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Low levels of sulphur dioxide contamination of Venusian phosphine spectra

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ABSTRACT

New analysis is presented of the 1.1 mm wavelength absorption lines in Venus’ atmosphere that suggested the presence of phosphine. We retrieve a sulphur dioxide observation from the JCMT archive that was simultaneous within a few days of the PH₃ 1-0 spectrum obtained in June 2017, and demonstrate via a radiative transfer calculation that contamination of PH₃ by SO₂ was $\approx 10\%$. We also present ALMA 2019 spectra of PH₃ 1-0 and an SO₂ transition acquired simultaneously, and infer that SO₂ line-contamination was $\lesssim 2\%$ (for the least-noisy half of the planetary disc). The contamination-subtracted ALMA and JCMT spectra (of 6-8 sigma confidence) are now consistent with similar absorption-depths at the two epochs. The two values span $-1.9(\pm 0.2) 10^{-4}$ of the continuum signal (which was re-estimated for ALMA), albeit for differing planetary areas. This suggests that the abundance attributed to phosphine in Venus’ atmosphere was broadly similar in 2017 and 2019.

Key words: planets and satellites: individual: Venus – radio lines: planetary systems

1 INTRODUCTION

There is presently little consensus about the possible presence of phosphine, PH₃, in Venus’ atmosphere. This trace-gas would be very unexpected for an oxidised planet, but could come from unknown chemical routes (Bains et al. 2021a), or even be a biological by-product. Ultra-dry/acidic cloud conditions would be uninhabitable by any known life (Seager et al. 2021a, Hallsworth et al. 2021), but neutralisation of some of the acid in droplets could provide better habitats (Bains et al. 2021b). In Greaves et al. (2020) we presented 1.1 mm-wavelength absorption features interpreted as from PH₃ in Venus’ atmosphere, owing to close alignment with the 1-0 rotational-transition frequency. Mogul et al. (2021) then retrospectively attributed to phosphine a signal from the Pioneer-Venus mass spectrometer LNMS, which sampled the clouds in 1978. All three of these signals were at $\geq 5\sigma$ confidence after careful re-processing. Further searches for phosphine are currently difficult — shorter-wavelength absorption only traces above-cloud layers (Trompet et al. 2021), and further in-situ sampling awaits new missions. Planned future instruments include the mass spectrometer VMS on NASA’s

DAVINCI, and a balloon-borne tunable laser spectrometer as part of the Venus Life Finder programme (Seager et al. 2021b).

Critiques of our results have posed three main questions: (1) are the 1.1 mm features robust? (2) could they be due to SO₂ absorption rather than PH₃? (3) do the line-widths observed suggest the absorbing gas is at high altitude, where PH₃-presence is problematic as it should be rapidly photo-chemically destroyed? Regarding (1), Greaves et al. (2021a,b) presented new data-processing addressing technical issues (Villanueva et al. 2021) and statistics on false-positives (Snellen et al. 2020; Thompson 2020). We here expand on some of the technical issues in (1), and then focus on (2), with new analysis quantifying the level of SO₂ contamination of the 1.1 mm features we attributed to PH₃. We find that SO₂ contamination levels are insignificant compared to those from ad-hoc models (Akins et al. 2021; Lincowski et al. 2021). Addressing (3) will require new observations and better laboratory data, as inversion of line-shapes to altitude-profiles of abundance needs lower-noise spectra and a PH₃-CO₂ broadening-coefficient that improves on current theoretical estimates.

The 1.1 mm data discussed here include: from the James Clerk Maxwell Telescope (JCMT), a centred-weighted whole-planet spectrum observed over a week in June 2017, and from the Atacama Large Millimeter/submillimeter Array (ALMA), a datacube from

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Table 1. Details of the observations made with JCMT and ALMA. The JCMT data are single-dish spectra covering the planetary areas listed. The ALMA interferometer was configured with baselines between antennas of 15-314m, but data shown here exclude baselines of <33m to reduce noise; the largest angular scale detected is then smaller than Venus.

facility	project id	dates	integration times	frequency centres and bands	planetary area covered
JCMT	S16BP007	2017 June 16/14/12/11/9	30 minutes \times 10	266.946 GHz, 250 MHz band	75% (at \geq half-power of beam)
JCMT	M17AP081	2017 June 6, May 26/17	25-40 minutes /day	346.590 GHz, 1 GHz band	\sim 30% (at \geq half-power of beam); also offset beams viewing limb (see text)
ALMA	2019.A.00023.S	2019 March 5	3.5 hour block	266.1 & 266.9 GHz, with 1875 & 117 MHz bands	100% at \geq 70% power, but largest scale detected \approx Venus-radius (see text)

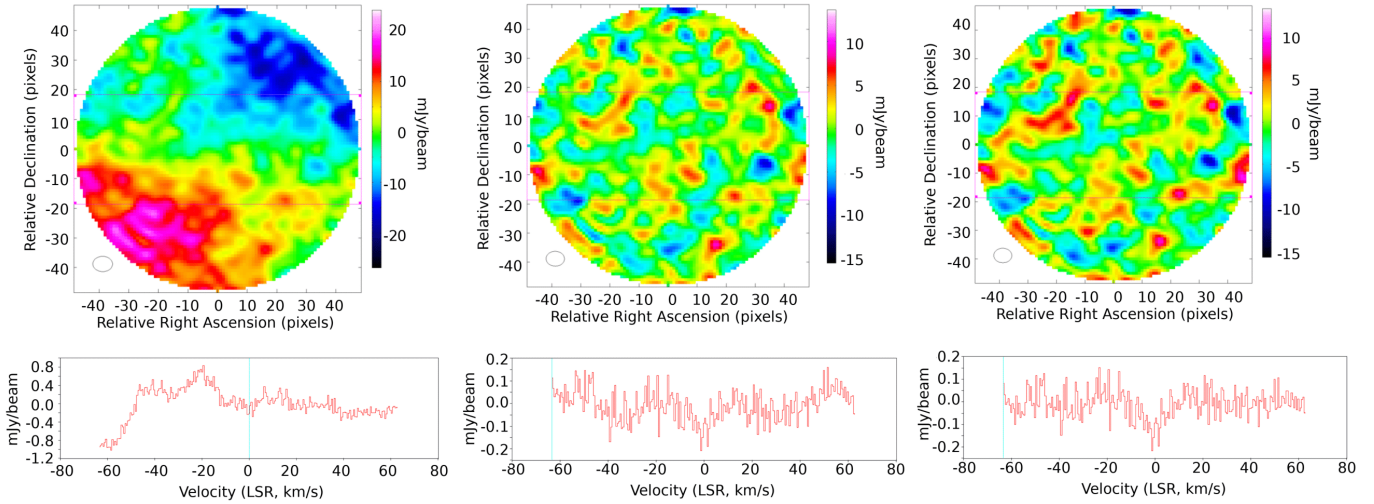


Figure 1. Final stages of the ALMA processing, as performed for this project. Each top panel shows the zero-velocity slice of the calibrated PH₃ 1-0 datacube. From left to right: Venus continuum-subtracted cube using all antenna baselines (15-314m) and subtracting only a 1st-order image-plane fit; using only baselines of 33-314m and with a 1st-order image-plane fit; using only baselines of 33-314m and with a 6th-order image-plane fit. The axes are RA,Dec with 0.16 arcsec pixels. Flux scales are Jy per beam with beam size shown by the ellipses at lower-left of each panel. The lower panels show the corresponding spectrum from each of the identical boxes (of 97 \times 37 pixels) outlined in purple in the upper panels. The axes are flux in mJy/beam against radio-definition velocity with respect to Venus. Spectral ripple is more suppressed at velocities away from zero with the higher-order image-plane fit, and so the lower-right spectrum has the lowest residuals. The box in which extraction was performed was chosen to illustrate a good balance of planetary coverage and ripple cancellation.

one morning in March 2019, where the planet was spatially resolved. With ALMA, issues with spatial filtering (Villanueva et al. 2021, Akins et al. 2021, Greaves et al. 2021a) resulted in least smooth regions, e.g. the limb, being the best-sampled. Full details are given in Table 1.

2 DATA PROCESSING

2.1 ALMA

The original ALMA processing suffered from several issues in bandpass calibration and flux-scaling. The observations were non-optimal in calibration, being exploratory in high dynamic range for line:continuum. (For comparison, only one similar ALMA dataset on Venus has been published – by Encrenaz et al. (2015); Vandaele et al. (2017); Piccialli et al. (2017) – with only around half the observing time and one-third of the antennas employed for our project, or $\sim \sqrt{6}$ times the sensitivity.) After the observatory (JAO/ESO) re-calibrated and re-released our Venus data in late 2020, the line-shapes were seen to be improved – i.e. were more "V-shaped" as expected for a narrow line with faint pressure-broadened wings, after the removal of the more "bowl-shaped" artefacts. However, there are still caveats on

recoverable planetary area and line:continuum fidelity, as discussed below.

Going beyond the JAO-released re-processing, Greaves et al. (2021a) excluded short antenna-baselines, and applied low-order image-plane fits. The first procedure removes at an early stage the data that contribute the most spectral "ripple" and noise – Greaves et al. (2021a) demonstrated that including the shorter antenna-baselines increases the noise by a factor ≈ 2.5 . However, without the short baselines, the largest angular scale that is reliably imaged is 4.3 arcsec and the largest detected is 7.1 arcsec (Greaves et al. 2020). Hence, as Venus then subtended 15.2 arcsec, most of the centre of the planet is heavily downweighted, with most of the line signal coming from an annulus inwards of the limb. The second additional procedure involved subtracting image-plane fits, which were of 6th-order for the narrowband data including PH₃ 1-0, and of 3rd-order for the simultaneous wideband data covering a strong SO₂ transition. This procedure removes the need for any trendlines (which could be user-biased) to be fitted to spectra extracted from the final datacubes. The orders were chosen as the lowest that could effectively flatten the spectral baselines. Figure 1 illustrates the improvements to spectral quality from these two procedures. Spectra can then be extracted over broad

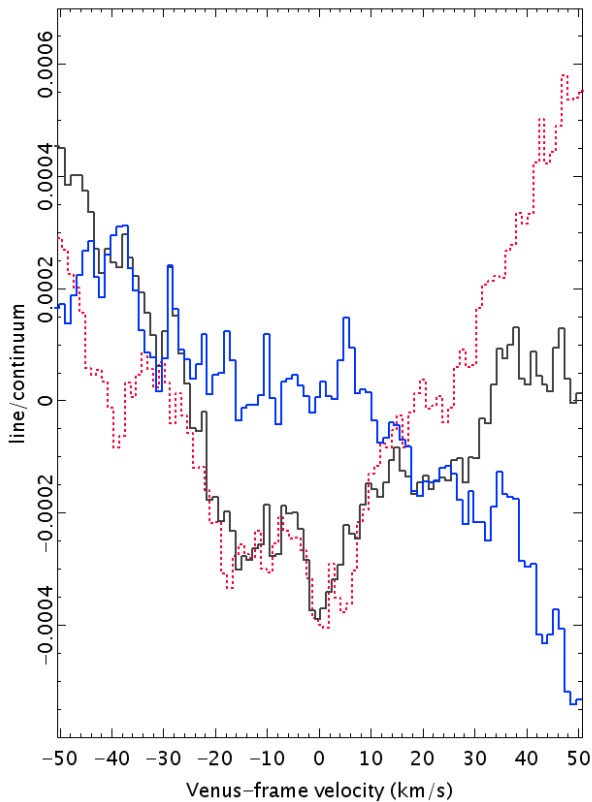


Figure 2. Additional processing of the ALMA wideband SO_2 spectrum. The black histogram is a spectral cut around the SO_2 13(3,11)-13(2,12) frequency, for the half-planet area of Section 4.1. The dotted red histogram is a “template” line-free section of the same spectrum, after an applied shift of +145 km/s. Subtracting the template from the line-region produces the thick blue histogram, representing the SO_2 spectrum with reduced ripple.

planetary areas, where residual spectral ripples tend to self-cancel¹, as shown by the lower-right panel of Figure 1. Line:continuum ratios are finally obtained via a similarly-processed continuum signal extracted from the same area. This overcomes the difficulties in appropriately calibrating models of Venus, but involves the assumption that line and continuum sources are similarly spatially distributed, as discussed below. The spectra presented here use the processing scripts first published in Greaves et al. (2021a), but here we have recovered phosphine over a larger planetary area.

The ALMA wideband data were useful as they serendipitously covered several transitions of SO_2 , with none of these frequencies covered in the narrow-band mode. One post-processing step is also applied here, as the wideband data suffered particularly from spectral ripple (not improved by higher-order image-plane fitting). These wideband ripples are notably quasi-periodic on the frequency axis, and so we experimented with self-cancellation around the strong SO_2 transition at 267.537 GHz. A “template” line-free section of spectral baseline was identified around -145 km/s, which has similar structure to the line region, and so can be shifted in velocity and sub-

¹ The combination of signals from pairs of telescopes in radio interferometry produces complex visibilities which can be expressed as a combination of sinusoidal functions, generally producing in the image plane amplitude errors that are symmetric and phase errors that are anti-symmetric about the image centre (Taylor et al. 1999), as is the case here. Hence, the errors tend to cancel for a selected region that is symmetric about the centre.

tracted – see Figure 2. This procedure partially cancelled the largest ripples around the SO_2 line.

2.2 JCMT

The JCMT PH_3 spectra of Greaves et al. (2020) were acquired with bandwidth insufficient to cover any strong SO_2 transitions. However, we have now found nearly contemporaneous monitoring of SO_2 in the JCMT public archive. The JCMT’s HARP camera-spectrometer monitored Venus from March to June 2017 (most relevant dates listed in Table 1), with the 6 June 2017 data acquired very shortly before our PH_3 observations on 9-16 June 2017. These raw archival spectra from HARP (0.98 MHz spectral resolution) were downloaded, and one-(x,y)-pixel datacubes were created with the ‘makecube’ task in SMURF², with output spectra viewed and manually corrected for Venus-Earth velocity-differences (>10 km/s) within SPLAT³. The resulting SO_2 19(1,19)-18(0,18) (346.65217 GHz) lines have high S/N but some spectral ripple is evident.

HARP observed at 346.6 GHz with a telescope beam of ≈ 14 arcsec, while Venus’ diameter on 6 June 2017 was 23 arcsec. The planet was thus undersampled by the on-source receptor (Table 1), but HARP receptors at 30 arcsec-offsets saw the planetary limb in the first sidelobe. We tested co-adding these offset line:continuum spectra with the planet-centre spectrum, with various offset-weights up to 50%, and found only up to $\sim 10\%$ changes in net SO_2 line-depth. The planet-centre spectrum (with the best S/N) is thus adopted as representing net planetary SO_2 .

3 MODELLING

Here we model SO_2 spectra using the simplified radiative-transfer code of Greaves et al. (2021a) — the implementation is described here in Appendix A, where a link is provided to the code. The model uses the temperature-pressure profile of the Venus International Reference Atmosphere (VIRA), with details of the altitude and diffusion profiles listed in Greaves et al. (2020). Spectra are produced in absorption against a “quasi-”continuum formed by broad blended emission features of molecules deeper in the atmosphere. Appendix A below describes how the SO_2 line profiles are calculated. The aim here is for the results from simple pencil-beam calculations to be reproducible and to use transparent methods. We have neglected convolution with the telescope beam, as these effects should be similar for line and continuum. (There could be some differences if an absorbing molecule has a spatial distribution unlike the molecules producing the quasi-continuum – for example, if absorption favours the day- or night-side – however, prior ALMA data do not indicate any such clear trends (e.g. see Figures 15-16 in Piccialli et al. 2017).) All the lines we model have very low optical depths (line/continuum $\ll 1$), and so trace all altitudes above where the quasi-continuum is opaque, but there is a strong weighting function according to local temperature gradient (e.g. Figure 7 of Piccialli et al. 2017). We also neglect the decrease in absorption towards the planetary limb, having described above the JCMT case where this is found to influence the whole-planet spectrum by only $\sim 10\%$.

The abundances inferred here are intended to be *representative*

² The Sub-Millimetre User Reduction Facility; the online manual is located at starlink.eao.hawaii.edu/docs/sun258.htm/sun258.html.

³ The Spectral Analysis Tool: the online manual is located at astro.dur.ac.uk/~pdraper/splat/sun243.htm/sun243.html.

only, as they are set to be constant over the atmospheric column where absorption arises. Verification tests (against Lincowski et al. 2021, Figure 2 and Greaves et al. 2020, Figure 4) found that our simple code generates SO₂ lines that are 15-25% less deep than from more detailed models (see discussion in Appendix A). If our SO₂ model-lines are $\approx 0.8 \times$ true line-depths, then representative abundances we infer by fitting the depths of observed spectra will be too high by a factor ≈ 1.25 (i.e. by $1/0.8$). This systematic uncertainty is negligible compared to the altitude-dependent variations of molecular abundances in Venus' atmosphere (e.g. Rimmer et al. 2021, and discussion below).

Here we generate our model SO₂ spectra at spectral resolutions used in the ALMA and JCMT observations. We adopt as pressure-broadening coefficient the mean-estimate of $0.18 \text{ cm}^{-1}/\text{atm}$ from Lincowski et al. (2021). The SO₂ line-strengths are from Underwood et al. (2016, via the HITRAN database), but our code now additionally⁴ scales line-strengths for temperature as a function of altitude, as described in Appendix A. This is important for modelling the “contaminating” SO₂ line, as its absorbing energy level is significantly different to that of other transitions that were observed, at 613 K versus 93-152 K. The temperature-pressure profile for Venus' atmosphere is well-defined, with for example a temperature-related uncertainty in the altitude where the 1.1. mm continuum is most strongly generated of ~ 2 -3 km (best-estimate value of 56 km). Since the high-J contaminating SO₂ transition will vary the most with adopted temperature of the warm clouds, we tested varying the lowest altitude of absorbing SO₂ molecules within these upper/lower bounds. The line-depth of this high-J SO₂ transition was found to be uncertain by only $\pm 5\%$ by this method.

For verification of line-ratios, we used the SO₂ line-pair of 30(9,21)–31(8,24)/13(3,11)–13(2,12) relevant to the ALMA observations. Detailed codes (Greaves et al. 2020, Lincowski et al. 2021) have given line-depth ratios for this pair of 1:40(± 2), while the simplified code gives 1:31. The model used here thus tends to slightly over-estimate SO₂ (J=31) contamination – i.e. using more detailed calculations would further decrease the negligible contamination we find here.

4 RESULTS

4.1 ALMA 2019 data

We first note that, after the observatory-led re-processing, absorption near the PH₃ 1-0 frequency is clearly detected. Figure 3 shows an example spectrum where we have sought to balance the largest retainable planetary area against the best ripple-cancellation, given that Declination-extremes in the field exhibit worse noise (Greaves et al. 2021a). After further testing of these systematics, we have now extracted a higher signal-to-noise (S/N) detection of PH₃ 1-0, from an area that is $\approx 50\%$ larger than in Greaves et al. (2021a – their Supplementary Figure 2). The new extracted spectrum is from a planet-spanning RA,Dec “box”, of 97×37 pixels where 1 pixel = 0.16 arcseconds. The long axis of the box is nearly aligned with the planetary equator (which was tilted from RA by 13°), and 49% of the planetary disc is included (no latitudes above 40°).

This spectrum has 7.7 sigma confidence when line-integrated over ± 6 km/s. The line-centroid is at -0.2 ± 0.5 km/s in the Venus-centric PH₃ 1-0 reference-frame, fully in agreement with zero as expected if the absorption is dominated by phosphine. This measured velocity

is however 3-sigma discrepant with the alternative attribution (Lincowski et al. 2021, e.g.) to SO₂ 30(9,21)–3(18,24) absorption, which would be centred in this frame at $+1.3$ km/s.

We also checked whether the choice of a particular box affected the results. Test-extractions were made for PH₃ for bands of latitude (instead of Declination) that extended to 20, 30, 40 or 50 degrees from the equator. The fitted PH₃ line-depths varied by only $\sim \pm 10\%$, at the level of noise.

Figure 3 also shows the spectrum from the 97×37 -pixel box for the SO₂ 13(3,11)–13(2,12) transition that ALMA observed simultaneously. Spectral ripple has been suppressed as shown in Figure 2. The overlaid grey curve employs 3 ppb of SO₂ at altitudes ≥ 80 km, to demonstrate that mesospheric sulphur dioxide at greater abundances would likely have been detected (at ≥ 3 -sigma at line-minimum). We then ran the same model for the SO₂ 30(9,21)–3(18,24) transition. Comparing this model to the PH₃ 1-0 observation, the SO₂ contamination is $< 2\%$, when integrated over ± 10 km/s (Figure 3b).

4.2 JCMT 2017 data

The JCMT acquired SO₂ 19(1,19)–18(0,18) spectra on mornings 26, 17 and 6 days before the mid-point of the PH₃ run. The SO₂ line-continuum ratios were found to be similar, at -0.0043 , -0.0029 and -0.0044 at line-minimum respectively, suggesting an SO₂ abundance variation of $\sim \pm 20\%$ about the mean. Figure 4 shows the SO₂ spectrum observed on 6 June 2017, closest in time to the PH₃ observing run. There is some spectral ripple present, for which a suitable least-parameters approximation is a 4th-order polynomial. After subtracting this trendline from the data, we overlay two line models: one best matching the line core and one with a better match to the wings. The former model is for 20 ppb of SO₂ at ≥ 75 km and the latter for 25 ppb at ≥ 80 km. These fits have reduced- χ^2 of 1.8 and 1.65 respectively, over ± 20 km/s in velocity – they are representative only (i.e. use constant abundance), but within these limitations the fits match the observed line adequately, and net-abundance and minimum-altitude are quite tightly constrained.

We then generated models for the contaminating transition SO₂ 30(9,21)–31(8,24) using these two abundance profiles. Quadratic baseline-fits were subtracted from these models, over the same ± 8 km/s region as for the data. (Greaves et al. (2020) applied a higher 8th-order to the data; duplicating this for the model would further reduce the inferred contamination.) Figure 4 shows the results, demonstrating that the SO₂ (J=31) line-contribution must be small. The model signal, over ± 8 km/s, is only 9-11% of the total absorption seen in the PH₃ 1-0 observation. The PH₃ 1-0 detection shown has 6.7-sigma confidence when integrated over ± 8 km/s.

Given the rather constant SO₂ that JCMT observed in May-June 2017, it seems unlikely that the planet-wide abundance soared by an order of magnitude in the three days between the last SO₂ spectrum and the start of PH₃ observing. Large jumps in SO₂ are rare for big areas of Venus (Marcq et al. 2020). An extreme example is a 2.5-fold decline seen by HST over 5 days (Jessup et al. 2015), but this was restricted to latitudes inside $\pm 10^\circ$, whereas the JCMT SO₂ spectrum shown here represents the whole planet and a ten-fold increase would be needed. We conclude that while SO₂ does vary strongly on various cadences, the SO₂ and PH₃ JCMT spectra here are sufficiently contemporaneous for a robust contamination test.

⁴ This temperature dependence was not included in Greaves et al. (2021a).

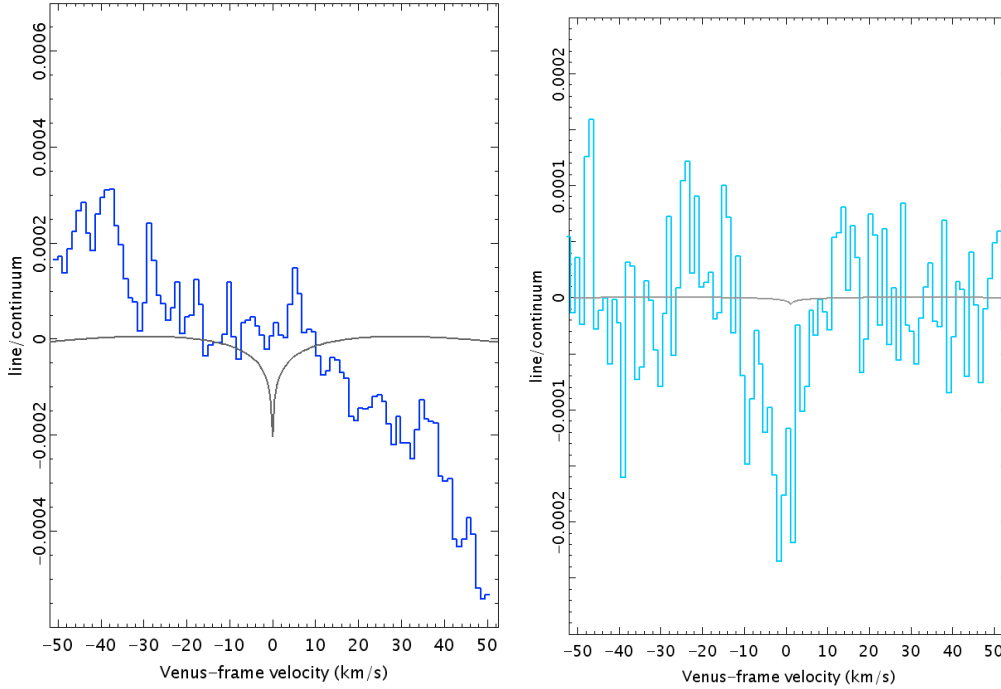


Figure 3. Left panel, (a): ALMA wideband spectrum of SO_2 13(3,11)-13(2,12) (dark blue histogram), extracted from half of the planetary disc as described in the text. Spectral ripple has been suppressed as shown in Figure 2. The grey curve is an upper-limit model, for 3 ppb of SO_2 at all altitudes ≥ 80 km, after removal of a quadratic baseline fitted outside ± 10 km/s, to simulate the processing of the real data. Right panel, (b): spectrum at the PH_3 1-0 frequency (blue histogram) for the same planetary area. The upper grey histogram is the corresponding (3 ppb, ≥ 80 km, quadratic-subtracted) model demonstrating the upper-limit on the SO_2 30(9,21)-3(18,24) contamination. The grey histogram encloses $<2\%$ of the line-area of the blue histogram.

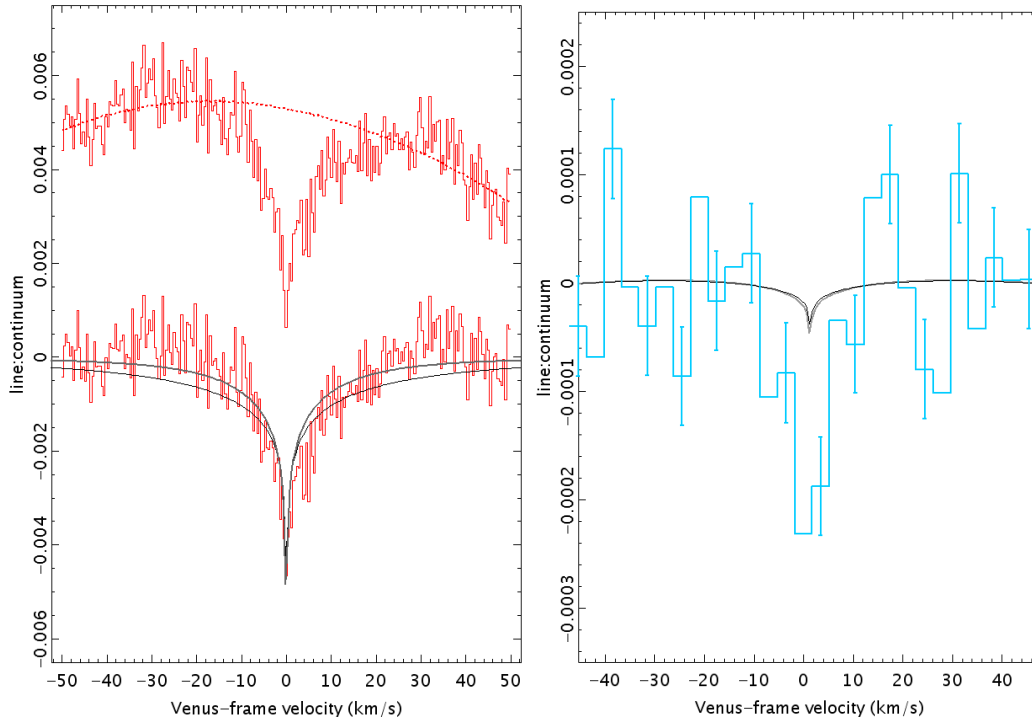


Figure 4. Left panel, (a): JCMT 346.6 GHz spectrum of SO_2 19(1,19)-18(0,18) observed on June 6 2017 (upper red histogram, offset vertically for clarity). The dashed trendline is a 4th-order polynomial fitted outside the line region. The lower histogram shows the trendline-subtracted residual spectrum, overlaid with two models: the thicker curve is for 25 ppb of SO_2 at ≥ 80 km and the thinner (lower) curve is for 20 ppb at ≥ 75 km. Right panel, (b): the net 9-16 June 2017 JCMT spectrum of PH_3 1-0 (blue histogram, spectrally binned and with representative 1-sigma errorbars), overlaid with the same two models as in (a) but for the contaminant SO_2 30(9,21)-3(18,24) line. Observed and model spectra have here both had line-wings suppressed outside ≥ 8 km/s (see text).

5 DISCUSSION

5.1 Contamination

Figures 3 and 4 show that the absorptions proposed as PH₃ 1-0 can not realistically be re-attributed to sulphur dioxide. Contamination of the observed spectra by the high-J SO₂ transition is inferred to be $\leq 10\%$, at both epochs. The ALMA-detection presented here has 7.7 sigma confidence, minimally affected by up to 2% SO₂ contamination. The JCMT spectrum has 6.7 sigma confidence, so is at ≈ 6.0 sigma after removing 10% contamination.

Lincowski et al. (2021) proposed that high abundances of SO₂ could escape detection when larger spatial scales are filtered out in ALMA processing, and Akins et al. (2021) simulated this for a range of 2D gas-distributions. We agree with their conclusions about spatial filtering, but emphasise that this can not enhance SO₂ 30(9,21)–31(8,24) relative to SO₂ 13(3,11)–13(2,12) absorption. Both line-signals will be similarly filtered, as they arise from the same spatial distribution of gas and the same column of absorbing atmosphere (line-frequencies differ by $<1\%$). Therefore, a strong upper limit on the observed SO₂ J=13 line imposes a stringent limit on the “contaminant” J=31 line – such that ALMA absorption detected at the PH₃ frequency can not be solely from SO₂.

The only pathological case that we can identify would involve weighting the SO₂ abundance-profile to the warmest gas-layer (where the J=31 level-population is higher), and making this layer particularly patchy (so J=31 spatial-filtering is reduced). Imagining a simple two-layer atmosphere, J=13 absorption could trace both a smooth cold mesosphere (temperatures down to ~ 175 K) and a warm patchy cloud deck (up to ~ 300 K). J=31 absorption (from an energy level above 600 K) would be more weighted by the warm cloud-decks, and less of this signal would be filtered out. The result would be a stronger “contaminant” SO₂ 30(9,21)–3(18,24) line than in standard models. However, this concept severely conflicts with observations. While millimetre-wavelength absorption-spectra have some sensitivity to the clouds (Piccialli et al. 2017, Figure 7, e.g.), these observations mainly find SO₂ in the mesosphere (above ~ 78 –85 km; Lincowski et al. 2021). Further, while this mesospheric SO₂ may be patchy (Encrenaz et al. 2015), lower altitudes are dominated by large-scale Hadley-cell circulation (Marcq et al. 2020), with SO₂ “plumes” rapidly smeared out by super-rotation (Encrenaz et al. 2019). A smoother SO₂ distribution at lower altitude is the opposite of what is needed for this enhanced-J=31 scenario to work.

5.2 Abundances

The net SO₂ abundances inferred here are typical for the gas-columns traced by millimetre-wavelength observations, e.g. the 4-year JCMT-monitoring programme of Sandor et al. (2010). Our 20–25 ppb of SO₂ from JCMT in June 2017 is near the mean, ≈ 23 ppb, in the Sandor et al. tabulation. Our ≤ 3 ppb ALMA SO₂ upper-limit from March 2019 lies in the lowest decile of their abundance table, but with correction for spatial-filtering the limit could be higher. Akins et al. (2021) show that filtering could reduce the SO₂ line-depth by a factor as much as ~ 30 (in their model D, covering an area similar to that outlined in Figure 1).

While our net-SO₂ abundances are normal for millimetre monitoring, abundance-profiles that have been inferred from comprehensive (multi-wavelength and in-situ) datasets tend to increase upwards. Such top-weighting enabled Lincowski et al. (2021) to approximately match our JCMT PH₃-frequency spectrum using SO₂ alone. However, we can now show that their model – Case D, SO₂ rising to ~ 400

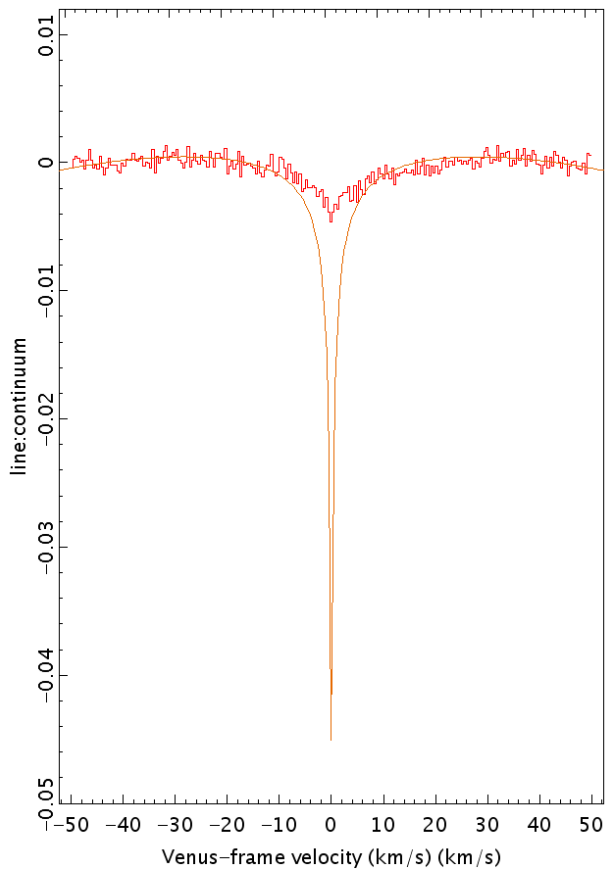


Figure 5. Test of a published ad-hoc model for SO₂. The red histogram is SO₂ 19(1,19)–18(0,18) as observed at JCMT, from Figure 4a. The red curve is a prediction from a SO₂ model based on Lincowski et al. (2021), as described in the text. A quadratic was subtracted from the model to remove line wings, similar to the data-processing of Figure 4a.

ppb at 100 km altitude – is inconsistent with the newly-retrieved JCMT data. We adapted our simple radiative-transfer code for the SO₂ 19(1,19)–18(0,18) transition to use the Case D abundance-profile from Lincowski et al. (2021; we made an empirical fit to the curve in their Figure 1b). The minimum height where absorption against the continuum can occur at this frequency was taken to be 60 km (Piccialli et al. 2017). Figure 5 demonstrates that this ad-hoc model – based on various historical SO₂ data – will produce $\approx 10\times$ deeper absorption than was actually seen at JCMT. Hence the ad-hoc model greatly over-estimates the amounts of SO₂ that were present near the time of the JCMT observations of PH₃.

Even after removing SO₂ contamination, it is still problematic to infer PH₃ abundances (assuming that the millimetre-absorber is phosphine, and not some mysterious uncatalogued molecule). Villanueva et al. (2021) argue that the narrow observed lines suggest PH₃ must be solely mesospheric, and so of high abundance given a limited gas-column to populate. We agree that our preliminary constant-abundance profile (Greaves et al. 2020) was not in fact suited to matching the observed spectra (discussed in Greaves et al. 2021a). Also, a purely mesospheric location is indeed problematic, because PH₃ molecules should rapidly photodissociate (unless upwards diffusion is much faster than expected: Greaves et al. 2021a). However, the cloud-level PH₃ contribution is unquantified here, given that line-wings are heavily suppressed in necessary processing. The Pioneer-Venus in-cloud data (Mogul et al. 2021) support at ~ 5 -sigma

confidence that PH₃ is indeed present in the clouds, likely in the mid-to-high ppb range (Bains et al. 2021c). More work is needed to reconcile all available PH₃ data with a consistent profile of abundance by altitude.

We highlight that, although abundances remain unknown due to poor altitude information, the line:continuum ratios for JCMT and ALMA are now similar. After subtracting contamination and adopting uniform ≈ 3.5 km/s spectral binning, the line-minimum for JCMT is $-2.1e-4$ and for ALMA it is $-1.7e-4$, i.e. a variation of $\sim 10\%$ around the mean. An important factor in this convergence is the assumed continuum in calculating the line/continuum depths. In the ALMA case, we are now using the observed continuum signal (which was always the case for JCMT). The true ALMA line-depth is uncertain due to the unknown effects of spatial filtering; in particular, the absorption could be significantly less deep with a Venus-model continuum rather than the observed filtered continuum. This effect was modelled by Akins et al. (2021), while Greaves et al. (2021a) calculated from the data that 22% of the continuum survives the spatial filtering. Modulo this uncertainty, ALMA and JCMT both sampled large areas of Venus (Table 1), and so the similar spectra hint that phosphine-attributed abundances were broadly comparable in 2017 and 2019.

6 CONCLUSIONS

(Quasi)-simultaneous data on sulphur dioxide absorption are used to infer bounds on the SO₂ contamination of absorption at the PH₃ 1-0 frequency. These limits are $<2\%$ to $\approx 10\%$, for large areas of Venus. Sulphur dioxide would need to have increased ten-fold planet-wide over only a few days for SO₂ to have mimicked PH₃ in the discovery data. We conclude that results from observations preclude re-attributing phosphine on Venus to sulphur dioxide.

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DATA AVAILABILITY

Raw and processed data are available in the open-access JCMT and ALMA archives, at <https://www.cadc-ccda.hia-ihp.nrc-cnrc.gc.ca/en/jcmt/> and <https://almascience.eso.org/alma-data> (and other ALMA repositories). The scripts to reproduce the ALMA results shown here were published in Greaves et al. (2021a). Files of the processed spectra shown here will be made available at zenodo.org.

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APPENDIX A: LINE PROFILE MODEL

We develop a semi-analytical one-dimensional model for the line profile, starting at the surface of Venus, height $z = 0$ km, and moving up in height increments based on the same temperature profile used by Greaves et al. (2021a), with the top of the atmosphere at 115 km.

We track the intensity as a function of height (z , km) and frequency (ν , Hz), with a line center at ν_0 (Hz):

$$I = I(\nu, \nu_0, z), \quad (\text{A1})$$

We set $I(\nu, \nu_0, 0)$ equal to unity over all frequencies. For each step, Δz (km), from 0 km to 115 km, we update:

$$I(\nu, \nu_0, z + \Delta z) = I(\nu, \nu_0, z) e^{-\tau(z, z + \Delta z)} + \frac{B_\nu(z)}{B_\nu(0)} e^{-\tau(z, z + \Delta z)}, \quad (\text{A2})$$

where τ is the optical depth between z and $z + \Delta z$, given by:

$$\tau(z, z + \Delta z) = f_V(\nu, \nu_0, z) S_{\nu_0}^*(z) \Delta z. \quad (\text{A3})$$

Here $f_V(\nu, \nu_0, z)$ is the Voigt profile, and depends on the gas temperature T (K) and pressure p (bar), both functions of height, z , and on the pressure-broadening coefficient γ ($\text{cm}^{-1}/\text{atm}$). The line-strength, $S_{\nu_0}^*$ ($\text{cm}^{-1} \text{s}^{-1}$) is:

$$S_{\nu_0}^*(z) = cn(z) e^{E_J/T_0} e^{-E_J/T(z)} S_{\nu_0}, \quad (\text{A4})$$

where $c = 2.9979 \times 10^{10}$ cm/s is the speed of light, $n(z)$ (cm^{-3}) is the number density of the absorbing species, E_J (K) is the value of the lower energy level, T (K) is the temperature and S_{ν_0} ($\text{cm}^{-1}/(\text{molecules cm}^{-2})$) is the line strength at $T_0 = 300$ K. The reason for the two Boltzmann terms is to scale S_{ν_0} to different temperatures. We assume that the atmospheric gas at each height is in local thermodynamic equilibrium and therefore the population of the lower level is proportional to $e^{-E_J/T}$. We also assume that the gas in the experiment used to measure S_{ν_0} at T_0 is also in local thermodynamic equilibrium, and therefore is proportional to e^{-E_J/T_0} . We can achieve the line strength appropriate for T by dividing the former Boltzmann factor by the latter. Finally $B_\nu(z)$ is the spectral radiance given by Planck's law:

$$B_\nu(z) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/(kT)} - 1}, \quad (\text{A5})$$

where $h = 6.62607 \times 10^{-27}$ erg s is Planck's constant and $k = 1.38065 \times 10^{-16}$ erg/K is Boltzmann's constant.

This one-dimensional model accounts for absorption and thermal emission, but does not treat scattering. Scattering will increase the path length traversed and is therefore expected to strengthen the absorption features. Unless scattering is steeply dependent on frequency, this effect will be approximately the same for each line, and so the ratio of line strengths will not be affected.

This program calculates a single line profile and is written in Python3. Example code to model the SO_2 13(3,11)-13(2,12) transition can be found at <http://www.mrao.cam.ac.uk/~pbr27/J13.py>.

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