiance and $F_{\odot}(\lambda)$ a reference top-of-atmosphere solar spectral irradiance. These solar spectral irradiance were extracted from the SOLSTICE II database

⁸⁷ (McClintock *et al.*, 2005) at the corresponding date to account for the solar

cycle variations. We also corrected a spectral feature in these solar spectra near 230-240 nm that our forward radiative transfer model was unable to reproduce, no matter the prescribed values of the atmospheric parameters.

91 3. Forward Model

92 3.1. Overview

A detailed description of the forward radiative transfer we use is available in Marcq *et al.* (2019). For the sake of convenience, we present below a summary of its features and free parameters. The radiative transfer equation solver we use is the pseudo-spherical version of DISORT (Dahlback and Stamnes, 1991) using 16 streams.

98 3.1.1. Aerosols

⁹⁹ The model encompasses the 50-110 km altitude range. We consider a ¹⁰⁰ bimodal log-normal size distribution ($r_{\rm eff} = 0.12$ and 0.8 µm respectively, ¹⁰¹ with an effective dimensionless variance of $\nu_{\rm eff} = 0.15$) of aerosol particles ¹⁰² following Luginin *et al.* (2016).

The vertical profiles for both modes that we consider are simplified from the same reference (Luginin *et al.*, 2016) a simplification from the retrieved profiles derived by Luginin *et al.* (2016) and can be seen in Fig. 1. Number density is capped for both particles at in the lower part the model (respectively $2 \cdot 10^8$ and 10^8 particles/m³ for mode 1 and mode Above a altitude named Z₂

- hereafter, mode 2), and the number density ratio $n_1/n_2 = 1000$ is fixed in the
- ¹⁰⁹ upper particle number density decreases following $n_2(z > Z_2) = 10^8 \exp\left(\frac{Z_2 z}{4.5 \text{ km}}\right)$ particles/m³.
- Below this altitude, we have a constant, capped value $n_2(z < Z_2) = 10^8$) particles/m³.

Figure 1: Synthetic number density profiles for both particle modes. Z_2 is a free parameter in our model, which captures cloud top altitude variations.



Mode 1 particles follow a similar profile, with a constant ratio $n_1/n_2 = 1000$ 111 in the upper part of the model, and a cap at $2 \cdot 10^8$ particles/m³ in the 112 <u>lower</u> part of the model. The altitude Z_2 above which mode 2 particles 113 decrease following a scale height of 4.5 km is a free parameter in our model, 114 representative of which is related to the cloud top altitude variations – 115 we find that $Z_{\text{TOP}}(250 \text{ nm})$, classically defined (Titov *et al.*, 2018) as the 116 altitude where nadir optical depth is equal to one (consdering only particulate 117 <u>opacity</u>). Numerical intergration yields $Z_{\text{TOP}}(250 \text{ nm}) = Z_2 + 4.95 \text{ km}$ for 118 the above described extinction profiles. 119

The real refractive index of both modes is taken from Hummel *et al.* (1988) for a 75%-25% H₂SO₄-H₂O mixture. Imaginary indices for both modes are discussed in §3.2, the imaginary index of mode 1 particles at 250 nmbeing $m_{i}(250 \text{ nm})$, being another free parameter.

124 3.1.2. Gaseous Species

The gaseous species involved in absorption and/or scattering are displayed in Fig. 2. CO_2 Rayleigh and absorption cross-section is unchanged since Marcq *et al.* (2013). SO_2 and SO cross-sections were compiled from various sources by Jessup *et al.* (2015), and we use the same. New gaseous species that we consider is O_3 and OCS, whose UV absorption cross-sections are taken from Sander *et al.* (2011).

 CO_2 vertical profile is computed from hydrostatic equilibrium assum-131 ing VIRA-2 temperature profile (Moroz and Zasova, 1997). Following recent 132 intercomparison between observations and models (Vandaele et al., 2017a; Marcq et al., 2018) 133 , we consider that SO_2 vertical profile is capped at 150 ppmv in the lower 134 part of the model, and decreases according to a scale height of 3 km in the 135 upper part of the model. Its mixing ratio at 70 km is a free parameter of our 136 model. Since we cannot distinguish individual SO and SO_2 absorption lines 137 at SPICAV-UV spectral resolution, we have to assume that SO vertical profile 138 is tied $\frac{10\%}{10\%}$ of SO_{2, according to the average values dervied from higher} 139 spectral resolution HST/STIS measurements (Jessup *et al.*, 2015). OCS ver-140 tical profile is taken from Haus *et al.* (2015), and O_3 is considered uniformly 141 mixed between 55 and 70 km. Its mixing ratio in this range is an optional 142 free parameter of the model. 143

¹⁴⁴ O₃ measurements is the main topic addressed by Marcq *et al.* (2019). O₃ ¹⁴⁵ absorption is considered only when including it yields a substantial reduction ¹⁴⁶ in the reduced χ^2 (namely, 5.5). We adopt the same criterion in the present ¹⁴⁷ study. Example of a fitted spectrum with and without O₃ can be found ¹⁴⁸ in Marcq *et al.* (2019, their Fig. 2)Marcq *et al.* (2019, their Fig. 3).



Figure 2: UV cross-sections of considered gaseous species

149 3.2. Model Sensitivity

The modeled effect of varying SO_2 (Fig. 3) is easy to understand: since 150 SO_2 has two broad electronic absorption bands peaking near 215 and 280 nm, 151 respectively, these two absorption bands have a relative depth that becomes 152 more pronounced with increasing SO_2 abundance. However, it is noteworthy 153 that the SO_2 influence extends throughout the whole spectrum, even though 154 the cross-section is a continuum between 240 and 270; nm reaching a local 155 minimum near 240 nm. Sensitivity of the inferred radiance factor to SO_2 156 absorption in the 240-270 nm region is a telltale sign that multiple scattering 157 is prevalent, so that most backscattered photons have traveled through long 158 enough optical paths into deep, SO_2 -rich atmospheric layers that its smaller 159 absorption cross-section is partially offset. This is important when consider-160 ing SO_2 measurement proxies such as image ratios between 280 and 240 nm: 161

Figure 3: Synthetic radiance factors for a cloud top altitude of 74 km, $m_i(250 \text{ nm}) = 10^{-2}$ and varying SO₂ abundances. The considered geometry is pure nadir viewing, with a solar zenith angle of 30°.



the image at 240 nm, though not dominated by SO_2 gaz gas absorption, is also not independent from the spatial SO_2 variations.

At Venus' cloud top, the observed SO_2 absorption band is primarily re-164 lated to the column density above the cloud top (Marcq et al., 2011, 2013). 165 Thus, altering the cloud top altitude results in a change in the total SO_2 col-166 umn density above the cloud top, according to the assumed vertical profile 167 of SO_2 number density. The primary effects of altering the cloud top alti-168 tude while making no change to SO_2 vertical profile would therefore be very 169 similar to the results displayed in Fig. 3, because the direct outcome of the 170 change in the cloud top altitude is a change in the SO_2 column density above 171 that altitude. However, as Fig. 4 shows, changing the cloud top altitude will 172 impact the total absorption occuring in the two SO_2 electronic absorption 173

Figure 4: Synthetic radiance factors for $m_i(250 \text{ nm}) = 10^{-2}$, and varying SO₂ abundances as well as cloud top altitudes et at 250 nm. The considered geometry is pure nadir viewing, with a solar zenith angle of 30°.



¹⁷⁴ bands differently, because the 280 nm band has a lower cross-section than
¹⁷⁵ the 215 nm band. Thus, for example, increasing the cloud top altitude re¹⁷⁶ sults in a lower relative depth for the 280 nm SO₂ absorption band compared
¹⁷⁷ to the 215 nm band. Similarly, the lower cross-section of the 280 nm band
¹⁷⁸ allows that band to probe deeper into the atmosphere than the 215 nm band.
¹⁷⁹ Notably, at lower altitudes both Rayleigh scattering and CO₂ absorption are
¹⁸⁰ stronger.

Altering the imaginary part \underline{m}_{i} of the refractive index of mode 1 particles yields the expected outcome, namely lowering the albedo when particles are darker (Fig. 5). However, altering the spectral slope of this mode 1 absorption results in a spectral distortion very much alike that of changing the cloud top altitude. This resulted in a fitting degeneracy when if we

tried to fit both the mode-1 absorption spectral slope and cloud top altitude 186 together. We therefore chose to keep only the cloud top altitude as a fit-187 ted parameter, and adopted a spectral dependency fixed spectral slope for 188 $m_i(\lambda) = m_i(250 \text{ nm}) \times \exp\left(\frac{\lambda - 250 \text{ nm}}{40 \text{ nm}}\right)$ where the exponential function, fitting 189 only $m_i(250 \text{ nm})$. The 40 nm slope accounts for the decreasing mode 1 single-190 scattering albedo with increasing wavelength. Using this relationship fixed 191 40 nm value, our low latitude cloud top average altitude near 250 nm was 192 then in agreement with the most recent IR measurements (Ignatiev et al., 193 2009) that do not suffer from this degeneracy. The This 40 nm value is 194 slightly less steep than our previous estimate of about 34 nm (Marcq et al., 195 2011), which can be explained by our updates to the spectral calibration 196 of radiance factors (Marcq et al., 2019). At first, we assumed that this de-197 pendency applied to both particle modes, but this assumption resulted in 198 spurious correlations between effective airmass and cloud top altitude as well 199 as imaginary refractive index retrievals – mode 2 particles contribute more 200 to backscattering at smaller airmass since they dominate at lower altitudes. 201 Empirically, we found that assuming a constant, fixed imaginary refractive 202 index of 10^{-3} for mode 2 particles minimized such spurious correlations. 203

Since this fixed value is much larger than the imaginary refractive index of pure H_2SO_4 - H_2O solutions in this wavelength range, this may be indicative of two different UV absorbers: one, well mixed with mode 2 and mode 1 particles and with little spectral dependency between 200 and 300 nm, and the other one, mixed with mode 1 particles only and horizontally variable, absorbing more towards longer wavelengths. This latter absorber is likely the same absorber than the infamous near UV-blue absorber peaking Figure 5: Synthetic radiance factors for a cloud top altitude of 74 km, SO₂ volume mixing ratio of 50 ppbv at 70 km and varying $m_i(250 \text{ nm})$. The considered geometry is pure nadir viewing, with a solar zenith angle of 30°.



²¹¹ near 365 nm, our retrieved imaginary indexes in the 10^{-2} - 10^{-1} range and ²¹² spectral slope being in agreement with recent determinations of this imag-²¹³ inary refractive index over a larger spectral range extending to the visible ²¹⁴ range (Pérez-Hoyos *et al.*, 2018).

We will further discuss the scientific implications in $\S5.1$.

216 4. Results

- 217 4.1. <u>Retrieval uncertainties</u>
- The above described forward model is then compared to 30-s binned
- 219 SPICAV-UV observations through a Levenberg-Marquardt iterative algorithm (Newville et al., 2014
- 220 . Three parameters are always fitted, namely: SO₂ mixing ratio at 70 km,
- Z_2 and $m_i(250 \text{ nm})$. O₃ mixing ratio is also fitted when its inclusion results

in a significant reduction in residual χ^2 – the interested reader should refer to Marcq *et al.* (2019) for further details about O₃ in the SPICAV-UV nadir data set.

The Levenberg-Marquardt algorithm yields a covariance matrix, from which $1 \cdot \sigma$ statistical uncertainties are derived for each fit, along with the residual reduced χ^2 . The median reduced χ^2 of the whole dataset is 16.6 (which indicates that systematic errors do exist, and/or that the observatoinal uncertainity may be underestimated). Hereafter, we only consider our fits valid if their χ^2 is less than 3 times this median value ($\chi^2 < 50$).

In this valid dataset, the median relative $1 \cdot \sigma$ uncertainty on SO₂ retrievals 231 is 38%, substantially less than the 3-order of magnitude spatial and temporal 232 variability of SO₂ (§4.2, §4.3.1): the lowest $3 \cdot \sigma$ detection of SO₂ is about 233 0.6 ppb, and the highest values on the order of 1000 ppby. Similarly, the 234 median relative $1 \cdot \sigma$ uncertainty on m_i retrievals is 25%, also substantially 235 less than its spatial and temporal variability ($\S4.2$, $\S4.3.2$). Finally, the 236 median relative uncertainty on our cloud top altitude retrievals is on the 237 order of 1 km. 238

239 4.2. Temporal variability

The long term evolution over the whole extent of *Venus Express* of our retrieved cloud top SO_2 and imaginary index of mode 1 particles are shown respectively on Fig. 6 and 7. We restricted the analysis of Since most SO_2 temporal variability to lower latitudes only so that we do not encompass any bias in latitude, since SO_2 and latitude are correlated in our data set content is actually located below $\pm 20^{\circ}$ in latitude (see §4.3), we will discuss hereafter the temporal variability of SO_2 temporal variability only in this low-latitude \underline{bin} . The most striking features in both retrieved parameters are: (i) shortterm dispersion is much larger than retrieval uncertainties, and spans two orders of magnitude for SO₂ and one for the imaginary index; (ii) despite this short-term variability, longer term trends can be observed.

For SO_2 , the overall trend consists in an overall decline by a factor 5 to 251 10 from 2007 (about 80 ppbv) 80 ppbv in median) to 2014 (about 10 ppbv). 252 This steady decline is not monotonous though: after the peak in 2007, surges 253 in SO_2 can observed in 2009, 2012, and late 2013. This trend is consistent 254 with our previous findings for 2006-2012 (Marcq et al., 2013), except for the 255 2009 peak that was not noticed at the time, probably due to an insufficient 256 number of analyzed observations compared to our extensive analysis pre-257 sented here. Comparison with STIS/HST retrievals (Jessup *et al.*, 2015) and 258 with TEXES retrievals (Encrenaz et al., 2012, 2016), extrapolated at 70 km 259 assuming a scale height of 3 kmis excellent, and, are fully consistent with 260 the statistical dispersion of SPICAV-UV retrievals, which highlights the fact 261 that these "snapshot" observations are actually representative of the median 262 state of cloud top SO_2 as observed statistically by SPICAV. More gener-263 ally, these variations are in agreement with the inter-comparison of available 264 SO_2 measurements detailed by Vandaele *et al.* (2017b), as well as recent 265 UVI/Akatsuki results (Lee et al., 2017). 266

Regarding UV darkness (as measured through mode 1 imaginary index at 250 nm), the long term trend can be divided in two time periods: first a 5fold increase from 2006 ($\sim 10^{-2}$) until 2010 ($\sim 5 \cdot 10^{-2}$), and then a constant, darker plateau from 2011 onward until the end of the mission in late 2014. These variations are most pronounced at lower and mid-latitudes, latitudes

Figure 6: Temporal evolution of SO_2 mixing ratio at 70 km for latitudes lower than 30° . The red line stands for the moving median value, and white diamondsare TEXES-/squares show other SO_2 mixing ratios from Enerenaz *et al.* (2016)measurements in the same time interval.



above 60° seem less affected by this trend. Here also, these results compare 272 well with our previous results (Marcq et al., 2013) where we accounted for 273 this UV darkening through a fitted scaling factor, but also with the 40% UV 274 albedo darkening observed in 2006-2011 by Venus Express/VMC at 365 nm 275 (Lee et al., 2015). This agreement between two diffrent instruments (VMC 276 and SPICAV) and the fact that the albedo latitude variation trends inferred 277 from either the VMC and SPICAV data sets are consistent, even though 278 the binning and the reduction of the two data sets is are unique lead us to 279 believe that this darkening is genuine, and not an artifact from the aging of 280 the SPICAV UV detector. 281

Figure 7: Temporal evolution of mode 1 imaginary refractive index at 250 nm. The red line stands for the moving median value. Absolute latitude is color-coded.



$_{282}$ 4.2.1. SO_2 periodogram

The SO₂ variations observed in Fig. 6 suggest they may exhibit some periodicity. In order to discuss them more quantitatively, we computed a Lomb-Scargle periodogram of both SO₂ mixing ratio as well as its logarithm (since we present all of our SO₂ results in a logarithmic scale). Lomb-Scargle periodograms are well suited when the temporal sampling of measurements is uneven (as it is the case here), but may exhibit "ghost" harmonics for integer multiple values of the genuine frequency.

These periodograms are shown in Fig. 8. Assuming that genuine frequencies would show up in both SO_2 and $log(SO_2)$ periodograms, we find that our frequency signal is dominated by a 400 Earth day period (and its ghost harmonics near 200, 135 and 100 days) component, that can be seen between the SO_2 surges in Fig. 6. A 110-day long component is also visible, Figure 8: Lomb-Scargle periodogram of low-latitude SO_2 in log and linear scales. Periods discussed in the main text are shown in dashed, with the 400-day period and its ghost harmonics shown in dashed black.



close to the solar day on Venus surface, suggesting a link between SO_2 variations and local solar time at the surface reminiscent of the similar period seen by Bertaux *et al.* (2016) for the UV brightness as observed by VMC. We present the correlation between topography and SO_2 in more detail in §4.3.1.

Other possible periods that are significantly above noise include a 155 Earth day component, as well as medium term components (40, 17 and 6 Earth days). Noticeably, a 4-day period is absent, implying that SO_2 patches are shorter lived than the super-rotation period at cloud top.

304 4.3. Spatial variability

305 4.3.1. SO₂

The binned latitudinal distribution of our SO_2 retrievals is shown in Fig. 9. 306 The main features from our previous analyses (Marcq et al., 2013, 2011) are 307 still valid, namely: (i) there is a large dispersion, spanning more than two 308 orders of magnitude at lower latitudes and about one order of magnitude at 309 higher latitudes (ii) the median SO_2 value is larger at lower latitudes (typ-310 ically 5 to 100 ppbv, median 20 ppbv below 30°), due to the occurrence of 311 SO_2 "plumes" (above 100 ppbv) that do not occur at higher latitudes. The 312 observed latitudinal pattern remains consistent with the SO_2 gas distribution 313 being dominantly controlled by a Hadley-cell type circulation as reported pre-314 viously (Jessup and Mills, 2019; Vandaele et al., 2017b; Jessup et al., 2015; 315 Marcq et al., 2013, 2011) – thus is linked to large-scale (or deep) convective 316 mixing process. The broad range of SO_2 abundance values observed at each 317 latitude points to the perpetual competition between general circulation and 318 the LST dependent photochemical destruction of SO_2 (Marcq *et al.*, 2013) 319 which may produce order of magnitude changes in the cloud top abundances 320 on a time scale of several Earth days (corresponding to 1-2 hours of LST) 321 considering the zonal super-rotation at cloud top) particularly at low lati-322 tudes. The SPICAV-observed variability patterns are fully consistent with 323 other measurements in UV from HST/STIS (Jessup et al., 2015) or in IR 324 with IRTF/TEXES (Encrenaz et al., 2012, 2016). 325

Our comprehensive data set also allows us to study the variability of SO₂ with respect to local solar time as shown in Fig. 10. A local minimum near noon (between 10am and 2pm) is evidenced. Interestingly, TEXES Figure 9: SO₂ mixing ratio at 70 km with respect to latitude for all LSt values. The red line stands for the moving-10°-moving boxcar median value, and red error bars for the $1 \cdot \sigma$ statistical dispersion.



measurements also confirm the inefficiency of upwelling SO_2 plumes in the 10h to 14h local time interval (Encrenaz *et al.*, 2019). We further discuss the SO_2 and overall UV brightness variations with respect to local solar time in $\S5.2$.

The SO_2 periodgram (§4.2.1) suggest that SO_2 and surface topography 333 may be correlated. Therefore, we have mapped our SO_2 retrievals with re-334 spect to latitude and geographic longitude in Fig. 11. Besides the latitudinal 335 trend already discussed, we notice a possible SO_2 enhancement located down-336 wind of the western edge of the large equatorial high-altitude plateau known 337 as Aphrodite Terra in the $30^{\circ}-45^{\circ}$ range. Similarly, the SO₂ volume mixing 338 ratio observed by HST at low latitudes in the 0°-45°E longitude range was 339 an order of magnitude higher than directly over Aphrodite Terra (Jessup and 340

Figure 10: SO₂ mixing ratio at 70 km for latitudes below 20° with respect to local solar time. The red line stands for the <u>1-hour</u> moving <u>boxcar</u> median value, and red error bars for the $1 \cdot \sigma$ statistical dispersion.



Mills, 2019). Yet TEXES measurements also displayed on Fig. 11 fail to re-341 port such an increase of SO_2 over the same ground location. Although the 342 70 km values inferred from TEXES data do not match the statistical averaged 343 SPICAV values, a trend of increased SO₂ plumes at $0^{\circ}-30^{\circ}E$ vs. $60^{\circ}-140^{\circ}E$ 344 is distinctly evident in the TEXES data (Encrenaz et al., 2019, their Fig. 345 8). One should also note that the polar orbit of Venus Express implies that 346 different longitudes were observed at different dates, so that longitudinal and 347 temporal variablity cannot be retrieved separately from these maps. 348

349 4.3.2. UV brightness

We have also investigated the correlation between topography and the retrieved absorption of mode 1 particles shown in Fig. 12 to determine if

Figure 11: Map (latitude vs. longitude) of SO_2 mixing ratio at 70 km. The contour lines follow topographic elevation – <u>Aphrodite Terre is peaking near 90°E-0°</u>. Crossed hatching indicated lack of meaningful data. Red diamonds show co-located day side TEXES retrievals, with red crosses showing the TEXES observations footprint.



relationships between the albedo and the underlying topography proposed 352 by Bertaux et al. (2016) are supported by our data, and to determine how 353 the observed albedo trends might relate to the retrieved SO_2 abundances. 354 We are able to do so, since the retrieved values of $m_i(250 \text{ nm})$ exhibit an 355 anti-correlation with the UV brightness of the cloud top (once SO_2 absorption 356 is taken into account). Comparison of Figures 11 and 12 highlights that 357 directly over Aphrodite Terra (60° -1 40° E, 15°S) where relatively SO₂ VMRs 358 have been retrieved, the m_i values are low, suggesting a bright cloud top – 359 this results confirms that the cloud top is brighter over Aphrodite but the 360 anti-correlation between the cloud top albedo and the SO_2 gas abundance 361 does not support that the abundance of both components $(SO_2 \text{ and } UV)$ 362 absorber) is controlled solely by linked vertical transport process (see $\S5$). 363

Fig. 11–12 also indicates that high m_i values are retrieved at lower lati-364 tudes, which is expected since convective activity is strongest at these lati-365 tudes due to the enhanced solar heating (Peralta et al., 2007; Titov et al., 366 2008, 2012). However, strong longitudinal variability in the cloud top bright-367 ness is observed within the low latitude region sampled by SPICAV; and the 368 inferred brightness distribution is not symmetric with respect to the equator. 369 Additionally, as already mentioned, the polar orbit of Venus Express leads 370 to an uneven longitudinal sampling with respect to observation date, so that 371 the observed distribution pattern may also be linked to long-term temporal 372 variability. 373

In terms of local time and latitudinal variability, Fig. 13 shows that (i) UV brightness increases with increasing latitude, reaching a high plateau near 60°N; and (ii) UV brightness is lower between 10:00 and 16:00 at lower

Figure 12: Map (latitude vs. longitude) of mode 1 imaginary refractive index at 250 nm. The contour lines follow topographic elevation - <u>Aphrodite Terre</u> is peaking near 90°E-0°. Crossed hatching indicates lack of meaningful data.



Figure 13: Pseudo-map (latitude vs. local solar time) of mode 1 imaginary refractive index at 250 nm. Hatched areas indicate lack of meaningful data



latitudes (below 30°). Both these patterns in latitude and local solar time are already known from previous studies (Titov *et al.*, 2008, 2012; Lee *et al.*, 2015). These already known trends, plus the fact that minimum UV brightness (correlated with maximum m_i values) is reached near 14:00 and not exactly at noon lead us to discard a spurious correlation of our retrievals with respect to airmass, which may occur if the assumed extinction vertical profiles are not representative of the real ones.

384 4.3.3. Cloud top altitude

Variations of cloud top altitude with respect to latitudes are shown in Fig. 14. The average low latitude cloud top altitude (defined as $\tau(250 \text{ nm}) =$ 1 nadir level) we find is $73 \pm 2 \text{ km}$ in good agreement with already known

values (Ignatiev et al., 2009; Pérez-Hoyos et al., 2018). This is not surprising, 388 since we adjusted the spectral slope of the UV absorber precisely to match 389 this mean value (see $\S3.2$). The already known decrease of cloud top altitude 390 towards higher latitudes (Ignatiev et al., 2009) is also observed, although 391 the amplitude – about 10 km from equator to pole here instead of about 392 3 km according to Ignatiev et al. (2009) – is somewhat larger, and starts 393 at lower latitudes (30° instead of 50°). Nevertheless, due to the aforemen-394 tioned degeneracy between the spectral slope and cloud top altitude, reach-395 ing a qualitative agreement for this poorly constrained parameter retrieval 396 is satisfactory, considering the need to keep as few free fitted parameters as 397 possible in our forward model. Please note that simultaneous and co-loacted 398 IR cloud top measurements would remove such a degeneracy, and allow for 399 a detailed investigation of the spatial and temporal variability of the aerosol 400 spectral slope. 401

402 5. Discussion

403 5.1. UV absorption

404 5.1.1. Nature of UV absorber

As already mentioned in §3.2, we suspect that our retrievals of the imaginary refractive index of mode 1 particles is directly related to the local abundance of the infamous UV absorber. Unfortunately, the only spectropscopic spectroscopic constraint we were able to derive is the spectral slope-related parameter of 40 nm. Such an a decrease of UV single scattering albedo with increasing wavelength in the SPICAV UV range is compatible with a large number of candidates for the UV absorber, including the most recent mix-

Figure 14: Cloud top altitude with respect to latitude. The red line stands for the 10° binned moving boxcar median value, and red error bars for the $1 \cdot \sigma$ statistical dispersion.



ture of cis- and trans-OSSO suggested by Frandsen et al. (2016). Actually, we 412 first tried to fit the average UV brightness not through the refractive index 413 of mode 1 particles, but with peak OSSO concentration following the theo-414 retical vertical profile given by Frandsen *et al.* (2016) peaking near 62 km. It 415 appeared then that we could not reach a satisfactory fit, the amount of OSSO 416 required to match the mean albedo was at up to two orders of magnitude 417 larger than the peak abundance given reported by Frandsen et al. (2016, 418 about 10 ppbv), and in such a case suppressed all other gaseous spectral 419 signatures (SO_2, SO, O_3) except for CO_2 . So, if the unknown UV absorber 420 were indeed OSSO, its vertical abundance profile and abundance would differ 421 significantly from the theoretical values given by Frandsen et al. (2016). 422





423 5.1.2. Correlation with SO_2

We already reported (§4.3) that low SO_2 abundances were observed within 424 2 hours of the subsolar point, and similarly the lowest UV brightness (min-425 imum absorber abundance) was detected in the afternoon hours. The long-426 term trends are opposite too, with an observed secular decrease for SO_2 , and 427 secular increase of the UV absorption, see $\S4.2$). This points to an anti-428 correlation between SO_2 and UV absorption that is confirmed in Fig. 15: 429 although the statistical dispersion for both SO_2 and the imaginary refrac-430 tive index $m_i(250 \text{ nm})$ is large, there is an average decrease of one order 431 magnitude for m_i relative to an increase of SO₂ of two orders of magnitude. 432 Such an anti-correlation using VMC 365 nm observations with respect to 433 our previous estimates of SO_2 (Marcq *et al.*, 2013) was reported by Lee *et al.* 434 (2015), as well as using high spectral resolution (line-resolving) retrievals of 435

 SO_2 and SO with HST/STIS from Jessup *et al.* (2015). Therefore, we can 436 safely dismiss that correlation would be a spurious artifact due to parasitic 437 trends in the photometric calibration of SPICAV-UV spectra. There are two 438 possible, non-mutually exclusive physical explanations already reported (Es-439 posito, 1984; Jessup *et al.*, 2015) and supported by this study: (i) injections 440 of SO_2 and H_2O from the deep atmosphere lead to an increased formation 441 rate of uncontaminated H_2SO_4 , UV-bright haze particles above the UV ab-442 sorber; and (ii) on longer time scales, SO_2 is a precursor species to the UV 443 absorber, so that there is a possible conversion of SO_2 into a sulfur-bearing 444 UV absorber $-SO_2$ and the UV absorber being competing reservoirs of sulfur 445 in such a case. 446

447 5.1.3. Comparison with VMC

Our SPICAV retrievals of m_i (mode 1 imaginary index) show a greater 448 level of longitudinal variation of the unknown UV absorber than inferred 449 from VMC (Lee et al., 2015; Bertaux et al., 2016); for example, Fig. 12 does 450 not indicate that Aphrodite is a region where the cloud top albedo is uniquely 451 bright compared to all other longitudes, unlike what is indicated by Bertaux 452 et al. (2016). Similarly, the latitude variation at southern latitudes is more 453 complex than what is seen in VMC at southern latitudes. On the other hand, 454 the latitudinal variations inferred from the SPICAV analysis at northern lat-455 itudes shows the expected pattern of low latitudes darker than high at for 456 almost all longitudes. These complexities complex spatial patterns are likely 457 more readily discernible in the SPICAV data, because these data may be 458 used to distinguish between different particle modes (effectively segregating 459 distinguishing between mode 2 H_2SO_4 particles mostly conservative scatter-460

ing from and mode 1 absorption), while VMC traces only the total absorption
in the 365 nm band, thus likely to include both mode 1 and mode 2 contributions. Moreover, SPICAV reconstructed maps include long-term temporal
variations due to the slow Venus Express orbital swath precession relative
to longitude and/or local solar time, which may explain the overall larger
variability seen by SPICAV compared to instantaneous VMC maps.

467 5.2. Requirements for deep vertical mixing

Since SO_2 transient enhancements and correlated UV brightenings are 468 caused by local upwellings – also called "plumes" by e.g. Encrenaz et al. 460 (2016), clues to the processes that support the observed SO₂ spatial dis-470 tributions and the impact of SO_2 enhancement plumes can be derived by 471 considering the LST, latitude and longitude patterns revealed in the statisti-472 cally averaged data. As described in $\S4.3$ and shown in Fig. 11, regions of SO₂ 473 enhancements have been observed primarily at latitudes smaller than 30° ex-474 cept at Aphrodite Terra longitudes ($60^{\circ}-140^{\circ}E$) where the SO₂ enhancement 475 extends to 40° S so that on average the SO₂ abundance from 0° tp 40° S is 476 higher than observed at the same latitudes in the 160°-240°E region. Addi-477 tionally, on average a very strong enhancement region is typically observed 478 downwind from Aphrodite at $30-45^{\circ}E$. On the other hand, depletion of SO₂ 479 noted between 10:00 to 14:00 local solar time (Fig. 10) implies that at these 480 local solar times replenishment of the cloud top SO_2 abundance via large-481 scale mixing cannot keep up with the high rate of photochemical loss that 482 would dominate at these local solar times at low latitude. 483

The prevalence of Venus' cloud top SO_2 abundance to peak at low latitudes was already noticed in our first analysis (Marcq *et al.*, 2011, 2013), and was then linked to the general meridional circulation causing upwelling
at lower latitudes and downwelling at higher latitudes. Therefore, the combined SPICAV, TEXES and HST results confirm that the mechanism driving
transient plume formation differs distinctely from shallow sub-solar mixing
and deep Hadley-cell circulation processes.

The observed increase in SO_2 abundance in the 0° to 40°S latitude re-491 gion at longitudes intersecting Aphrodite Terra relative to what is observed at 492 similar latitudes upwind provides further evidence to the unexpected connec-493 tion between surface topography and cloud top (Bertaux et al., 2016; Peralta 494 et al., 2017). In general, the current analysis shows that statistically on aver-495 age SO_2 is high at low latitudes from 40° to 120°E relative to other longitudes 496 except at $30^{\circ}-45^{\circ}E$ (downwind from Aphrodite) where the SO₂ abundance is 497 on average higher than at Aphrodite. We still do not completely understand 498 what controls the overall SO_2 longitudinal variation (provided it is genuine 499 and not an artifact from our temporal-longitudinal sampling). Nevertheless, 500 the relative increase in SO_2 between the region downwind of Aphrodite and 501 directly over Aphrodite are consistent with the differences in wind speed 502 within those two specific regions and the anticipated vertical wind speed re-503 sponse proposed by Bertaux et al. (2016), as we already suggested in $\S4.2.1$ 504 while discussing the possible 110-day period in SO_2 . The differences in wind 505 speed between these two regions are likely linked to the impact of gravity 506 waves (Navarro et al., 2018) momentum deposition on cloud top zonal wind 507 speeds as proposed by Bertaux et al. (2016). 508

Interestingly, Encrenaz *et al.* (2016) does not see any SO_2 plume over this location (see Fig. 11), which highlights that while the discussed SO_2 enhance-

ment over the western slopes of *Aphrodite Terra* is on average higher than 511 other longitude regions, other transient phenomena may also be relevant, 512 such as local time effects shown in Fig. 13. In fact, TEXES measurements 513 were acquired above Aphrodite Terra at 13:30 local time, further confirming 514 that transient plume activity is suppressed directly over *Aphrodite* near local 515 noon. Similarly, STIS observations from Jessup and Mills (2019) show that 516 increased 245 nm cloud top darkening occurs over regions of low elevation 2 517 hours LST prior to local noon, but these increases are not observed at similar 518 local times directly over Aphrodite Terra. 519

520 6. Conclusion

Our analysis of the full SPICAV-UV nadir data set has been performed 521 by fitting the observed radiance factors with respect to SO_2 abundance at 522 cloud top and UV absorption of mode 1 particles. Our previous conclusions 523 about SO₂ (Marcq *et al.*, 2011, 2013) are mostly confirmed: in average, SO₂ 524 is found to be decreasing with increasing latitude, from typically 5-100 ppby 525 at 70 km near the equator to 2-20 ppby polewards of 60°N and S. Statistical 526 dispersion is therefore much larger at lower latitudes, consistent with the 527 location of transient SO_2 plumes as seen by other observers (Encrenaz *et al.*, 528 2016). The 5-fold secular decrease in equatorial SO_2 reported by Marcq 529 et al. (2013) between 2007 and 2011 is now found to extend until 2015 at 530 least, albeit with a previously unreported secondary maximum in 2009. A 531 minimum near subsolar point is also found in average, likely caused by the 532 locally higher photochemical depletion rate. 533

⁵³⁴ UV absorption (Fig. 13) displays the familiar pattern of comparatively

⁵³⁵ brighter mid-to-high latitudes compared to lower latitudes (Titov *et al.*,
⁵³⁶ 2018), along with an already known darkening in the 12:00-14:00 local time
⁵³⁷ range at low latitudes (Titov *et al.*, 2012). Long-term evolution of UV dark⁵³⁸ ness (Fig. 7) shows at first an increase between 2006 and 2011, followed by
⁵³⁹ a variable, yet in avergae average darker UV albedo between 2011 and 2015.
⁵⁴⁰ Such a behavior is reminiscent of the other UV-sensitive instrument on board
⁵⁴¹ venus Express, namely VMC (Lee *et al.*, 2015, 2019).

We have also investigated possible correlations with topography. Since 542 longtudinal and temporal sampling are correlated to the slowly precessing 543 Venus Express polar orbit, such correlations are hard to disentangle from 544 temporal variability. With this *caveat* in mind, topographic signature of 545 Aphrodite Terra is possibly seen both in SO_2 , with high SO_2 levels reported 546 directly downwind of Aphrodite Terra in the $30^{\circ}-45^{\circ}E$ zonal region, and in 547 UV brightness with a comparatively brighter cloud top above and downwind 548 from Aphrodite Terra. Both findings are consistent with VMC studies of UV 540 albedo (Bertaux *et al.*, 2016) and SO_2 behavior as seen by STIS/HST (Jessup 550 et al., 2015), and explained through coupled variations in vertical mixing and 551 zonal wind speed through momentum deposition from topography-induced 552 gravity waves over the western edge of Aphrodite Terra. 553

In any case, the high temporal and spatial variability of both SO₂ and UV absorption over a large span of temporal (from days to decades) and spatial (from regional to planetary) scales highlight the need to continue the monitoring of Venus after the end of *Venus Express*, from orbiters like *Akatsuki* and Earth-based observations, at least until the next generation of UV instruments on board Venus orbiters may take over the legacy of *Venus* *Express* at some point in the late 2020s to early 2030s.

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